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THE CHEMICAL INTERACTIONS OF ACCELERATED CARBON-14 IONS AND ATOMS WITH BENZENE

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THE CHEMICAL INTERACTIONS OF ACCELERATED CARBON-14 IONS AND ATOMS WITH BENZENE

Tz-Hong Lin
(Ph. D. Thesis)

October 1969

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Solid benzene at -196° was irradiated with monoenergetic beams of $^{14}\text{C}^+$ ions and atoms with kinetic energy ranging from 5 eV to 15 KeV. About 28% of the ions striking the target benzene have been identified as $^{14}\text{C}$ labeled benzene, toluene, cycloheptatriene, phenylacetylene, styrene, biphenyl, diphenylmethane, phenylcycloheptatriene, benzaldehyde, tropone, phenol, and $\text{n-C}_3\text{C}_7$ unsaturated alkylbenzenes.

The nature of the reactions involved was investigated by total degradations of toluene; partial degradations of toluene (from 5–5000 eV irradiations) and benzaldehyde (from 15–5000 eV irradiations); and partial degradations of phenylacetylene, biphenyl, diphenylmethane, and phenylcycloheptatriene from a 5000 eV irradiation.
The mechanisms for the product formations were interpreted in terms of the intermediate carbenes and radicals resulting from the C-H and C=C bond insertions of hot C(3P), C(1D), and C(1S). These intermediates were evidenced by the presence of benzaldehyde, tropone, and phenol, which could result from the interactions of such intermediates with oxygen from an unknown source. The dependence of the radiochemical yields of the products upon the energy of the irradiating 14C\(^{+}\) ions was consistent with these hypotheses.

We conclude here that, in our accelerated C-benzene system, the hot and thermal C(1S) species react similarly. However, the reactions of hot C(3P) and C(1D) are different from that of the thermal counterparts.
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I. INTRODUCTION

A. The Scope

In a chemical reaction where positive activation energy is involved, reaction can be achieved by supplying the requisite energy (thermal or electromagnetic). A reaction mechanism may then be defined in terms of the structure of the transition state and its thermodynamic properties.

A high energy (above activation energy) species which is produced by a process other than thermal collision, however, displays behavior characteristic of an energy distribution which is non-equilibrium relative to the condition of statistical equilibrium for that species with its surroundings. Since the hot species possesses excess energy available for its reaction with a substrate molecule, the energy of the transition state or activated complex is always well above the energy barrier for various modes of reactions. The consequences are the participation of many competing reactions, an indiscriminate mode of reaction, and the existence of high energy processes which are not encountered in thermal reactions. The study of the energy degradation and the generally unique chemical reactions of atoms with high kinetic energy is called hot-atom chemistry.
The chemical reaction of hot carbon species with organic substrates has been intensively studied in the past two decades. Most of these investigations relied on the use of atoms produced by nuclear processes. The main features of the reaction of hot carbon (C\textsuperscript{11} and C\textsuperscript{14}) with organic molecules are the formation of reentry, synthesis, fragmentation, build-up and polymerization products.\textsuperscript{2} Such reactions are usually temperature and phase independent, insensitive to added radical scavenger, and inhibited by moderation by inert gas in the gas phase. The fact that isotopic carbon is always incorporated in the parent molecule has attracted attention in the preparation of labeled compounds. However, for many reasons, not the least of which is the appearance of labeled methyl analogs that are extremely difficult to remove, the carbon recoiling has not been used as successfully as that of tritium.

The present work is concerned with the study of the hot-atom chemistry of carbon-14 ions or atoms, produced by an ion accelerator,\textsuperscript{3} with solid benzene at liquid nitrogen temperature.

B. The Sources of Hot Carbon Atoms or Ions

The hot atoms can be produced by a variety of methods, including photolysis, ionizing radiation, nuclear recoiling, and accelerated ions\textsuperscript{3} (charge neutralized during deceleration).

If electromagnetic radiation, with energy per quantum higher than chemical bond energy is absorbed by a molecule, it may, following the law of conservation of energy, dissociate and give hot atoms
or radicals of well-defined energy. Although the production of hot hydrogen and deuterium from the photolysis of corresponding iodide was carefully studied, the chemistry of the carbon atom from this method is rarely investigated. Stief and DeCarlo reported the formation of carbon atoms in the photolysis of carbon suboxide at 1470 Å. The formation of traces of carbon ions was suspected by Jensen and Libby in their photolysis of CH₄ with 584 Å light. In neither case was the energy of the carbon species discussed.

Both radiolysis and electric discharge may give hot carbon species. However, the production of a spectrum of species with undefined energy is inevitable. In his gas phase irradiation of a mixture of organic substrates (benzene and pyridine) and CO₂ or C₂H₂ with β-rays from ⁸⁵Kr, Turton isolated the corresponding aldehyde and carboxylic acids. Kalyazin further modified this procedure and used it in the quantitative synthesis of carbonyl and carboxylic compounds from hydrocarbons. While there was no indication that hot carbon was involved in these systems, Turton's experiment (benzene-¹⁴CO₂ system) was repeated in the present research; we used ⁶⁰Co as radiation source. Various hot-reaction products similar to that of our ¹⁴C⁻benzene system were observed.

The nuclear transformations have been used as principal sources of energetic carbon in most carbon hot atom research. Table I lists the nuclear reactions capable of producing hot carbon isotopes.

The ¹⁴N(n,P)²⁴C reaction has been used in a huge number of investigations. The ¹⁴C is produced in situ in the thermal-neutron irradiation of either a nitrogen-containing compound or the
Table I. Recoil energies of hot carbons.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Incoming particle and its energy</th>
<th>Nuclear processes</th>
<th>Recoil energy of hot carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{14}$C</td>
<td>&gt;Therman n</td>
<td>$^{14}$N(n,p)$^{14}$C</td>
<td>0.045 MeV</td>
</tr>
<tr>
<td>$^{11}$C</td>
<td>&gt;18 MeV n</td>
<td>$^{12}$C(n,2n)$^{11}$C</td>
<td>1.1 MeV(max)</td>
</tr>
<tr>
<td>$^{11}$C</td>
<td>&gt;50 MeV P</td>
<td>$^{12}$C(P,Pn)$^{11}$C</td>
<td>1.8 MeV(mean)</td>
</tr>
<tr>
<td>$^{11}$C</td>
<td>&gt;27 MeV $\gamma$</td>
<td>$^{12}$C(\gamma,n)$^{11}$C</td>
<td>0.4 MeV(mean)</td>
</tr>
<tr>
<td>$^{11}$C</td>
<td>&gt;6 MeV P</td>
<td>$^{14}$N(P,\alpha)$^{11}$C</td>
<td>2.1 MeV(max)</td>
</tr>
<tr>
<td>$^{11}$C</td>
<td>2-3 GeV P</td>
<td>$^{16}$O(P,Pn\alpha)$^{11}$C</td>
<td>--</td>
</tr>
</tbody>
</table>

A homogenous mixture of the compound to be studied and some nitrogen source.

The disadvantages of this technique are the possible complications introduced by the presence of the nitrogen source, and serious radiation damage caused by the fast neutron and $\gamma$-rays in the thermal neutron flux. In order to minimize these disadvantages, $^{11}$C recoil reactions such as $^{12}$C(n,2n)$^{11}$C, $^{12}$C(P,Pn)$^{11}$C and $^{12}$C(\gamma,n)$^{11}$C were used in most of the mechanistic studies. Here, the nitrogen source was eliminated. Due to the short half-life of $^{11}$C (20.5 min, that of carbon-14 is 5760 years), only a factor of $10^8$ less $^{11}$C than $^{14}$C is needed for investigations. Thus, the irradiation can be completed within an hour (several days to weeks are required for $^{14}$N(n,p)$^{14}$C) and, consequently, the radiation damage effects are
greatly reduced. One obvious disadvantage of this technique is the
time available for the analysis (only several half-lives of $^{11}\text{C}$,
i.e., about 100 min). The $^{11}\text{C}$ can also be generated by nuclear
stripping reaction; $^{11}\text{C}$ is produced by focussing a pulsed beam of
120-MeV $^{12}\text{C}$ ions on a target consisting of gold and platinum foils
which strip a neutron from $^{12}\text{C}$ ions converting them to $^{11}\text{C}$. 11

The first study of energetic $^{14}\text{C}^+$ ions produced by a mass
spectrometer was reported by Croatto and Giacomello. 12 They bom-
barded solid benzoic acid, 13 stearic acid, cholesterol, 14 and
Vitamin B with $^{14}\text{C}^+$ ions; $^{14}\text{C}$-labeled parent compounds were found.
Lemmon, Reynolds, Mazetti and Calvin 15,16 then irradiated solid ben-
zene at $-160^\circ$ with 2 KeV $^{14}\text{C}^+$ ion beams; $^{14}\text{C}$-labeled benzene and
toluene, in agreement with carbon recoiling experiments, were found.
The irradiation of $\beta$-carotene and morphine with $^{14}\text{C}^+$ ions gave also
the labeled parent compounds. 17 These experiments were followed by
the construction of a special ion accelerator and a detailed study
of $^{14}\text{C}^+$-benzene (solid) interaction by Mullen. 18 After extensive
modification, the same ion accelerator was used in the present work.

C. The Chemistry of Hot Carbon Atoms with Organic Compounds

In spite of the extensive development of organic chemistry, the
chemistry of elemental carbon was not studied until 1946 when
Yankwich et al. 19 attempted unsuccessfully the labeling of glycine,
pyridine, and aniline by the $^{14}\text{N}(n,P)^{14}\text{C}$ reaction. The labeling of
pyridine and aniline was demonstrated by Edwards since three years later. Since then a huge number of investigations in this field have taken place. The study of the reactions of the thermal carbon atom was initiated by Skell and Engel, and Sprung, Winstein and Libby in 1965.

The hot-atom chemistry of carbon has been reviewed by Wolf, Wolfgang, Filatov, and many others. Much of the research was directed towards the finding of practical methods for preparation of labeled compounds. Most of it, however, involved the study of the mechanism of the elementary act of the atom-molecular collision and the subsequent chemical reaction brought about by the excess kinetic energy of the hot species.

The 14C or 11C atoms produced in a nuclear reaction possess kinetic energy in the range of 0.05 - 2 keV, where energy loss of the hot species is brought about mainly by electronic interactions and nuclear scattering. At around 5000 - 6000 eV, energy degradation by means of elastic and inelastic collision takes place. It is generally agreed that "chemical" reactions become meaningful only when the kinetic energy of the recoiling species becomes close to that of chemical bonds (<10 eV).

For the interpretation of the hot reaction, Libby was the first to suggest the elastic (billiard ball) collision model; the labeled parent molecules were formed by a process involving a high energy collision between a recoiling atom and an organically bound atom of like mass, resulting in a complete or nearly complete energy transfer to the struck atom which breaks the bonds and moves out of
the place of impact, followed by the combination of the thermalized recoil atom with the fragment it has created. This idea was modified by Fox and Libby to include the epithermal (above chemical bond energies) region in an effort to interpret products other than the parent compounds. Epithermal reactions were considered to be dependent on the nature of the solvent cage, the thermalized "hot species" were trapped in a solvent cage after producing various radicals in this vicinity, and the labeled compounds were then formed from radical recombinations. The "random fragmentation" or "brush-heap" hypothesis was then proposed by Willard to account for the hot reactions that could not be explained by Libby's model. Here, in the liquid and solid states, the collision of recoil atoms with their surrounding molecules resulted in the indiscriminate multi-bond-breaking which gave variety of radicals in its vicinity. The recoil atoms then combined with surrounding radicals to give stable compounds. While the inadequacies of these reaction models in describing overall hot atom reactions have been revealed as the new data accumulated, their significance should not be neglected.

There are numerous theoretical treatments of carbon hot-atom processes in the literature. The more recent ones are those of (i) Estrup and Wolfgang, which showed a remarkable agreement between theory and the experimental data for hot tritium, hydrogen, and fluorine atoms, (ii) that of Thomson, and (iii) those of Wong and Wiles.

Not surprisingly, classical mechanics can give only a very limited explanation for hot-atom processes. The chemical approach
has been more successful. Here, the reactions of hot carbon are explained in terms of abstraction, insertion, substitution, radical reactions, etc. Substantial evidence has accumulated to support the involvement of the hot carbon atom, and of methyne(CH), methylene(CH₂), methyl(CH₃)², and C₂Hₓ species.

The charge and spin state of hot carbon species have been discussed by Wolfgang. It was pointed out that recoiling carbon reacts with organic substrates in its neutral form (in its low-lying ¹D and ³P states). It was, therein, concluded that both hot and thermal carbon atoms reacted in similar ways, with thermal species more discriminative, favoring (in aliphatic compounds) π-bond over C-H bond insertion.¹¹,²²

D. Previous Studies on the Carbon-Benzene System

The carbon recoiling in benzene was first investigated by Zifferero and Masi in 1954. The clathrate of ammoniacal nickel cyanide was used as the nitrogen source for the ¹⁴C(n,p)¹⁴C reaction. Four percent of the recoiling ¹⁴C appeared as labeled benzene. The study of the same system by Wolf, Anderson and Redvanly revealed the formation of only 1.4% of benzene-¹⁴C.

In their study of the hot-atom chemistry of carbon in aliphatic and aromatic amines, Schrod and Libby thermal-neutron irradiated an 8 mole-% solution of aniline in benzene. For the first time, several ¹⁴C-containing compounds, in addition to
benzene-$^{14}$C, were identified. The radiochemical yield of $^{14}$C-labeled benzene, toluene, diphenylmethane, and triphenylmethane were found to be 2.5, 1.7, 3.2, and 2.1%, respectively. In the same year, Wolf, Gordon and Anderson$^{36}$ studied the same system using 2-methylpyrazine as the nitrogen source; the yields of benzene-$^{14}$C and toluene-$^{14}$C were 1.92 and 1.05%. Perhaps the most important result in this paper was the finding that 12% of the activity was incorporated into the aromatic ring of toluene. A later paper of Wolf's$^{37}$ on the benzene system reported 2.6 and 2.25% respectively for the yield of labeled benzene and toluene.

The radiocarbon-labeled product distribution resulting from the (n,2n) activation of carbon-12 in benzene was thoroughly studied by Suryanarayana and Wolf$^{38}$ in 1958. About 4.5 and 2.2% of the total $^{11}$C activity produced were found in benzene and toluene, respectively. Furthermore, added radical scavengers decreased the yield of benzene-$^{11}$C but did not significantly affect the formation of toluene-$^{11}$C. Change of phase from liquid to solid showed the same effect. The implication was that at least some of benzene-$^{11}$C was produced via thermal reactions involving free radicals while toluene-$^{11}$C and some of benzene-$^{11}$C were formed through the hot process. The $^{14}$C distribution in toluene-$^{14}$C obtained from irradiation of benzene-2-methylpyrazine was then determined by Visser et al.$^{39}$ The results are shown on the following page.

In 1961 Mullen,$^{18}$ by using the ion accelerator, showed the ring-methyl activity distribution of the toluene-$^{14}$C obtained from the $^{14}$C+-benzene system to be similar to that observed by
Wolf. The essential equivalence of the recoil and the ion accelerator techniques was therefore indicated. Further, Mullen found the presence of labeled cycloheptatriene, allene, propyne, 1,2-butadiene, 1,3-butadiene, 1 and/or isobutane, 1-butyne, and trace amounts of n-butane.

Voigt and coworkers\textsuperscript{40,41} have studied the hot-atom chemistry of benzene by the labeled acetylene formation. The $^{12}\text{C}(\gamma,n)^{11}\text{C}$ reaction was used. The results were in agreement with a mechanism involving the insertion of an energetic $^{11}\text{C}$ or $^{11}\text{CH}$ into a C-H bond followed by the fragmentation of the resulting intermediate. An investigation involving three phases (solid, liquid and gas), neon moderation, and the presence or absence of oxygen was reported in 1967 by Rose et al.\textsuperscript{42} The yields of benzene, toluene, and cycloheptatriene were comparable to the previous data. An increase in polymeric products were observed in the neon moderated system. It was found that the reactivity of benzene was comparable to that of oxygen, which was, in turn, similar to that of the alkenes (toward hot carbon).

The most recent and detailed study of the carbon-benzene system was carried out by Williams and Voigt\textsuperscript{43} where $^{11}\text{C}$ recoiling was
examined in liquid benzene, toluene, and p-xylene (with and without scavenger). Labeled methane, acetylene, allene, methylacetylene, vinylacetylene, diacetylene, benzene, toluene, cycloheptatriene, o-m- and p-xylene, ethylbenzene, styrene and phenylacetylene were found in benzene. The yields of benzene, toluene, cycloheptatriene and phenylacetylene were 3.54, 2.64, 3.19 and 1.9%, respectively. The mechanism was discussed in terms of insertion-fragmentation of C atom, and the C-H insertion of CH₂.

It may be worthwhile to mention that the reaction of thermal carbon with benzene was reported by Sprung et al. 22 in 1965. Here the thermal carbon was produced by electrically heating a spectrographic quality carbon rod. The exposure of solid benzene (liquid nitrogen temperature) to carbon vapor gave both toluene and cycloheptatriene.

E. The Purposes of this Research

The reaction of hot carbon atom with benzene is by no means well understood. The mechanism of the formations of the major known products (benzene, toluene and cycloheptatriene), the nature of intramolecular activity distribution, the paths to particular products, the energy dependence of products formation, and the nature of possible high molecular weight (7C₁₃) products, etc., are still to be disclosed.

Part of this work was concerned with the identification of major aromatic products with more than six carbons. No attempt was made
to study the products smaller than C₆, although, for the reason discussed later, the existence of C₆ hydrocarbons was checked thoroughly. Gas-liquid partition chromatography (glc) and several chemical reactions were used in this study.

In order to study the energy requirement for the reactions leading to product formations, the yield of all identified major products was determined in the kinetic energy range, of the irradiating ¹⁴C⁺ ions, between 5 - 5000 eV. Carbon-14 atoms, instead of ions, were used in some experiments.

The total degradation of toluene-¹⁴C obtained from the ¹⁴C⁺-benzene reaction was the main goal of this research. This was carried out with at least two different procedures. The partial degradation of all known products was also investigated.
II. IRRADIATION, PRODUCT IDENTIFICATION, AND YIELD DETERMINATION

A. Irradiations

The earlier arrangement of the ion accelerator was described by Mullen. The detailed description, operation, and discussion of the modified accelerator will be found in the Ph.D. Thesis (1969) of H. Pohlit. The schematic drawing is shown in Figure 1. The ion source is a low voltage capillary arc type. The $^{14}$CO$_2$ (admixed with He) is introduced into the ion source from a low pressure supply system. A constant beam of accelerated electrons produced by a hot tungsten filament then ionizes the molecules. The ions are extracted, focused on a slit, accelerated in an electric field, and separated by the magnetic field. The purified $^{14}$C$^+$ beam is then focused and allowed to impinge upon target solid benzene which is coated on a cold finger at liquid nitrogen temperature. A constant stream of benzene vapor is fed into the target area through a low pressure supply unit during the irradiation so that only the flesh surface of benzene is exposed to the irradiating ions. For the low energy ion and the neutral-atom irradiations, the ions are decelerated by a decelerating lens, and neutralized by grazing a metal surface before reaching the target.

All the irradiations were performed by H. Pohlit and W. Erwin. Table II lists all the irradiations and their relevant conditions.
SCHEMATIC DRAWING OF 10 KV - ION ACCELERATOR

Figure 1
<table>
<thead>
<tr>
<th>No. of Irradiation</th>
<th>Energy eV</th>
<th>Species</th>
<th>Time hr:min</th>
<th>Ion or atom beam, μA</th>
<th>Benzene input, λ</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5000</td>
<td>$^{14}\text{C}$</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>a</td>
</tr>
<tr>
<td>2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>a</td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>&quot;</td>
<td>4:00</td>
<td>0.8 - 1.1</td>
<td>360</td>
<td>a, c</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>&quot;</td>
<td>2:45</td>
<td>0.75 - 1</td>
<td>200</td>
<td>a</td>
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<tr>
<td>5</td>
<td>&quot;</td>
<td>&quot;</td>
<td>3:00</td>
<td>1 ± 0.2</td>
<td>450</td>
<td>a</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>&quot;</td>
<td>1:00</td>
<td>0.8 - 1.2</td>
<td>140</td>
<td>b</td>
</tr>
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<td>7</td>
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<td>&quot;</td>
<td>0:45</td>
<td>1</td>
<td>80</td>
<td>b</td>
</tr>
<tr>
<td>8</td>
<td>15000</td>
<td>&quot;</td>
<td>0:55</td>
<td>0.8 - 1.2</td>
<td>170</td>
<td>a, b</td>
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<td>9</td>
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<td>&quot;</td>
<td>0:44</td>
<td>1</td>
<td>170</td>
<td>a, b</td>
</tr>
<tr>
<td>10</td>
<td>5000</td>
<td>&quot;</td>
<td>1:07</td>
<td>1</td>
<td>160</td>
<td>a, b, spread beam</td>
</tr>
<tr>
<td>11</td>
<td>&quot;</td>
<td>&quot;</td>
<td>1:00</td>
<td>0.9 - 1.4</td>
<td>320</td>
<td>toluene used instead of benzene</td>
</tr>
<tr>
<td>12</td>
<td>&quot;</td>
<td>$^{14}\text{C}$</td>
<td>1:00</td>
<td>1</td>
<td>120</td>
<td>a</td>
</tr>
<tr>
<td>13</td>
<td>&quot;</td>
<td>&quot;</td>
<td>1:00</td>
<td>1</td>
<td>250</td>
<td>a, b</td>
</tr>
<tr>
<td>14</td>
<td>&quot;</td>
<td>&quot;</td>
<td>1:05</td>
<td>--</td>
<td>400</td>
<td>a, b</td>
</tr>
<tr>
<td>15</td>
<td>&quot;</td>
<td>&quot;</td>
<td>1:05</td>
<td>1.5</td>
<td>370</td>
<td>b</td>
</tr>
<tr>
<td>16</td>
<td>&quot;</td>
<td>$^{14}\text{C}^+$</td>
<td>3:00</td>
<td>1.5</td>
<td>200</td>
<td>c</td>
</tr>
<tr>
<td>17</td>
<td>200</td>
<td>&quot;</td>
<td>1:00</td>
<td>0.8</td>
<td>140</td>
<td>c</td>
</tr>
<tr>
<td>18</td>
<td>5000</td>
<td>$^{12}\text{C}$</td>
<td>2:00</td>
<td>0.4 - 0.8</td>
<td>150</td>
<td>check $^{12}\text{C}$ products</td>
</tr>
<tr>
<td>19</td>
<td>0</td>
<td>$^{14}\text{C}^+$</td>
<td>0:15</td>
<td>--</td>
<td>--</td>
<td>a, b</td>
</tr>
<tr>
<td>20</td>
<td>5000</td>
<td>&quot;</td>
<td>0:15</td>
<td>0.6</td>
<td>--</td>
<td>a</td>
</tr>
<tr>
<td>21</td>
<td>350</td>
<td>&quot;</td>
<td>0:15</td>
<td>0.2</td>
<td>--</td>
<td>b, c</td>
</tr>
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<td>Species</td>
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<td>Benzene input, l</td>
<td>Remarks</td>
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<td>49</td>
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<td>0.6</td>
<td>--</td>
<td>c</td>
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<tr>
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<td>--</td>
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<td>a, b</td>
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<td>--</td>
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</tr>
<tr>
<td>53</td>
<td>100</td>
<td></td>
<td>1:07</td>
<td>1.3 - 1.6</td>
<td>--</td>
<td>b, c</td>
</tr>
<tr>
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<td>31</td>
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<td>0.8 - 1.1</td>
<td>--</td>
<td>b, c</td>
</tr>
<tr>
<td>55</td>
<td>5</td>
<td></td>
<td>0:42</td>
<td>1.4</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

Remarks:  
- **a**: used in product identification  
- **b**: used in yield determination  
- **c**: used in degradation
After the irradiation, the product mixture was scraped off from the surface of the target cold finger into a small vial (1-2 cc) equipped with a rubber septem and a screw cap. The appropriate amounts of cold carrier compounds were then added by means of a syringe through the rubber septem. The stock solution thus obtained was stored in a dry-ice bath.

B. Product Identification

An aliquot of the sample mixture prepared as above was injected into a glc column. The peaks that emerged from the column were detected both with a mass detector (thermal conductivity) and a radioactivity detector (proportional counter). The match in the mass and radioactivity in a peak was taken as preliminary identification of a product. Series of chemical reactions were then used to confirm the nature of the compound.

For the better overall separation of the reaction mixture, the efficiency of several glc columns were checked. Figures 2 and 3 show the chromatogram of aliquot of reaction mixture obtained from FFAP, 1/4" x 10', and from Apiezon L (20% on chromosorb W, 1/4" x 10'). Figure 4 shows that chromatogram of the same sample mixture from CW20M, 15% on DMCS treated chromosorb W, 1/4" x 10'. CW20M was used in most of the analyses. Helium was used as carrier gas in glc (40 ml/min). The effluent was then mixed with the same amount of methane and was counted by proportional tube.
**Figure 2.** Glc tracing for an aliquot of IR-1 on FFAP. Temperature: programmed from 30° to 80° (10°/min), after 35 minutes, programmed again to 220°.
Figure 3. Glc tracing for an aliquot of IR-1 on Apiezon L. Temperature: programmed from 30° to 100° (10°/min), after 55 minutes, programmed again to 250°.
**Figure 4.** Glc tracing (without added carrier compound) for an aliquot of IR-1 on CW20M. Temperature: programmed from 45° to 250° (6°/min).
Each experiment, which will be described, was repeated several times, reproducibility thus being assured. Only a typical chromatogram will be presented for each experiment. In all cases, the smooth line of our glc traces represents mass (thermal conductivity) detection and the jagged line represents radioactivity (proportional counter) detection.

The preliminary experiments included the hydrogenation (see Figure 27) and bromination (Figure 5) of aliquots of irradiated samples, and the oxidation of individually trapped compounds.

The catalytic hydrogenations were performed conveniently using a "Parr hydrogenation" apparatus. A small test tube (3/8" x 3") was used as the reaction vessel. About 0.1 - 1 µl (or mg) of the sample, usually collected in a U-shaped capillary tube (or disposable pipette), was washed out with about 100 µl of suitable solvent (introduced into the capillary tube by means of a hypodermic syringe) into the test tube. A small quantity of catalyst (usually PtO₂, about 1 mg) was added. The tube was then connected to the apparatus using pressure tubing. The system was flashed five times with hydrogen, 2 atm of hydrogen was then introduced, and the tube shaken for the desired time.

1. Major Products

A CW20M (1/4" x 11', 5% Cu20M on DMCS-treated chromosorb W (70-80 mesh)) column was used in the glc. Since the "prebenzene" (compounds with shorter retention times than benzene) products
**Figure 5.** Glc tracing of IR-2 after bromination (on CN20M). Temperature: programmed from 45° to 250° (6°/min).
were previously examined by Mullen,\(^{18}\) they were not the concern of this investigation. Only the products which had molecular weight greater than benzene were extensively studied. The retention times on glc of the suspected products were checked on CW20M. The compounds checked were bicyclo(2.2.1)heptadiene, xylenes (o-, m-, and p-), ethylbenzene, benzo[cyclobutene, styrene, cyclooctatetraene, phenylacetylene, n- and isoalkylbenzenes, indene, benzocyclooctatetraene, biphenyl, diphenylmethane, triphenylmethane, o-phenyl-toluene, diphenylethane, stilbene, tropone, phenylcycloheptatriene and fluorene.

Figure 4 shows the radio tracing (no carrier except benzene) of an aliquot of sample from IR-1. The major activity peaks appearing after toluene were numbered as U-1 to U-5.

Upon bromine treatment (see Figure 5) of the aliquot of the reaction mixture, the destruction of cycloheptatriene, U-1, U-3(?), and U-5 was observed. The catalytic hydrogenation (Pt\(O_2\)) gave a similar result. Therefore, U-1 and U-5 were unsaturated hydrocarbons which reacted with bromine and hydrogen.

In order to obtain further information about the nature of the major products, an aliquot of the target material from IR-2 was cochromatographed with a carrier mixture of 3-phenylpropene (for U-1), hexylbenzene (for U-2), diphenylmethane (U-4) and phenylcycloheptatriene (U-5). Moreover, each fraction was trapped separately with a U-shaped capillary tube at liquid nitrogen temperature. Each purified compound was dissolved in 500 \(\lambda\) of toluene (used as cold carrier for benzoic acid) and was oxidized with basic
permanganate solution. The benzoic acid formed was isolated, purified by sublimation, methylated with diazomethane, repurified on glc (CW20M), and counted. The results are shown in Table III.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Starting specific activity calculated as toluene dpm/umole</th>
<th>Activity in methyl benzoate dpm/umole</th>
<th>% activity of methyl benzoate acid from parent compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-1 ((\phi C=CH))</td>
<td>0.97</td>
<td>0.34</td>
<td>35.5</td>
</tr>
<tr>
<td>U-2 ((\phi CHO))</td>
<td>1.67</td>
<td>1.22</td>
<td>73.2</td>
</tr>
<tr>
<td>U-4 ((\phi_2 CH_2))</td>
<td>4.02</td>
<td>4.35</td>
<td>100</td>
</tr>
<tr>
<td>U-5 ((\phi CH_T))</td>
<td>5.36</td>
<td>4.53</td>
<td>81.1</td>
</tr>
</tbody>
</table>

Toluene was added in all of the samples as the cold carrier for the product benzoic acid. Since the rate of reaction of toluene might be quite different from that of each individual compound, the last term "% of activity of methyl benzoate from parent compound" might not be meaningful. However, for qualitative purposes, this experiment served to indicate the presence of the \(\phi-C\) partial structure in U-1, U-2, U-4, and U-5.

The retention times of phenylacetylene, hexylbenzene (or indene), biphenyl, diphenylmethane, and phenylcycloheptatriene matched those of U-1, U-2, U-3, U-4, and U-5, respectively. Figure 6 shows the typical radio and mass tracing of the aliquot
Figure 6. Glc tracing (on CW20M) of IR-6.
from IR-5 (with added carriers). In order to prove the structures of these compounds, aliquots of each carrier (0.1 - 1 μ) were added to aliquots of the target material and injected on the glc column. The individual "peaks" were then collected with a capillary tube (a disposable pipette) which was connected to the exit of the glc through a rubber septum, the only exception was that phenylacetylene, the most volatile compound of this series, was trapped with a U-shaped capillary which was immersed in a liquid nitrogen bath. The collected, purified fractions were then subjected to confirmatory tests, such as hydrogenation, oxidation, halogenation, or hydrohalogenation.

a) Products other than U-2

Phenylacetylene. As shown in Figure 5, the activity in U-1 disappeared when the sample was treated with bromine and hydrogen (PtO₂ catalysis). The unsaturated character of this compound was clearly shown. At the time the sample from IR-3 was available, no other information about the structure of U-3 was known. Several unsuccessful attempts were made to trap this compound from glc without added carriers. It was not until IR-4 that the correspondence of retention time of phenylacetylene and U-1 was recognized. U-1 activity was then trapped with cochromatographed phenylacetylene and hydrogenated (PtO₂, 2 atm H₂ 15 min, in benzene), phenylacetylene was added to the hydrogenate and the solution analyzed with glc. As shown in Figure 7, the activity in U-1 was converted to ethylbenzene.
Figure 7. Glc tracing (on CW20M) of the trapped phenylacetylene (from IR-5) after hydrogenation. Temperature: 6 minutes at 80°, then programmed 8°/min to 250°.
Biphenyl and Tropone. There was an unfortunate incident in which a bottle of bibenzyl (1,2-diphenylethane) had been mislabeled as biphenyl. U-3 was not considered as biphenyl for quite some time since this erroneous "biphenyl" appeared on glc at phenylcycloheptatriene position. Later, the U-3 peak was found to match one of the impurities in an old benzene solution of 7-phenylcycloheptatriene. (The 7-phenylcycloheptatriene used in this experiment did not contain any detectable impurity on glc. Originally, this old benzene solution was obtained from dissolution of about 0.1 g pure 7-phenyl CHT in 1 ml of benzene and the solution left on the bench for several months; presumably the impurities were formed by photochemical decomposition of phenyl CHT). This impurity was then separated and purified on glc. It was not hydrogenated (PtO₂ 2 atm, 2 hrs) under normal conditions and the UV spectrum of this compound matched exactly with that reported for biphenyl. The mixed fusion of this compound with biphenyl from new bottle did not depress the melting point. The original bottle of biphenyl was found to be bibenzyl!

The U-3 activity was then cochromatographed with cold biphenyl and collected. The hydrogenation (PtO₂, 2 atm, H₂, 2,5 hrs) in benzene did not affect the nature of the activity. Figure 8 shows the tracing of the hydrogenated biphenyl. Further, the trapped biphenyl peak was reinjected on glc on SE30, Poropak Q, and Apiezon L. The matching of the mass and radioactivity was observed in all cases. Therefore, the activity in U-3 was established as biphenyl.
Figure 8. Gc tracing (on C42DM) of trapped biphenyl (from IR-12) after hydrogenation.
Temperature: 12 minutes at 75°, then programmed 10°/min to 200°.
As will be described later, most of the activity in U-2 was identified as benzaldehyde. If this implied that benzaldehyde was formed by the quenching of one of the key intermediates, phenylcarbene, by scavenging oxygen (from any O-containing compound), then it was similarly possible that oxygen might react with another intermediate, cycloheptatrienylidene to give tropone. The presence of tropone was therefore sought.

The tropone had a retention time on CW20M column similar to that of biphenyl. They also behaved similarly on SE30 column. When U-3 activity was collected with carrier biphenyl and tropone, and hydrogenated (Pd/C, 2 atm, H₂, 1 hr) in alcohol solution, about 1/2 of the activity was converted to cycloheptanone (see Figure 9). When the hydrogenation was repeated without added tropone, only biphenyl could be detected. Here, presumably, the resultant micro amount of cycloheptanone was adsorbed by the catalyst.

**Diphenylmethane.** From its retention time (RT) on the glc, it was thought that U-4 could be diphenylmethane; this compound was therefore used as a carrier. Rechromatography (glc) of this material showed only one major activity peak at diphenylmethane. The hydrogenation (PtO₂, 1 hr, 2 atm, H₂) in benzene solution with added hexylbenzene, spiro(6.6)tridecane, phenylcycloheptane, phenylbarrelane, and phenylcycloheptatriene gave a tracing shown in Figure 10. About 50% of the activity was retained as diphenylmethane.

When purified (on glc) diphenylmethane (with carrier) was oxidized with SeO₂ (see degradation) in a sealed tube, the activity was converted to benzophenone along with the added cold carrier.
Figure 9. Glc tracing (on CW20M) of trapped biphenyl-tropone peak (from IR-37) after hydrogenation. Temperature: 12 minutes at 70°, then programmed 6°/min to 200°.
Figure 10. Glc tracing (on CW20M) for trapped diphenylmethane (from IR-5) after hydrogenation. Temperature: 12 minutes at 100°, then programmed 10°/min to 250°.
Phenylcycloheptatriene. The activity tracing of U-5 matched that of the mass peak of synthesized 7-phenylcycloheptatriene \(^{46}\) (see synthesis). The U-5 was thus cochromatographed with carrier 7-phenylcycloheptatriene and collected. The rechromatography of this material on SE30, CW20M, and Apiezon L showed perfect matches of both mass and radioactivity peaks. When this sample was hydrogenated \((\text{PtO}, 2 \text{ atm}, 1 \text{ hr})\) in benzene, and 0.2 mg of 7-phenylcycloheptatriene added afterwards, the tracing shown in Figure 11 was obtained. Here, most of the activity was converted to phenylcycloheptane.

b) U-2

The identity of the compound U-2 had presented considerable difficulty. We had assumed that, although our \(^{14}\)C was produced from \(^{14}\)CO\(_2\), the ion accelerator was efficient enough to eliminate the participation of any oxygen-containing species (either from the ion beam itself or the diffusion of an O-containing molecule from the ion source). Our efforts at product identification were, therefore, concentrated on hydrocarbon products.

U-2 had a retention time close to n-hexylbenzene and indene; this was far longer than that of any known C\(_7\) compound. The rechromatography of the trapped U-2 (with hexylbenzene as a quasi-carrier) showed a 10% conversion into a volatile compound which had a retention time that corresponded to cycloheptatriene (this decomposed product was proved indeed to be cycloheptatriene by catalytic hydrogenation), (see Figure 12). The following experiments were carried out in the course of structural determination of U-2.
Figure 11. Glc tracing (on CN20M) for trapped phenylcycloheptatriene (from IR-3) after hydrogenation. Temperature: 6 minutes at 80°, then programmed 8°/min to 250°.
Figure 12. The reinjection of trapped U-2 activity (from IR-5) on CW20M. Temperature: 12 minutes at 100°, programmed 10°/min to 200°.
i) Bromination and hydrobromination. A solution of 100 \( \lambda \) benzene and a trapped (from glc) peak of U-2 and n-hexylbenzene was placed in a 3/8" x 3" test tube equipped with a rubber stopper, 1 ml of HBr (or 1 \( \lambda \) of bromine) was injected (using a syringe) into the tube. The solution was then shaken at room temperature for one hour. 0.5 \( \lambda \) each of benzylbromide and p-bromotoluene (or p-bromobenzylbromide) were added and the mixture was chromatographed on CW20M. No activity was found in any of the added bromo compounds, about 60% of the activity remained with the n-hexylbenzene.

ii) Hydrogenation. The hydrogenation of the trapped U-2 n-hexylbenzene peaks in a benzene solution (PtO\(_2\), 2 atm, \( \text{H}_2 \), 1 hr) gave toluene and methylcyclohexane in close to 1:1 ratio as shown in Figure 13. When this toluene peak was trapped and oxidized, radioactive benzoic acid was obtained. The methylcyclohexane was identified by its dehydrogenation to toluene. Thus, our initial assumption that U-2 was a hydrocarbon seemed established.

iii) Stability. In order to investigate whether the above hydrogenation products were really the products of the reaction, an aliquot of the sample (U-2 and n-hexylbenzene) was dissolved in 100 \( \lambda \) of benzene and was shaken up with 1 mg of PtO\(_2\) for 1 hour at room temperature (no \( \text{H}_2 \) was present). About 1/2 \( \lambda \) each of methylcyclohexane, toluene, and cycloheptatriene were then added and the whole mixture injected on glc (CW20M). The individual carrier peaks were trapped in a liquid scintillation counting solution and counted. No activity was found in toluene and methylcyclohexane peaks. About
Figure 13. Glc tracing (on CW20M) of trapped U-2 activity (from IR-5) after hydrogenation.
Temperature: 12 minutes at 100°C, then programmed 10°C/min to 200°C.
50% of the activity was found in the n-hexylbenzene fraction. It was interesting to see that a few percent of the activity was found in the CHT fraction.

The next experiment was to check the stability of U-2 at elevated temperature. U-2 activity was chromatographed and collected with n-hexylbenzene in a capillary tube. This tube was then sealed under helium and heated at various temperatures for 1 hour. One-half lambda each of methylcyclohexane, toluene, and CHT were again added and the mixture treated as above. The radioactivity was found only in the n-hexylbenzene fraction. Table IV summarizes the results.

<table>
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<tr>
<th>Activity of U-2(n-hex)$^<em>$ used, cpm$^</em>$</th>
<th>Condition</th>
<th>Time (hr)</th>
<th>Tol cpm$^*$</th>
<th>CHT cpm$^*$</th>
<th>U-2(n-hex)$^<em>$ cpm$^</em>$ after treatment</th>
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</thead>
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<td>10$^4$</td>
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<td>0</td>
<td>0</td>
<td>22</td>
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<tr>
<td>5 x 10$^3$</td>
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<td>0</td>
<td>0</td>
<td>31</td>
</tr>
<tr>
<td>1.4 x 10$^3$</td>
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<tr>
<td>3 x 10$^3$</td>
<td>250° sealed tube</td>
<td>1</td>
<td>0</td>
<td>0</td>
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</tr>
</tbody>
</table>

* Above background (about 20 cpm)

** Low recovery, probably due to the absorption by PtO$_2$
The toluene and methylcyclohexane from hydrogenated U-2 could have three possible origins: 1) It could be formed from the C_{7}H_{6}; the attack of hydrogen on different sites of the molecule leading to either the toluene or methylcyclohexane, 2) the hydrogenolysis of a U-2 which has more than seven carbons, and 3) the hydrogenolysis of an oxygen-containing U-2. 2) was unlikely because fragmentation of a hydrocarbon by hydrogenolysis was unknown to us. There was nothing against 3) except our strong belief that the participation of oxygen-containing species was not to be expected. Although the retention time of U-2 was far longer than any known C_{7} compound, there was slight hope that U-2 could indeed be C_{7}H_{6}. Benzocyclopropene was the obvious choice since it gave toluene, methylcyclohexane and cycloheptane on hydrogenation. The possibility of U-2's being this compound was eliminated by cochromatography with the authentic sample,\textsuperscript{47,*} and by thermostability test.

iv) Attempted synthesis. Consideration of possible reaction mechanisms suggested that methylene and phenylcarbene\textsuperscript{42} might be a precursor of U-2. A promising approach was to simulate the reaction which hopefully had taken place in the bombardment of benzene with \textsuperscript{14}C\textsuperscript{+}. Methylene and phenylcarbene were, therefore, generated in benzene solution and the product analyzed. No U-2 was found when methylene was generated by mean of Simmon-Smith reagent\textsuperscript{65} (CH_{2}X_{2}, Ag-Cu). The generation of phenylcarbene in benzene solution was

\textsuperscript{*}Kindly provided by Professor E. Vogel of the Institut für Organische Chemie der Universität Köln, Germany.
investigated as follows: a 0.1 M benzene solution of stilbene oxide or phenyldiazomethane was irradiated in a Vycor flask with a high pressure mercury vapor lamp (A-H6) for four days at a distance of approximately 10 inches. The glc of the resulting mixture indicated the presence of about 1% toluene, 4% of U-2-like compound, and 3% of phenylcycloheptatriene. This U-2-like compound was isolated (from glc), and purified by repeated glc. The hydrogenation of this compound gave only small amounts (about 1%) of toluene and methylcycloheptane. The structure of this compound was found to be benzaldehyde from the mass spectrometry (parent ion at 106). It was hard for us to believe that benzaldehyde could be easily hydrogenated to toluene and methyl cyclohexane (1 hr, 2 atm, PtO2 in pentane). Nevertheless, the possibility of U-2 as benzaldehyde was investigated as follows:

When benzaldehyde was added to an aliquot of the target material an exact match of the RT with U-2 was observed. The rechromatography of the trapped U-2 activity and benzaldehyde (from CW20M) on various columns (CW20M, SE30, FFAP, Polapak Q and Apiezon L) again showed perfect matches of the mass and the major activity peak.

The U-2 activity was then trapped with benzaldehyde, and hydrogenated (PtO2, 2 atm, H2, 1 hr) in benzene. The activity was found in benzyl alcohol. However, no appreciable amount of toluene nor methylcyclohexane was observable (see Figure 14).

Figure 15 shows the tracing of a partially hydrogenated sample (PtO2, 2 atm, H2, 15 min) of U-2 (cotrapped with n-hexylbenzene) in
Figure 14. Glc tracing (on CW20M) of trapped U-2 activity (benzaldehyde as carrier, from IR-37) after hydrogenation. Temperature: 12 minutes at 70°, then programmed 6°/min to 200°.
Figure 15. Glc tracing (on CW20M) for the trapped U-2 activity (from IR-29-32) after partial hydrogenation. Temperature: 12 minutes at 75°, then programmed 10°/min to 200°.
pentane solution. Here, the carrier compounds (1/2 \( \lambda \) each), methyl-
cyclohexane, toluene, and benzyl alcohol were added after the hydro-
genation. The activities were found in all four compounds.

When U-2 was collected with hexylbenzene from CW20M and the
trapped material was cochromatographed with benzaldehyde on Apiezon
L, the tracing shown in Figure 16 was obtained. Again, about 10%
of the activity appeared before the main peak (notice that counting
sensitivity for the first peak was greater, 3000 cpm full-scale
deflection, while that of the benzaldehyde was less, 10,000 cpm
full-scale deflection). The hexylbenzene was well separated from
benzaldehyde.

In order to check the nature of the main activity in Figure 16,
this peak was trapped and reinjected on the same column. This
time, the activity was found only in benzaldehyde (see Figure 17).
Furthermore, only benzyl alcohol was obtained when this fraction
was hydrogenated.

The air oxidation of U-2 was also studied: The U-2 activity
was cotrapped with carrier benzaldehyde in a capillary tube which
was allowed to stand for two days. The material in the capillary
was washed out with ether and then methylated with diazomethane.
The solution was gas chromatographed on CW20M. The methylbenzoate
and benzaldehyde were trapped in a liquid scintillation solution
and were counted. Most of the activity (80\%) originally in benz-
aldehyde was found in the benzoate.

Thus, the side product in our attempted synthesis of the un-
known compound resulted in the breakthrough in the structural
Figure 16. The reinjection of the U-2 activity (from IR-29-32) on Apiezon L. Temperature: programmed from 75° to 225° (10°/min).
Figure 17. The reinjection of the trapped benzaldehyde activity in Figure 16 on Apiezon L. Temperature: 7.5 minutes at 150°, then programmed 10°/min to 200°.
determination of the major portion of the U-2 peak.

As can be seen in Figures 12 and 16, about 10% of the activity, from a reinjection of the U-2 peak trapped with hexylbenzene, appeared slightly after toluene. There is also some activity with an identical RT as that of cycloheptane in hydrogenated U-2 (barely before the benzene peak; see Figures 13, 14 and 15). Furthermore, Table IV showed the appearance of trace activity in cycloheptatriene. Therefore, the first peak in Figure 16 was trapped and rechromatographed with added methylcyclohexane and toluene. Figure 18 shows that this activity did not match with either compound. When it was chromatographed with methylcyclohexane, toluene, and cycloheptatriene, a perfect match of the activity with cycloheptatriene was observed (see Figure 19). Finally, the confirmation of this result (the identity of the peak as CHT) was obtained by the hydrogenation of trapped activity (along with carrier cycloheptatriene, PtO₂, 2 atm, H₂, 40 min in pentane). Toluene and cycloheptatriene were added after the hydrogenation. The glc trace is shown in Figure 20. The cycloheptatriene activity was clearly converted to cycloheptane.

2. Minor Products and the Compound Sought

When styrene and cyclooctatetraene, along with carriers of other known compounds were added to an aliquot of the target, the glc tracing shown in Figure 21 was obtained. These two compounds were then collected and hydrogenated separately. Figure 22 shows the glc tracing of the hydrogenated styrene fraction. The activity originally in styrene was converted to ethylbenzene. The styrene
Figure 18. The reinjection of the trapped minor activity peak in Figure 16 on Apiezon L. Temperature: 150°.
Figure 19. The reinjection (with added carrier cycloheptatriene) of the trapped minor activity peak in Figure 16 on Apiezon L. Temperature: 125°.
Figure 20. Glc tracing (on CW20M) for the minor activity peak in Figure 16 (co-trapped with cycloheptatriene) after hydrogenation. Temperature: 80°.
Figure 21. Glc tracing for an aliquot of IR-8 (with added carriers) on CW20M. Temperature: 12 minutes at 75°, then programmed 10°/min to 225°.
Figure 22. Glc tracing (on CW20M) for the trapped and hydrogenated styrene fraction. Temperature: 12 minutes at 70°, then programmed 6°/min to 200°.
was, therefore, known to be formed. The similar glc injection of hydrogenated cyclooctatetraene gave no activity under the cyclo- octane peak. However, as will be described later, this compound could be formed with an upper limit yield of 0.074%.

The possible appearances of naphthalene, benzobarrelene,* and benzocyclooctatetraene* were also investigated. The result is shown in Figure 23. These three compounds were trapped individually and were hydrogenated. No activity was found in the naphthalene fraction. The major portion of the activity under benzobarrelene and benzocyclooctatetraene did not match the hydrogenated analogs as shown in Figures 24 and 25.

The finding of benzaldehyde and tropone have promoted our effort to find the existence of other oxygenated products, such as formaldehyde, trioxane, benzoic acid, and phenol. Only phenol was found to be formed (about 0.5% of incident 14C+ ions, the identity was confirmed by the catalytic hydrogenation to cyclohexanone and cyclohexanol).

The existence of o-phenyltoluene, bicycloheptadiene, indene, fluorene, and triphenylmethane were also investigated. None was detectable except that small amount (maximum of 0.04%) o-phenyltoluene might be formed.

The possibility for the existence of methylcyclopentane, n-hexane, and cyclohexane in the hydrogenated sample was also carefully examined. Figure 26 shows the tracing of the hydrogenated

*Kindly provided by Professor M. Stiles of the University of Michigan and Professor L. Friedman of Case Western Reserve University.
Figure 23. Glc tracing (on CW20M) of an aliquot of IR-37 with added naphthalene, benzobarrelene, and benzocyclooctatetraene. Temperature: 12 minutes at 70°, then programmed 6°/min to 200°.
Figure 24. Glc tracing (on CW20M) of the trapped benzobarrelene (from Figure 23) after hydrogenation. Temperature: 12 minutes at 70°, then programmed 6°/min to 200°.
Figure 25. Glc tracing (on CW20M) of the trapped benzocyclooctatetraene (from Figure 23) after hydrogenation. Temperature: 12 minutes at 70°, then programmed 10°/min to 200°.
Figure 26. Glc tracing (on G20M) of the pre-benzene compound after hydrogenation. Temperature: 75°.
sample with the added unlabeled carriers. No activity was found in these compounds. These were confirmed by reinjection of individually trapped peaks on suitable glc columns. Similar experiments showed the absence of n-heptane, n-hexane, and 3-methylpentane in the hydrogenated aliquot.

3. Products from the Hydrogenation of the Product Mixture

The catalytic hydrogenation of the aliquot of the reaction mixture showed the appearance of abundant distinct peaks which were not observed prior to hydrogenation. Besides methylcyclohexane, cycloheptane, ethylbenzene and phenylcycloheptane (which were derived from the known major unsaturated compounds), there were many peaks rather close to C₃ - C₇ alkylbenzenes. This was reasonable because of the possible formation of the corresponding C₃ - C₇ fragments, or the possible fragmentation of the [φ-C₇Hₓ]⁺ species.

Figure 27 shows the mass and radio tracings after the entire target material was hydrogenated (PtO₂, 2 atm, 1 hr in benzene) with 1/2 λ each of added n-propyl-, n-butyl-, n-pentyl-, n-hexyl-, and n-heptylbenzene. Some coincidences of mass and radioactivity are observable.

Spiro(6,6)tridecahexaene could have been formed by the insertion of cycloheptatrienylidene into a C-C bond of benzene. However, this compound has not been reported in the literature. Therefore, the corresponding hydrogenated form spiro(6,6)tridecane
Figure 27. Glc tracing (on CW20M) for the hydrogenated aliquot from IR-4. Temperature: 6 minutes at 80°, then programmed 10°/min to 250°.
was synthesized and checked. The hot acetylene and/or its derivative could be expected to perform Diels-Alder condensation to give corresponding barrelenes. Thus barrelane, methylbarrelane and phenylbarrelane were also checked.

A hydrogenation with added methylcyclohexane, bicyclo(2.2.1)-heptane, cycloheptane, barrelane, methylbarrelane, spiro(6.6)tridecane, and phenylbarrelane gave a tracing shown in Figure 28. The result seems to be less appealing. Nevertheless, a search was made for all these compounds in the hydrogenated sample:

To 335 A of the reaction mixture from IR-25, 30 A each of methylcyclohexane, cyclooctane, propylbenzene, butylbenzene, amylbenzene, hexylbenzene, heptylbenzene, o-phenylbenzene, and phenylbarrelane, and 30 mg each of barrelane, methylbarrelane, bicyclo(2.2.1)-heptane, and spiro(6.6)-tridecane were added. This mixture was hydrogenated (PtO₂, 2 atm, H₂) for 2 hours at room temperature. The compounds were separated by a "Prep Master" glc on CW20M (70° for 30 min, 2.5°/min to 230°, hold) and trapped in a "U" tube at -196°. They were separately purified by rechromatography on various columns until the specific activities were constant or nearly constant. The results are listed in Tables V and VI.

4. The Hydrogenation of Between-Peak Areas

In order to study the nature of the compounds that appeared on the glc between major peaks, the activities of these fractions were collected and hydrogenated individually. The identity of the product molecules were assigned only by comparison of retention times.
Figure 28. Glc tracing (on CM200) for the hydrogenated aliquot from LB-5. Temperature: 75°C, then programmed 10°C/min to 200°C.
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(A pool of sample was prepared from PrepMaster on SE30.)

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#### n-Heptylbenzene

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#### o-Phenyltoluene

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*These weights are reliable only to ± 10 µg.

a) Between Cycloheptatriene and Phenylacetylene

The activity appeared between cycloheptatriene and phenylacetylene peaks were trapped with an U-shaped capillary tube at liquid nitrogen temperature, about 1 λ each of carriers were added and the mixture hydrogenated. The result is shown in Figure 29. The activities were found under the mass peaks of methylcyclohexane, cycloheptane, benzene, toluene, and ethylbenzene.
Figure 29. Glc tracing (on CW20M) for the trapped activity eluted out between phenylacetylene and cycloheptatriene (from IR-5) after hydrogenation. Temperature: 6 minutes at 80°, then programmed 8°/min to 250°.
Table VI. The yields or upper limits of yields (U.L.) of the products from hydrogenation of the irradiation sample.

<table>
<thead>
<tr>
<th>Compound</th>
<th>% Yield*</th>
<th>Compound</th>
<th>% Yield*</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Propylbenzene</td>
<td>0.46</td>
<td>n-Butylbenzene</td>
<td>0.63</td>
</tr>
<tr>
<td>~background (0.0005) U.L.</td>
<td></td>
<td>Amylbenzene</td>
<td>0.44</td>
</tr>
<tr>
<td>0.004 (U.L.)</td>
<td></td>
<td>Hexylbenzene</td>
<td>0.72</td>
</tr>
<tr>
<td>0.055 (U.L.)</td>
<td></td>
<td>Neptylbenzene</td>
<td>0.91</td>
</tr>
<tr>
<td>Spiro(6,6)tridecane</td>
<td>0.033 (U.L.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.074</td>
<td></td>
<td>o-Phenyltoluene</td>
<td>0.039 (U.L.)</td>
</tr>
</tbody>
</table>

*Based on total activity incorporated during irradiation.

b) Between Benzaldehyde and Biphenyl

The activity eluted off between benzaldehyde and biphenyl from glc was similarly trapped. The injection of the trapped material with added cold carrier showed the presence of an impressive amount of cycloheptatriene (see Figure 30). When an aliquot of the same sample was hydrogenated with added cold carriers, a chromatogram similar to that of hydrogenated total irradiated solution was obtained (Figure 31). The existence of cycloheptatriene was further confirmed by trapping and hydrogenation to cycloheptane.
Figure 30. The reinsertion of the trapped activity between U-2 and biphenyl (from IR-29-32), on CN20H. Temperature: 6 minutes at 75°, then programmed 10°/min to 200°.
Figure 31. Glc tracing (on CW2OM) for the aliquot used in Figure 30, after hydrogenation.

Temperature: 6 minutes at 80°, then programmed 10°/min to 250°.
C. The Yield Determinations

The yield of the individual major products were determined by injecting an aliquot of the target material (with added carrier) into the glc, trapping each compound by bubbling the effluent compound into a counting vial containing liquid scintillation solution, and counting the trapped activity. The yields were calculated from the total recovered activity which was determined by liquid scintillation counting of a known volume of an aliquot of the original sample. The detailed description and discussion are presented in the Ph.D. thesis (1969) of H. Pohlit. 44

The yields of the major products, as a function of different kinetic energies and charge states of the irradiating carbon are listed in Table VII.
Table VII. Effect of charge and energy on the incorporation of $^{14}$C into products

<table>
<thead>
<tr>
<th>Energy and charge state$^a$</th>
<th>Benz.</th>
<th>Tol.</th>
<th>CHT</th>
<th>$\phi$C $\phi$H</th>
<th>U-2</th>
<th>$\phi$-$\phi$</th>
<th>$\phi$-CH$_2$-$\phi$</th>
<th>$\phi$-CHT</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 KeV $^{14}$C$^+$ ion</td>
<td>3.6+0.2</td>
<td>1.5+0.3</td>
<td>4.1+0.2</td>
<td>2.0+0.2</td>
<td>2.4+0.3</td>
<td>1.3+0.2</td>
<td>2.3+0.2</td>
<td>5.8+0.6</td>
</tr>
<tr>
<td>5 KeV $^{14}$C$^+$ ion</td>
<td>4.2+0.2</td>
<td>1.3+0.1</td>
<td>3.3+0.2</td>
<td>2.1+0.1</td>
<td>3.4+0.2</td>
<td>---</td>
<td>2.4+0.4</td>
<td>6.3+0.3</td>
</tr>
<tr>
<td>5 KeV spread $^{14}$C$^+$ ion beam</td>
<td>4.4+0.2</td>
<td>1.5+0.1</td>
<td>3.3+0.2</td>
<td>2.1+0.1</td>
<td>3.4+0.2</td>
<td>2.1+0.1</td>
<td>2.3+0.1</td>
<td>6.0+0.2</td>
</tr>
<tr>
<td>5 KeV $^{14}$C atoms</td>
<td>3.4+0.4</td>
<td>1.0+0.1</td>
<td>2.5+0.3</td>
<td>1.6+0.4</td>
<td>2.6+0.8</td>
<td>1.3+0.2</td>
<td>1.5+0.1</td>
<td>5.3+1.8</td>
</tr>
<tr>
<td>1.5 KeV $^{14}$C$^+$ ion</td>
<td>5.7+0.2</td>
<td>1.3+0.1</td>
<td>2.9+0.1</td>
<td>2.3+0.2</td>
<td>4.1+0.3</td>
<td>2.3+0.6</td>
<td>2.5+0.4</td>
<td>5.5+0.4</td>
</tr>
<tr>
<td>0.5 KeV $^{14}$C$^+$ ion</td>
<td>4.8+0.2</td>
<td>1.0+0.1</td>
<td>2.3+0.1</td>
<td>2.2+0.1</td>
<td>5.1+0.3</td>
<td>1.7+0.2</td>
<td>2.8+0.1</td>
<td>6.0+0.2</td>
</tr>
<tr>
<td>0.5 KeV $^{14}$C atoms</td>
<td>3.7+0.2</td>
<td>0.9+0.1</td>
<td>1.8+0.1</td>
<td>1.9+0.1</td>
<td>5.5+0.1</td>
<td>2.5+0.1</td>
<td>1.9+0.3</td>
<td>5.5+0.5</td>
</tr>
<tr>
<td>0.1 KeV $^{14}$C$^+$ ion</td>
<td>5.7+0.2</td>
<td>1.1+0.1</td>
<td>2.2+0.1</td>
<td>3.1+0.1</td>
<td>8.3+0.5</td>
<td>2.9+0.5</td>
<td>3.8+0.1</td>
<td>6.6+0.2</td>
</tr>
<tr>
<td>31 eV $^{14}$C$^+$ ion</td>
<td>2.8+0.2</td>
<td>0.5+0.1</td>
<td>1.1+0.1</td>
<td>1.4+0.1</td>
<td>4.5+0.1</td>
<td>1.3+0.2</td>
<td>2.7+0.3</td>
<td>5.9+0.3</td>
</tr>
<tr>
<td>5 eV $^{14}$C$^+$ ion</td>
<td>2.6</td>
<td>0.2+0.1</td>
<td>0.5+0.1</td>
<td>0.3+0.1</td>
<td>5.5+1.5</td>
<td>1.6+0.2</td>
<td>2.2+0.1</td>
<td>4.6+0.1</td>
</tr>
<tr>
<td>4 KeV $^{14}$C$^+$ + O$_2$</td>
<td>4.2</td>
<td>1.2</td>
<td>3.3</td>
<td>2.1</td>
<td>2.1</td>
<td>1.6</td>
<td>2.8</td>
<td>6.8</td>
</tr>
</tbody>
</table>
III. DEGRADATIONS

A. Degradation of Toluene

1. Total Degradation

   a) Introduction

   The degradation of toluene and/or alkylbenzenes has been used in the mechanistic study of the toluene formation in the hot reaction of carbon with benzene\(^{39,50}\) and the study of the rearrangement of alkylbenzenes\(^{52,54}\). On the surface, these appeared to be suitable for our degradation. Unfortunately, because of the limited source of our toluene sample (a few tenths of a microcurie per 10 hour irradiation), only that via reduction was used in actual degradation.

   Mullen\(^{18}\) described a rather tedious procedure involving oxidation of toluene to benzoic acid and subsequent Schmidt reaction of the benzoic acid; the aniline obtained was converted to phenol, cyclohexanol, and cyclohexanone. Three different sequences of reaction were then used in the degradation of the phenol, cyclohexanol, and cyclohexanone to obtain the activity distribution in the aromatic ring. This method was not attempted because of its complicated sequences and poor yields of the reactions.\(^{49}\)
Figure 33. Degradation of toluene via heptanoic acid.
This scheme has some advantages: (1) Most of the intermediate compounds are sufficiently volatile and can be purified by glc, thus, maximum purifications can be obtained. (2) Fair yields are obtained in most of the reactions, except in the KOH fusion of the heptenoic acid (about 30%). The yield of carbon at the para position was about 3%, i.e., this method can be used on a toluene sample of total activity of about two tenths of a microcurie. This method was checked with toluene-1\(^{14}\)C and was applied successfully to a sample with an activity as low as 1.3 \(\times\) 10\(^5\) dpm.

When 6-keto-n-heptanoic acid was converted to the oxime, a Beckmann rearrangement\(^{55}\) of the oxime gave a quantitative yield of 5-acetamidopentanoic acid; hydrolysis of the latter with dilute \(\text{H}_2\text{SO}_4\) gave, again, a quantitative yield of acetic acid and the corresponding amino acid which can be oxidized easily to glutaric acid.

A reasonable scheme of degrading glutaric acid could, therefore, provide a simple route for our degradation. The possibility of the degradation of glutaric acid was investigated; the attempts included the conversion of glutaric acid to malonic acid, 1,3-propanedihalide, and 1,3-propanediamine.

i) Barbier-Wieland degradation:\(^{56}\) The glutaric acid was methylated and treated with phenyl lithium; the diol obtained was then dehydrated to the diene\(^{57}\) as the following:
The oxidation of 1,1,5,5-tetraphenyl-1,4-pentadiene was attempted using KMnO₄, NaIO₄, O₃, and UV-O₂ oxidations. This scheme of degradation was abandoned since no suitable oxidation condition was found for the tetraphenylpentadiene.

ii) Hundsdiecker decarboxylation: When the disilver salt of glutaric acid was refluxed with bromine and iodine in various solvents, only trace amounts of dihalide were obtained. The adoption of a modified method did not improve the result.

iii) Photochemical decarboxylation: Barton et al. reported that when glutaric acid was irradiated (with 300 W tungsten lamp for 3 hours) and refluxed in benzene-sulpholan solution with t-butylhypoiiodite, as high as 85% CO₂ and 69% of diiodide were obtained. However, we were only able to obtain about 30% of diiodide. Although the diiodide could be hydrolyzed and then oxidized to malonic acid in about 50% yield, this route was given up due to the low yield of diiodide, and the difficulty of purification. The intended degradative scheme is shown as below:
iv) Schmidt degradation: In an alternative way, glutaric acid was decarboxylated by the Schmidt method to carbon dioxide and trimethylenediamine. By varying the ratio of HN₃ to glutaric acid, we were able to obtain up to 60% diamine. This was attractive, provided that the degradation of the diamine was feasible. Various attempts were made to convert the diamine to the corresponding diacid, i.e., malonic acid. Amines are known to react with hypo-halite to give N,N-dihalo compounds, whose subsequent dehydrohalogenation affords cyano compounds which can be hydrolyzed to the carboxylic acids:

However, these reactions were not successful for our diamine.

We also tried the oxidation of the amine to oxime, followed by hydrolysis and oxidation to a carboxylic acid:
This reaction also failed; we were unable to identify the oxime.

The direct oxidation of diamine was also attempted. The oxidation using Tollen's reagent resulted in a formation of explosive reaction mixture from which none of the useful acid was obtained. Only in the case of aqueous basic KMnO₄ oxidation were we able to isolate about 50% of oxalic acid. Therefore, this oxidation was adopted for our degradation of trimethylene diamine. The whole reaction scheme is shown in Figure 34.

Although the activity in C₃ and C₄ must be obtained from the subtraction of activity in oxalic acid from that of trimethylene diamine, this scheme has its advantages in its simplicity, in the relatively high total yield of individual carbons, and in the possibility of a complete purification of every intermediate compound by glc. One of the irradiated samples was degraded by this method, the other by the previously outlined route through heptanoic acid.

b) Experimental

i) Degradation of toluene-1-¹⁴C via Steinberg and Sixma's method: Nitrotoluene-1-¹⁴C: Toluene-1-¹⁴C (11.1 g, 16 dpm/µmole) was nitrated with an HNO₃-H₂SO₄ mixture, at 0°, as described by Sixma. The product was steam distilled, but the yield was not determined.
Figure 34. Degradation of toluene via glutaric acid.
Nitrobenzoic acid-1-^{14}C: To the steam distillate obtained above (nitrotoluene-1-^{14}C and about 100 ml of water), 100 ml of water was added, and the mixture was oxidized with alkaline KMnO₄. The yield of nitrobenzoic acids was 8.36 g (41.5% yield from toluene).

o- and p-Aminobenzoic acid-1-^{14}C: In a round-bottomed flask fitted with a reflux condenser were placed 8.36 g of nitrobenzoic acid-1-^{14}C, 12.4 g of cyclohexane, 168 ml of ethanol, and 250 mg of palladium black. The mixture was refluxed vigorously for 17 hours (during the heating, the initially-formed yellow color gradually disappeared). The mixture was cooled and the solvent evaporated by means of a rotating evaporator, under reduced pressure. The residue was extracted with ether and the ether extract was filtered and dried over 2 g of anhydrous MgSO₄. After the MgSO₄ was filtered off, dry HCl was bubbled into the solution until the precipitation of the aminobenzoic acid hydrochloride was complete. The white precipitate was filtered off and washed with anhydrous ether. The yield of hydrochlorides was 7.7 g (88.7%, from nitrobenzoic acid, and 36.8% from toluene).

Quinoline 8- and 6-carboxylic acid-8- and 6-^{14}C: To a 100 ml round-bottomed flask fitted with a reflux condenser a mixture of 7.7 g of aminobenzoic acid-1-^{14}C hydrochloride, 1.7 g of p-nitrobenzoic acid (inactive), 3.3 g o-nitrobenzoic acid (inactive), 1.6 g FeSO₄, 2.93 g boric acid, 23 g glycerol and 16 ml conc. sulfuric acid were added. The flask was heated in an oil bath at 150 - 160° for 2 hours. The reaction was stopped by removing the heating bath
when the mixture started to foam. Water (100 ml) and concentrated (16 N) ammonia were added until the mixture was strongly alkaline to litmus. The resinous material was then filtered off using a filter aid (10 g of Celite) and the filtrate was adjusted to pH 4-5. The precipitate that formed upon lowering the pH was again removed by filtration and the filtrate extracted for two days with chloroform (using a liquid-liquid extractor). Five g of crude quinoline carboxylic acid was obtained by evaporation of the chloroform. It was purified by fractional sublimation. 51

From 5 g of crude acid mixture, 1.5 g of quinoline-6-carboxylic acid (7.7% yield from toluene) and 2.6 g quinoline-8-carboxylic acid (12.0% yield from toluene) were obtained.

Quinoline-6-carboxylic acid-6\(^{14}\)C: 10.14 ± 0.06 dpm/µmole.

mp 280 - 284\(^\circ\)

Anal. calcd. for C\(_{10}\)H\(_7\)NO\(_2\): C, 69.36; H, 4.04; N, 8.09

Found: C, 69.21; H, 4.22; N, 8.1

Quinoline-8-carboxylic acid-8\(^{14}\)C: 10.21 ± 0.07 dpm/µmole

mp 186 - 189\(^\circ\)

Anal. calcd. for C\(_{10}\)H\(_7\)NO\(_2\): C, 69.36; H, 4.04; N, 8.09

Found: C, 69.09; H, 3.91; N, 8.31

There was a considerable decrease (16 dpm/µmole to 10.2 dpm/µmole) in the specific activity of the quinoline carboxylic acids. This was probably due to the dilution of the labeled aminobenzoic acids by the production of aminobenzoic acids from the nitrobenzoic acids used in the Skraup procedure. The nitrobenzoic acids were used in this
procedure to oxidize the intermediate dihydroquinoline carboxylic acids to quinoline carboxylic acids.

Quinolinic acid-1-carboxyl-$^{14}$C: 1.14 g of quinoline-8-carboxylic acid-8-$^{14}$C was oxidized with potassium permanganate as described by Sixma; 0.35 g of crude quinolinic acid-1-carboxyl-$^{14}$C was obtained. To aid in purification, 1 g of inactive quinolinic acid carrier was added. After 4 recrystallizations from water, 0.315 g of pure quinolinic acid was obtained, mp 195 - 197°, 2.27 ± 0.02 dpm/μmole.

Anal. calcd. for C$_7$H$_5$N$_2$O$_4$: C, 50.32; H, 2.99; N, 8.38

Found: C, 50.48; H, 2.92; N, 8.58

From 1.14 g of quinoline-6-carboxylic acid, 0.4 g of crude quinolinic acid was obtained. Recrystallization from water gave 0.1 g of pure acid; mp 194 - 195°. No activity was found in this compound—an expected result since the 1-carbon of the starting toluene was lost on this oxidation.

Nicotinic acid: A mixture of 0.306 g of quinolinic acid-1-carboxyl-$^{14}$C and 50 ml glacial acetic acid was boiled for 30 minutes. The carbon dioxide was swept out by a stream of nitrogen through a dry-ice trap (to trap any acetic acid and water) into a liquid-nitrogen trap. The trapped CO$_2$ was then transferred into a vial containing 10 ml of the phenethylamine counting solution. The activity found was 2.24 ± 0.02 dpm/μmole.

The nicotinic acid was obtained by removal of the solvent and sublimation in vacuo. The yield was 0.231 g (90.1%) from the
quinolinic acid; mp 225 - 230°. The radioactivity determination on a small aliquot (5 mg) indicated that no activity remained. The results are summarized in Table VIII:

<table>
<thead>
<tr>
<th>Series</th>
<th>Active Compounds</th>
<th>Carbon atom</th>
<th>Activity, *dpm/μmole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quinolinic acid</td>
<td>C₁, C₄</td>
<td>2.27 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>ortho</td>
<td>CO₂ from quinolinic acid</td>
<td>C₁</td>
<td>2.24 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>CO₂ from nicotinic acid</td>
<td>C₄</td>
<td>0**</td>
</tr>
<tr>
<td>para</td>
<td>Quinolinic acid</td>
<td>C₂, C₃</td>
<td>0**</td>
</tr>
</tbody>
</table>

* above background
** this sample counted slightly below background

ii) Degradation of toluene via heptanoic acid: 54

(1) Degradation of toluene-1-¹⁴C:

1-Methylcyclohexene-1-¹⁴C: 67 A 500 ml three-necked round-bottomed flask was fitted with a Friedrich condenser, a thermometer, a dropping funnel, and a magnetic stirrer. The apparatus was flushed with dry nitrogen. A mixture of 100 ml ethylenediamine and 200 ml morpholine was added and heated to 90°. Six grams of sliced lithium were added in small portions over a period of 1.5 hours while the reaction mixture was stirred and maintained at 90°.
The rate of addition of lithium was determined by the amount of hydrogen evolution. After all of the lithium had been added, the heating mantle was removed and 20 g of toluene-\(^{14}\)C (6.66 ± 0.07 dpm/\(\mu\)mole) was added dropwise from the dropping funnel. Stirring was continued and the reaction was allowed to proceed for 6 hours with occasional heating to 90°. The flask was then cooled to 0°, and water was cautiously added until most of the initially-formed solid had dissolved. The mixture was then steam distilled, and the organic layer in the distillate was extracted with three 25 ml portions of ether. The extracts were combined, washed with 5% HCl and water, and dried over anhydrous MgSO\(_4\). Fractional distillation of the dried ether solution gave 18 g of crude 1-methylcyclohexene-\(^{14}\)C (bp 100 - 108°). The glc (30% butanediol succinate on Chromosorb W, 20' x 3/8", 120°) showed the presence of 65.4% of 1-methyl-1-cyclohexene. The yield of 1-methyl-1-cyclohexene was 56.5%. About 50 \(\lambda\) of the pure compound was obtained by glc and the activity counted. The specific activity was 6.51 ± 0.07 dpm/\(\mu\)mole.

6-Ketoheptanoic acid-6-\(^{14}\)C: A 250 ml flask fitted with a thermometer and a stirrer was charged with 11 g of the crude 1-methylcyclohexene-\(^{14}\)C and 300 ml of water. With vigorous stirring, 44.5 g of finely ground potassium permanganate was added over a period of 6 hours. During this addition, the reaction mixture was maintained at 0 - 2°. The mixture was then allowed to stand overnight at room temperature. The precipitate of MnO\(_2\) was removed by filtration and washed with 100 ml of hot water. The water wash
was added to the filtered reaction mixture and this solution extracted with ether to remove unreacted 1-methylcyclohexene. The aqueous solution of crude keto acid remaining was then saturated with ammonium sulfate and acidified with H₂SO₄. The precipitated keto acid was extracted with ether and converted to the semicarbazone with semicarbazide hydrochloride according to standard procedure. The yield was 7 g (mp 143 - 145°, 41.8% yield). Specific activity: 6.55 ± 0.07 dpm/μmole.

Anal. calcd. for C₈H₁₅N₃O₃: C, 47.76; H, 7.46; N, 20.89
Found: C, 47.79; H, 7.74; N, 21.62

Heptanoic acid-6-¹⁴C: Seven grains of the semicarbazone of 6-ketoheptanoic acid were heated with 8.4 g of potassium hydroxide and 42 g of diethylene glycol at 195° for 6 hours. The mixture was poured into water and neutralized with 10% hydrochloric acid, and the organic layer was extracted with ether. After distillation of the ether extract, 3.5 g (77.2% from semicarbazone) of heptanoic acid-6-¹⁴C, bp 222 - 225°, was obtained. Specific activity: 6.66 ± 0.07 dpm/μmole.

Neopentyl α-bromoheptanoate-6-¹⁴C: 3.5 g was heated under reflux with 5 ml of thionyl chloride for 1 hour. The excess of reagent was removed by distillation and 1.4 ml of bromine was added to the residue. The mixture was heated under reflux at 80 - 100° for 2 hours until practically all the color of bromine had disappeared. The reaction mixture was cooled
and poured into 3.5 g of neopentyl alcohol. The resulting dark brown solution was allowed to stand overnight, then extracted with 100 ml of ether. The ether extract was washed with 5% NaHCO₃ and water and dried over MgSO₄. The ether was removed by distillation and the residue distilled under reduced pressure. Four grams (53.3% yield) of the ester, boiling at 86 - 87°/0.35 mm, was obtained. Specific activity: 6.50 ± 0.07 dpm/μmole.

**Anal. calcd. for C₁₂H₂₉O₂Br:**

*Found: C, 51.51; H, 8.30; Br, 28.96*

**Neopentylheptenoate-6-¹⁴C: 68**

Four grams of neopentyl bromoheptanoate was refluxed with 7 ml of diethylaniline for 6 hours. The solution was then poured into a large excess of 20% sulfuric acid, and the resulting aqueous solution extracted with three 50-ml portions of ether. The ethereal extract was dried over anhydrous MgSO₄ and the ether removed by distillation. The residue was distilled under reduced pressure at 107 - 111°/17 mm. 1.8 grams (40.3% from bromo ester) of neopentylheptenoate-6-¹⁴C were obtained as a colorless oil. The specific activity was 7.68 ± 0.08 dpm/μmole. The activity indicated the presence of impurities; however, no further purification was attempted.

**Anal. calcd. for C₁₂H₂₂O₂: C, 72.73; H, 11.11**

*Found: C, 71.70; H, 11.67*

**Alkali fusion of heptenoic acid-6-¹⁴C: 68**

Neopentylheptenoate (0.42 g) was dissolved in 3 ml of ethanol and solution of 0.5 g KOH in 1.5 ml of water added. The mixture was heated under reflux
for 2 hours and evaporated to dryness on the steam bath. To the crude heptenoic acid thus obtained 2 g KOH was added, and the fusion carried out at 300 - 350° (sand bath) until bubbling ceased. The solid was dissolved in water and acidified with sulfuric acid, and the acidic solution was then steam distilled. The steam distillate was neutralized with KOH and evaporated to dryness to give the potassium salts of the two acids. Ten ml of 50% H₂SO₄ were added and the solution extracted with three 25-ml portions of ether. The ether extracts were combined and the ether removed by distillation. 61.5 mg of valeric acid-4-C and 90 mg of acetic acid were obtained from the separation by glc on FFAP column, and were titrated with standard NaOH solution using phenolphthalein as indicator. No activity was found in the acetic acid. The activity for the valeric acid was 6.44 ± 0.06 dpm/µmole.

Degradation of valeric acid-4-C: The titrated solution of valeric acid-14C was evaporated under vacuum to dryness. After the flask was cooled in an ice bath, 1 ml of concentrated H₂SO₄ was carefully added. The sodium valerate was dissolved by gentle warming and shaking. After the flask was again cooled in an ice bath, 0.1 g of sodium azide was added, and the mixture was allowed to warm up until the azide was nearly dissolved. The flask was connected to the traps, placed in a bath at 35°, and the temperature was raised over a period of 1 hour to 60 - 70°. The temperature was kept at 60 - 70° for about 30 minutes and the CO₂ was swept out with nitrogen stream for 10 minutes. The CO₂ was trapped in a spiral bubbler
containing 50 ml of anhydrous ether and 3 g of phenethylamine. The precipitated phenethylammonium phenethylcarbamate was filtered in a nitrogen chamber, and washed several times with anhydrous ether. 50 mg of carbamate (about 29% recovery), mp 92 - 95°, was obtained. No activity was found in this compound.

To the residue of the above reaction, NaOH was added until the solution was strongly basic. The solution was distilled and the butylamine was collected in a test tube immersed in a dry ice-acetone bath. To the collected liquid (about 0.5 g), 0.5 g of phenylisothiocyanate was added, and the mixture allowed to stand at room temperature for 2 hours. The crystallized solid was filtered, washed with petroleum ether, and then with water. After several recrystallizations from alcohol, 40 mg of N-butyl-N'-phenylthiourea, mp 68°, was obtained. The specific activity was 6.57 ± 0.07 dpm/μmole.

The results are listed in Table IX.

(2) Degradation of toluene-14C from 5000 eV 14C+ irradiation: The route via heptanoic acid was used (see (1)). The toluene-14C obtained from a 3-hour irradiation of solid benzene with 5 KeV 14C+ ions was purified once by glc on CW20M at 80°. It was diluted with 10 g of toluene (1.22 ± 0.01 dpm/μmole) and degraded. The 14CO2 was converted to benzoic acid-7-14C methyl ester by using phenylmagnesium bromide and counted. The details of the CO2 trapping and counting will be reported in the section "Partial Degradation".
Table IX. Degradation of toluene-1-\(^{14}\)C via heptanoic acid.

<table>
<thead>
<tr>
<th>Active compounds</th>
<th>Carbon atom* in toluene</th>
<th>Activity** dpm/μmole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene-1-(^{14})C</td>
<td>C(<em>{3}), C(</em>{1-4})</td>
<td>6.66 ± 0.07</td>
</tr>
<tr>
<td>1-Methyl-1-cyclohexene-1-(^{14})C</td>
<td>&quot;</td>
<td>6.51 ± 0.07</td>
</tr>
<tr>
<td>6-Ketoheptanoic acid-6-(^{14})C</td>
<td>&quot;</td>
<td>6.55 ± 0.07</td>
</tr>
<tr>
<td>Heptanoic acid-6-(^{14})C</td>
<td>&quot;</td>
<td>6.66 ± 0.07</td>
</tr>
<tr>
<td>Neopentyl-(\alpha)-bromoheptanoate-6-(^{14})C</td>
<td>&quot;</td>
<td>6.50 ± 0.08</td>
</tr>
<tr>
<td>Neopentyl heptenoate-6-(^{14})C</td>
<td>&quot;</td>
<td>7.68 (impure)</td>
</tr>
<tr>
<td>Valeric acid-4-(^{14})C</td>
<td>&quot;</td>
<td>6.44 ± 0.06</td>
</tr>
<tr>
<td>N-n-butyl-3-(^{14})C, N'-phenylthiourea</td>
<td>&quot; , C(_{1-3})</td>
<td>6.57 ± 0.07</td>
</tr>
<tr>
<td>Phenethylammonium phenethyl-carbamate</td>
<td>C(_{4})</td>
<td>0</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>C(<em>{2}), C(</em>{3})</td>
<td>0</td>
</tr>
</tbody>
</table>

* Toluene is numbered here as

** Above background
The acetic acid from C\textsubscript{2,3} was, unfortunately, contaminated by the glc column during rechromatography; it was therefore discarded. In order to obtain the activity in C\textsubscript{3}, the butylamine obtained from the pentanoic acid was degraded.

The residue from the Schmidt reaction of 2.5 mmole pentanoic acid\textsuperscript{14C} was oxidized with 50 ml of basic 5% KMnO\textsubscript{4}, a steam distillation of the acidified (with H\textsubscript{2}SO\textsubscript{4}) reaction mixture yielded, after glc purification, 1 mmole of butyric acid\textsuperscript{14C}. This was Schmidt degraded, and the CO\textsubscript{2} trapped and counted as benzoic acid. The specific activity was 13.5 ± 0.1 dpm/mmole.

The C\textsubscript{2} activity was obtained from the degradation of the recovered and purified heptanoic acid; 0.5 g of the recovered heptanoic acid from the KOH fusion was hydrogenated (PtO\textsubscript{2}, 2 atm, 3 hrs, in alcohol) to heptanoic acid. The heptanoic acid was purified with glc on Poropak Q column (Prep Master). 184.3 mg of heptanoic acid was collected; its specific activity was 1.17 ± 0.01 dpm/μmole.

The heptanoic acid\textsuperscript{14C} (184.3 mg) was then Schmidt degraded, and the CO\textsubscript{2} was trapped and counted as benzoic acid (100 mg). The specific activity was 30.2 ± 0.3 dpm/mmole.

The hexylamine obtained above was oxidized to acetic acid by a Kuhn-Roth oxidation. The residue from the degradation of heptanoic acid was made basic with NaOH, and the amine was then vacuum distilled with water. The aqueous hexylamine solution was then oxidized with 50 ml of 15% H\textsubscript{2}SO\textsubscript{4} containing 1 g of chromic anhydride (refluxed for 1.5 hr). The distillation of the resulting
solution gave about 1.2 mmole of acetic acid. One mmole of pure acetic acid was obtained from the glc purification (Prep Master) on CW20M column.

When this acetic acid was Schmidt degraded, about 100 mg of benzoic acid was obtained from the CO₂. The specific activity was 86.5 + 0.9 dpm/m mole. The methylamine was counted as phenyl-thiourea (purified by column chromatography on neutral alumina). The specific activity was 0.997 ± 5 dpm/μmole. All the data on this degradation are summarized in Table X.

iii) Degradation of toluene via glutaric acid

(1) Preliminary investigation

(a) Barbier-Wieland degradation

1,1,5,5-Tetraphenyl-1,5-pentadiol: Metallic Li (2.4 g) and 40 ml of anhydrous ether were placed in a 500 ml Erlenmeyer flask provided with a condenser, dropping funnel, and magnetic stirrer. A solution of 26.8 g of bromobenzene in 40 ml of ether was added dropwise during a period of 30 minutes. After all the metal had reacted, 6 g of dimethyl glutarate was added. The resulting solution was stirred for one hour and was poured into a separatory funnel containing 200 g of ice. The mixture was shaken well and the ether layer separated. The ether solution was dried over Na₂SO₄ and decolorized with 5 g of charcoal. The evaporation of the ether gave 12.6 g of a white solid that melted at 106 - 107°. The yield was 69.2%.
Table X. Degradation of toluene-$^{14}$C via heptanoic acid

<table>
<thead>
<tr>
<th>Compound</th>
<th>Carbon atom in toluene</th>
<th>% Yield from previous cpd.</th>
<th>Sp. Act. above background dpm/μmole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>All</td>
<td>--</td>
<td>$1.3 \pm 0.01^{***}$</td>
</tr>
<tr>
<td>1-Methyl-1-cyclohexene*</td>
<td>&quot;</td>
<td>66.2</td>
<td>$1.23 \pm 0.01$</td>
</tr>
<tr>
<td>6-Ketoheptanoic acid</td>
<td>&quot;</td>
<td>70.5 (crude)</td>
<td>--</td>
</tr>
<tr>
<td>6-Ketoheptanoic acid semicarbazone</td>
<td>&quot;</td>
<td>--</td>
<td>$1.1 \pm 0.01$</td>
</tr>
<tr>
<td>Heptanoic acid</td>
<td>&quot;</td>
<td>78.4</td>
<td>$0.98 \pm 0.01$</td>
</tr>
<tr>
<td>Neopentyl-2-bromoheptanoate</td>
<td>&quot;</td>
<td>67.0</td>
<td>$1.04 \pm 0.01$</td>
</tr>
<tr>
<td>Neopentyl-$\Delta^{2,3}$-heptanoate</td>
<td>&quot;</td>
<td>85.8</td>
<td>$1.01 \pm 0.01$</td>
</tr>
<tr>
<td>Acetic acid*</td>
<td>C$_2$,3</td>
<td>16.3</td>
<td>$0.0395 \pm 0.0004$</td>
</tr>
<tr>
<td>Pentanoic acid*</td>
<td>C$_{Me}$, C$_1$, C$_4$ &amp; C$_2$,3</td>
<td>26.2</td>
<td>$0.94 \pm 0.01$</td>
</tr>
<tr>
<td>CO$_2$ from pentanoic acid</td>
<td>C$_4$</td>
<td>49.2</td>
<td>$0.013 \pm 0.0001$</td>
</tr>
<tr>
<td>CO$_2$ from butyric acid</td>
<td>C$_3$</td>
<td>82</td>
<td>$0.014 \pm 0.0001$</td>
</tr>
<tr>
<td>Heptanoic acid*</td>
<td>All</td>
<td>--</td>
<td>$1.17 \pm 0.01$</td>
</tr>
<tr>
<td>CO$_2$ from heptanoic acid</td>
<td>C$_2$</td>
<td>58</td>
<td>$0.03 \pm 0.0003$</td>
</tr>
<tr>
<td>CO$_2$ from acetic acid</td>
<td>C$_1$</td>
<td>82</td>
<td>$0.0865 \pm 0.0009$</td>
</tr>
<tr>
<td>Methylamine from acetic acid</td>
<td>C$_{Me}$</td>
<td>--</td>
<td>$0.997 \pm 0.005$</td>
</tr>
<tr>
<td>6-Ketoheptanoic acid oxime</td>
<td>All</td>
<td>--</td>
<td>$1.19 \pm 0.01$</td>
</tr>
</tbody>
</table>

* purified on glc  
** counted as benzoic acid  
*** including radio impurity from target
1,1,5,5-Tetraphenyl-1,4-pentadiene: Ten grams of the 1,1,5,5-tetraphenyl-1,5-pentadiol were heated with 50 ml of glacial acetic acid to boiling. Concentrated H$_2$SO$_4$ (about 1 ml) was then added. The solution turned blue upon the addition of the sulfuric acid, but the color faded away quickly. The solution was boiled for 2 minutes and was then cooled. The precipitated crystals were filtered and recrystallized from glacial acetic acid. 7.8 g of the diene, mp 69 - 70°, was obtained. The yield was 67.2%.

Oxidation of 1,1,5,5-tetraphenyl-1,4-pentadiene:
The compound was not oxidized by O$_3$, 2% permanganate solution at 80°, nor by 3% NaIO$_4$ (with an added catalytic amount of KMnO$_4$) in 25% dioxane solution at room temperature.

Oxidation by O$_2$ and heat: Two g of the diene were heated to 120° in a slow stream of O$_2$ for 10 hours; no malonic acid was found. A trace of the benzophenone was detected by its semicarbazone.

UV oxidation in the solid state: One gram of diene was dissolved in 5 ml chloroform, then evaporated as a thin film in a 200 ml round-bottomed quartz flask. The compound was then irradiated with a high-pressure mercury lamp (A-H6) under an oxygen atmosphere for 10 hours. The volatile fraction was collected in a trap immersed in a dry ice-acetone bath. Gas-liquid chromatography (FFAP column) showed the presence of acetic acid (only a very small yield) in the volatile fraction. Benzophenone was also detected by its semicarbazone.
(b) Hunsdiecker reaction: The treatment of the dried silver salt of glutaric acid with one mole equivalent of bromine or iodine in various solvents (CCl₄, cyclohexane, and benzene) in the dark gave only a trace (if any, barely detectable on glc) of dihalide. Since the only interest here was the formation of dihalide, no effort was made to study other products.

The modified Hunsdiecker reaction was also checked. The reaction of 0.25 mole of glutaric acid with 0.25 mole of bromine (or iodine) and 0.19 mole of red mercuric oxide in 200 ml of refluxing carbon tetrachloride gave less than 5% of the corresponding dihalide. t-Butyl alcohol and sulfolane were then added to increase the solubility of glutaric acid; however, the yield of the dihalide was not improved.

(c) Photochemical decarboxylation: All the experiments were done as described by Barton et al., except that t-butylhypoiiodite was prepared and introduced directly into the reaction flask by suction filtration within a closed system. Pure helium was used, instead of nitrogen, to flush out the reaction flask (1 hr). The photolysis (300 W tungsten lamp, 2 hrs, at a 5-inch distance) of the refluxing solution of 1 mmole glutaric acid and 5.8 mmoles of t-butylhypoioidite in 135 ml of benzene (1.25 ml of sulfolane added) gave, after glc analysis, a maximum yield of 32% of 1,3-propanediiodide. The reported yield was 69%. Although the photolysis was repeated 3 times, the yield was not increased. It was not known whether this was caused by the impure potassium.
t-butoxide (purchased from K and K Lab.), or by the incomplete elimination of oxygen from the system.

(d) Schmidt reaction: Although Schmidt degradation of glutaric acid was reported to give 85% propanediamine, this procedure was not adopted because of the need for a tedious addition of a solid reactant (NaN₃) over a 10-hour period.

The Schmidt degradation procedure described by Phares gave about 30% yield of 1,3-propanediamine even when varying amounts of sodium azide were used. It was found that the reverse addition of reactant into reagent increased the yield by about 2-fold. Therefore, this method was used in the degradation. The CO₂ was counted as benzoic acid.

The residue of the Schmidt reaction was then made basic with sodium hydroxide and was extracted with three 25-ml portions of ether. The glc analysis of the combined ether extracts showed the presence of about 63% 1,3-diaminopropane.

(e) The oxidation of 1,3-propanediamine: The following reagents were used in an attempt to oxidize the diamine to malonic acid. None of them gave isolatable malonic acid.

- 5% KMnO₄ (neutral, basic and MgSO₄)
- Ag(NH₃)₂⁺
- Diazotization, followed by hydrolysis and KMnO₄ oxidation
- H₂O₂ - FeSO₄, followed by basic KMnO₄ oxidation
NaOBr – NaOH (intended for malononitrile)

H₂O₂ – Na₂WO₄

The basic permanganate oxidation gave, instead, a fair yield of about 50% of oxalic acid. Therefore, it was adopted in the degradation (see below).

(2) Degradation of toluene-1⁻¹⁴C

1-Methyl-1-cyclohexene-1⁻¹⁴C: Eighteen grams of crude 1-methyl-1-cyclohexene-1⁻¹⁴C were obtained from reduction of 20 g toluene-1⁻¹⁴C (32.01 dpm/µmole) with 12 g Li in a mixture of 100 g each of ethylamine and dimethylamine. After rough purification by glc on butanediol succinate (Craig) column, 12.3 g of 1-methyl-1-cyclohexene-1⁻¹⁴C was collected (31.54 dpm/µmole; the glc trace showed the presence of 14.4% impurity). The yield was 50.2%.

6-Ketoheptanoic acid-6⁻¹⁴C: A mixture of 4 g 1-methyl-1-cyclohexene-1⁻¹⁴C and 7 g of unlabeled 1-methyl-1-cyclohexene (supplied by Aldrich Chemical Co., Inc.) was oxidized with 44.5 g of KMnO₄. Thirteen grams of crude keto acid was obtained. The yield was 78.8%.

Two grams of the crude keto acids were heated on steam bath for 30 minutes with 5 g of NH₂OH·HCl, 5 g of NaOH, and 45 ml of water. The mixture was cooled, acidified with sulfuric acid, and extracted with ethyl acetate. The solvent was evaporated to 10 ml and was cooled in an ice bath. The crystallized solid was filtered.
After several recrystallizations from ethyl acetate, 1.1 g of oxime were obtained, mp 94 - 95°. The yield was 50%. Specific activity was 11.13 ± 0.11 dpm/μmole.

*Anal. calcd. for C<sub>7</sub>H<sub>13</sub>NO<sub>3</sub>: C, 52.83; H, 8.18; N, 8.81
*Found: C, 52.51; H, 8.21; N, 8.65*

Beckmann rearrangement of 6-ketoheptanoic acid oxime-6-<sup>14</sup>C and the subsequent hydrolysis: 1.1 g (6.92 mmole) of the oxime (11.13 ± 0.11 dpm/μmole) was added in small portions to 5 ml concentrated sulfuric acid. This solution was added dropwise to 20 ml of concentrated sulfuric acid at 120 - 130°. The mixture was heated at this temperature for another 5 minutes. Twenty-five ml of water was added and the solution refluxed for 2 hours. Two hundred ml of water was then added and the solution was steam distilled. The distillate was titrated with 0.5 N NaOH solution. 6.35 mmole of acetic acid was obtained (91.7% yield). Identity of the acetic acid was checked by glc (FFAP column).

The sodium acetate solution from the titration was evaporated under vacuum. The Schmidt reaction was carried out as described. 0.662 g (36.6% recovery) of phenethylammonium phenethylcarbamate, mp 93 - 94°, was obtained. The specific activity was 10.55 ± 0.11 dpm/μmole.

*Anal. calcd. for C<sub>17</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>: C, 71.33; H, 7.69; N, 9.79
*Found: C, 70.76; H, 7.31; N, 9.62*

To the residue of the Schmidt reaction, 10 g of NaOH in 50 ml water was added, and the methylamine was distilled off by warming
the solution to 90°. The amine was collected in a trap at -196°. One g of phenylisothiocyanate was then added and the mixture allowed to react at room temperature for 2 hours. The precipitated solid was filtered and recrystallized for 6 times from dilute alcohol. 0.4 g (40% recovery) of N-methyl-N'-phenylthiourea, mp 113 - 115°, was obtained. The specific activity was 0.26 ± 0.03 dpm/µmole.

Anal. calcd. for C₈H₁₀N₂S: C, 57.83; H, 6.02; N, 16.87
Found: C, 57.53; H, 4.69; N, 16.87

To the residual solution from the steam distillation, concentrated NaOH solution was added until the solution was basic. Seventy ml of 5% KMnO₄ was added and the mixture refluxed for 15 minutes. The MnO₂ was filtered, and the filtrate concentrated to 100 ml. This was acidified with concentrated sulfuric acid and extracted with ether. The crystals, obtained by evaporation of the ether, were recrystallized from ethyl acetate. 0.58 g (69.9% yield) of glutaric acid, mp 95 - 96°, was obtained. The melting point was not depressed by mixed fusion with authentic glutaric acid. The specific activity was 0.36 ± 0.04 dpm/µmole. The results are summarized in Table XI.

The validity of the Schmidt degradation of glutaric acid was investigated as follows:

The degradation of glutaric acid-2⁻¹⁴C: Glutaric acid-2⁻¹⁴C (0.15 mmoles, 7.13 x 10⁵ dpm/µmole, synthesized from malonic acid-2⁻¹⁴C--see Synthesis section) was degraded by the Schmidt reaction as described. 0.183 mmoles (61% yield) of
Table XI. Degradation of toluene-1-$^{14}$C via Beckmann rearrangement

<table>
<thead>
<tr>
<th>Active compounds</th>
<th>Carbon atom in toluene</th>
<th>Activity** dpm/µmole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Methylcyclohexene</td>
<td>C$<em>{Me}$, C$</em>{1-4}$</td>
<td>11.01 ± 0.11</td>
</tr>
<tr>
<td>6-Ketoheptanoic acid-6-$^{14}$C oxime</td>
<td>&quot; &quot;</td>
<td>11.13 ± 0.11</td>
</tr>
<tr>
<td>Acetic acid-1-$^{14}$C (phenethylammonium phenethylcarbamate)</td>
<td>C$_1$</td>
<td>10.55 ± 0.11</td>
</tr>
<tr>
<td>N-Methyl-N'-phenylthiourea</td>
<td>C$_{Me}$</td>
<td>0.26 ± 0.03</td>
</tr>
<tr>
<td>Glutaric acid</td>
<td>C$_{2-4}$</td>
<td>0.36 ± 0.03</td>
</tr>
</tbody>
</table>

* The starting toluene-$^{14}$C was diluted with inactive methylcyclohexene after the reduction

** Above background

methylbenzoate-7-$^{14}$C (from $^{14}$CO$_2$) was obtained after glc purification on CW20M column. No activity was found in this benzoate.

To the residue of the Schmidt reaction, cold 50% NaOH was added carefully until the solution was basic to litmus paper. The diamine was then vacuum distilled (with water). Three ml of 5% KMnO$_4$, and 2 mmole of NaOH were added to the distillate and the mixture refluxed for 15 minutes. After the excess KMnO$_4$ was destroyed by NaHSO$_3$, the MnO$_2$ was filtered and washed with hot water.
The aqueous filtrate was vacuum evaporated to near dryness and was acidified with concentrated HCl. The acidic solution was extracted with 3 10-ml portions of ethylacetate. The oxalic acid obtained by evaporation of the ethylacetate was methylated with diazomethane and then purified on glc (CW20M). About 0.07 mmoles (46.7%) of dimethyloxalate (3.45 x 10^5 dpm/mmmole) was obtained.

It might be mentioned here that when 1,3-propanediamine was extracted with ether, the oxidation after evaporation of the solvent resulted in the dilution of about 30% of the activity of oxalate.

(3) Degradation of toluene-^{14}C from 4000 eV^{14}C^{+} irradiation: The toluene-^{14}C was obtained from IR-29-32. The isolated toluene was hydrogenated to avoid any contamination of cycloheptatriene. The hydrogenate was then purified by glc on CW20M column. Three ml of carrier toluene was added and an aliquot counted. The specific activity was (1.72 ± 0.02) x 10^4 dpm/mmole.

The degradation was carried out as described in the test run (see section (1)). The ^{14}CO_2 was trapped as benzoic acid-1-^{14}C and counted. The 1,3-propanediamine was counted as dibenzoyl derivative. Table XII summarizes the data obtained.
Table XII. The degradation of toluene-\textsuperscript{14}C via glutaric acid

<table>
<thead>
<tr>
<th>Compound</th>
<th>Carbon atom in toluene</th>
<th>% Yield from previous cpd.</th>
<th>Specific activity dpm/mmole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>All</td>
<td>--</td>
<td>$(1.72 \pm 0.02) \times 10^4$</td>
</tr>
<tr>
<td>1-Methylcyclohexene</td>
<td>&quot;</td>
<td>55.1</td>
<td>&quot;</td>
</tr>
<tr>
<td>6-Ketoheptanoic acid oxime</td>
<td>&quot;</td>
<td>49.5</td>
<td>$(1.7 \pm 0.02) \times 10^4$</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>$C_{Me}, C_1$</td>
<td>90.8</td>
<td>$(1.58 \pm 0.02) \times 10^4$</td>
</tr>
<tr>
<td>$CO_2$ from acetic acid</td>
<td>$C_1$</td>
<td>44</td>
<td>$(1.36 \pm 0.01) \times 10^3$</td>
</tr>
<tr>
<td>Methylamine from acetic acid</td>
<td>$C_{Me}$</td>
<td>22</td>
<td>$(1.45 \pm 0.02) \times 10^4$</td>
</tr>
<tr>
<td>Glutaric acid</td>
<td>$2C_{2,3}, C_4$</td>
<td>80</td>
<td>$(1.17 \pm 0.01) \times 10^3$</td>
</tr>
<tr>
<td>$CO_2$ from glutaric acid</td>
<td>$C_2$</td>
<td>40.5</td>
<td>$(3.95 \pm 0.04) \times 10^2$</td>
</tr>
<tr>
<td>1,3-Propanediamine</td>
<td>$2C_{3,4}$</td>
<td>--</td>
<td>$(3.02 \pm 0.03) \times 10^2$</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>$C_{3,4}$</td>
<td>47</td>
<td>$(2.05 \pm 0.02) \times 10^2$</td>
</tr>
</tbody>
</table>

2. Partial Degradation

The toluene was oxidized by $CrO_3$ in acetic acid solution to benzoic acid (see p. 106). The benzoic acid was then Schmidt degraded to carbon dioxide and aniline. The $^{14}CO_2$ was trapped and counted as benzoic acid-7-$^{14}$C (see Counting of $^{14}CO_2$ below). Several samples were obtained from the irradiation with $^{14}C^+$ of varying energy and partially degraded:
IR-16: The sample was obtained from the irradiation of benzene with 5 KeV $^{14}$C$^+$. The toluene-$^{14}$C (100 $\lambda$) was hydrogenated and purified on glc. Sixty-seven mg of benzoic acid was obtained from the oxidation. The Schmidt reaction of the acid gave the specific activity shown below:

- Methylbenzoate from toluene: $1.09 \times 10^5$ dpm/mmmole
- CO$_2$ (-CH$_3$ of toluene, counted as methylbenzoate): $9.85 \times 10^4$ dpm/mmmole
- Aniline (phenyl group of toluene): $1.30 \times 10^4$ dpm/mmmole

IR-27: The toluene-$^{14}$C from the irradiation of benzene with 500 eV $^{14}$C$^+$ ion was purified, oxidized to benzoic acid, and partially degraded:

- Methylbenzoate from toluene: $1.55 \times 10^4$ dpm/mmmole
- CO$_2$ ($C_{Me}$, as methylbenzoate): $1.266 \times 10^4$ dpm/mmmole
- Aniline (as phenylthiourea): $2.46 \times 10^3$ dpm/mmmole

IR-28: The toluene-$^{14}$C from the irradiation of benzene with 100 eV $^{14}$C$^+$ ion was degraded as described:

- Methylbenzoate from toluene: $5.48 \times 10^3$ dpm/mmmole
- CO$_2$ ($C_{Me}$, as methylbenzoate): $4.38 \times 10^3$ dpm/mmmole
- Aniline: $8.52 \times 10^2$ dpm/mmmole

IR-58: The toluene-$^{14}$C was obtained from the irradiation of benzene with 31 eV $^{14}$C$^+$:

- Methylbenzoate from toluene: $3.37 \times 10^3$ dpm/mmmole
IR-59: The toluene-\(^{14}\)C was obtained from the irradiation of benzene with 5 eV \(^{14}\)C\(^{+}\):

- CO\(_2\) (C\(_7\), as methylbenzoate) \(2.81 \times 10^3\) dpm/mmole
- Aniline \(2.59 \times 10^3\) dpm/mmole

Methylbenzoate from toluene \(3.94 \times 10^3\) dpm/mmole

CO\(_2\) (C\(_7\), as methylbenzoate) \(1.14 \times 10^3\) dpm/mmole

Aniline \(2.59 \times 10^3\) dpm/mmole

B. Degradation of Benzaldehyde

The activity distribution of benzaldehyde was determined by degrading both the compound itself, and its hydrogenation (no carriers present) products, toluene and methylcyclohexane. Methylcyclohexane was first aromatized (Pd/C, 350\(^\circ\)) to toluene and was degraded as above. Benzaldehyde was air oxidized to benzoic acid, which was then degraded by the Schmidt reaction.

IR-16: The sample was obtained from the irradiation of benzene with 5 KeV \(^{14}\)C\(^{+}\). At the time of this degradation, this compound was known only as U-2. It was cotrapped with n-hexylbenzene. The hydrogenation of the trapped mixture (with added toluene and methylcyclohexane as carriers) resulted in almost quantitative conversion of the activity into toluene and methylcyclohexane. Both compounds were purified on glc.
Toluene-\textsuperscript{14}C from benzaldehyde: Toluene was degraded as above. The specific activities were:

- Methylbenzoate from toluene: \(7.63 \times 10^4\) dpm/mmole
- \(\text{CO}_2\) (\(C_{\text{Me}}\), as methylbenzoate): \(5.02 \times 10^4\) dpm/mmole
- Aniline: \(2.75 \times 10^4\) dpm/mmole

Methylcyclohexane from benzaldehyde: 110 \(\mu\)l of methylcyclohexane were dehydrogenated (in the vapor phase) with 1 g of 30\% Pd-C, loosely packed in a glass tube (0.5 cm in diameter, 40 cm long), which was heated at 515\(^\circ\). About 30 \(\mu\)l of toluene was obtained after separation on the "Prep Master". The toluene was degraded as described. The specific activities were:

- Methylbenzoate from methylcyclohexane: \(1.07 \times 10^4\) dpm/mmole
- \(\text{CO}_2\) (\(C_{\text{Me}}\), lost): ---
- Aniline: \(4.16 \times 10^3\) dpm/mmole

IR-28: The benzaldehyde activity from the irradiation of benzene with 100 eV \(^{14}\text{C}\) ions was cochromatographed and collected with 1 mg of benzaldehyde. The benzaldehyde was allowed to stand open to the atmosphere for two days. In such a way, benzaldehyde could be oxidized to benzoic acid quantitatively. The carrier benzoic acid was then added and was degraded and counted as described. The specific activities were:

- Methylbenzoate from benzaldehyde: \(1.25 \times 10^4\) dpm/mmole
IR-36: The benzaldehyde from the irradiation of benzene with 15 eV $^{14}$CO$^+$ ions was degraded. The specific activities were:

- Methylbenzoate from benzaldehyde: $2.43 \times 10^3$ dpm/m mole
- CO$_2$ (C$_7$, as methylbenzoate): $1.72 \times 10^3$ dpm/m mole
- Aniline (as N-methyl-N'-phenylthiourea): $6.23 \times 10^2$ dpm/m mole

IR-37: The benzaldehyde from the irradiation of benzene with 4000 eV $^{14}$CO$^+$ ions was degraded as above. The specific activities were:

- Methylbenzoate from benzaldehyde: $2.63 \times 10^4$ dpm/m mole
- CO$_2$ (C$_7$, as methylbenzoate): $1.75 \times 10^4$ dpm/m mole
- Aniline: $0.86 \times 10^4$ dpm/m mole

IR-52: In order to check the possible oxygen source, the $^{12}$C$^+$ was generated from a 1:1 mixture of CO$_2$ and $^{14}$CO$_2$ and the benzene was irradiated with 4000 eV $^{12}$C$^+$. Some benzaldehyde-$^{14}$C (3000 dpm) was obtained. The degradation of benzoic acid obtained from this benzaldehyde gave the following results:

- Methylbenzoate from benzaldehyde: $1.51 \times 10^4$ dpm/m mole
- CO$_2$ (C$_7$, as methylbenzoate): $1.46 \times 10^4$ dpm/m mole
Aniline (counted as N-methyl-N'-phenythiourea)  58.6 dpm/m mole

C. Partial Degradation of Benzene Derivatives

All the major products were partially degraded. The partial degradation of toluene-$^{14}$C and benzaldehyde-$^{14}$C were described in the previous sections.

Phenylacetylene was first hydrogenated to the ethylbenzene, which was oxidized to a benzoic acid. The benzoic acid was degraded by Schmidt reaction. The activity of the β-carbon was obtained by subtraction of the activity of benzoic acid from that of ethylbenzene.

Biphenyl-$^{14}$C was similarly oxidized to benzoic acid and was degraded.

Diphenylmethane was degraded as follows: The oxidation of diphenylmethane with SeO$_2$ in a sealed tube gave benzophenone. The treatment of benzophenone with hydrazoic acid$^{62}$ gave benzoylanilide and the subsequent hydrolysis gave benzoic acid and aniline. For double checking the result, this benzoic acid was Schmidt degraded as usual.

\[
\begin{align*}
\text{PhCH}_2\text{Ph} & \xrightarrow{\text{SeO}_2} \text{PhCO} \xrightarrow{\text{HN}_3} \text{PhCONHPh} \xrightarrow{\text{H}^+} \text{PhCOOH} + \text{PhNH}_3^+ \\
\text{H}_2\text{O} &
\end{align*}
\]

The phenylcycloheptatriene was catalytically hydrogenated to phenylcycloheptane; this was then oxidized, with chromic acid in
acetic acid, to a mixture of benzoic acid, adipic acid, and glutaric acid (see Figure 35). The benzoic acid was degraded as before. In order to determine the activity distribution in the cycloheptane ring, the adipic acid was Schmidt degraded to CO₂ and 1,4-butanediamine, which was oxidized to a mixture of succinic acid and oxalic acid. The activity in oxalic acid was taken as that of C₃ in phenylcycloheptatriene:

![Chemical diagram](image)

**Figure 35.** The degradation of phenylcycloheptatriene.

The labeled phenylacetylene, biphenyl, diphenylmethane and phenylcycloheptatriene obtained from IR-16 (5 KeV ¹⁴C⁺ ions irradiation) were degraded.
General procedure for the oxidation of benzene derivative

About 100 λ of alkylbenzene was dissolved in 5 ml of glacial acetic acid, 12 drops of concentrated sulfuric acid were added, and the mixture heated to 70 - 80°. With vigorous stirring, a saturated aqueous solution of chromic acid was added dropwise so that the temperature of the reaction mixture did not exceed 100°. The addition of chromic acid was continued until no further consumption of the acid was observed. The reaction was allowed to continue for 20 - 30 minutes and the excess of chromic acid removed by addition of methyl alcohol. The solvent was then evaporated by a stream of N₂. The residue was dissolved in 2 ml of water, and was extracted by three 50-ml portions of ether. Sublimations and/or methylation with diazomethane, followed by glc, were used in the purification of the organic acids.

General procedure for the Schmidt reaction and the counting of CO₂

The apparatus used is sketched in Figure 36. The oxidizing trap was not used. The acid or sodium salt of the acid (>0.2 mmoles) was dissolved in 2 ml of 100% H₂SO₄ in a three-necked 25 ml conical flask (flat bottom, in order to stir the mixture with a magnetic stirrer) fitted with a gas inlet, a gas outlet system, and a tube bent at right angles into which 1.5 mole equivalent of NaN₃ were placed. The solution was stirred until the organic acid was dissolved. With stirring, the NaN₃ was added portionwise during a period of 30 minutes. The stirring was continued until all the
Figure 36. Apparatus for Schmidt Reaction and trapping of CO$_2$. 
solid dissolved. The temperature was then raised slowly to 60°
(during 30 min) and was kept at this temperature for another hour. During the reaction the evolved gas was swept through a drying tube containing anhydride, a U-trap at -80° (dry ice-IPA) and a triple U-trap at -196° (liquid N₂). The CO₂ trapped in liquid nitrogen was vacuum transferred into a 25 ml conical flask containing 5-fold excess of 3 M ether solution of phenylmagnesium bromide at liquid nitrogen temperature. The Grignard reaction mixture was allowed to warm up to room temperature (15 - 30 min). It was then hydrolyzed with 5 ml of ice-water, extracted with ether to remove the by-product biphenyl, and was acidified. The extraction of acidic aqueous solution with ether (3 x 25 ml) gave crude benzoic acid. The benzoic acid was methylated with diazomethane, and the methylbenzoate purified by glc. The benzoate was trapped from the exit port of the glc column by means of a disposable pipette. The weighing and the counting of the benzoate gave the specific activity of the CO₂.

The amine from the Schmidt reaction was extracted, purified on glc (or oxidized to the corresponding acid), weighed and counted.

Phenylacetylene-¹⁴C: Phenylacetylene was hydrogenated to ethylbenzene, purified on glc (CW20M), oxidized to benzoic acid, and degraded. The specific activities were:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Specific Activity (dpm/m mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylbenzene</td>
<td>1.34 x 10⁵</td>
</tr>
<tr>
<td>Methylbenzoate</td>
<td>9.05 x 10⁴</td>
</tr>
<tr>
<td>CO₂ (α-carbon counted as methylbenzoate)</td>
<td>9.03 x 10⁴</td>
</tr>
</tbody>
</table>
Aniline  \(4.95 \times 10^3\) dpm/m mole

**Biphenyl-\(^{14}\text{C}^\)**: The purified biphenyl was oxidized to benzoic acid. The Schmidt reaction gave the following specific activities:

- Biphenyl  \(4.62 \times 10^4\) dpm/m mole
- Methylbenzoate  \(4.18 \times 10^4\) dpm/m mole
- \(\text{CO}_2\) (as benzoate)  \(1.86 \times 10^4\) dpm/m mole
- Aniline  \(2.29 \times 10^4\) dpm/m mole

**Diphenylmethane-\(^{14}\text{C}^\)**: The diphenylmethane was oxidized (sealed tube, 250°, 10 hours) to benzophenone, which was in turn converted to benzanilide. Two ml of 100% sulfuric acid were placed in an Erlenmeyer flask, and 2 ml of benzene were then added to cover the acid. The flask was cooled to 0° and, with stirring, 75 mg of \(\text{NaN}_3\) was added. After the \(\text{NaN}_3\) was dissolved, a solution of 82 mg of benzophenone in 3 ml of benzene was added. The mixture was stirred overnight at room temperature and then heated at 70 - 80° for 1 hour. About 15 ml of water was added and the solution refluxed for 6 hours. Extraction of the acidic reaction mixture with ether gave about 40 mg (crude) of benzoic acid. The aqueous solution was then made basic with \(\text{NaOH}\), and was extracted with ether. About 30 mg of aniline were obtained. The specific activities were:

- Diphenylmethane  \(1.77 \times 10^5\) dpm/m mole
- Benzophenone  \(1.58 \times 10^5\) dpm/m mole
Methylbenzoate $1.46 \times 10^5$ dpm/m mole
Aniline $7.32 \times 10^3$ dpm/m mole

The benzoate and adipate (about 10 mg each) were diluted with 30 $\mu$L each of carrier benzoate and adipate. Both compounds were degraded further by the Schmidt reaction. In the latter case, the 1,4-butanediamine product was oxidized with basic KMnO$_4$ to a mixture of succinic and oxalic acid. The specific activities were:

- Methylbenzoate $9.11 \times 10^4$ dpm/m mole
- CO$_2$ (as methylbenzoate) $6.97 \times 10^4$ dpm/m mole
- Aniline $2.15 \times 10^4$ dpm/m mole
- Dimethyladipate $3.89 \times 10^4$ dpm/m mole
- CO$_2$ from adipic acid (as methylbenzoate) $7.93 \times 10^3$ dpm/m mole
- Dimethylsuccinate $2.295 \times 10^4$ dpm/m mole
- Dimethyloxalate $1.07 \times 10^4$ dpm/m mole

The dependability of the above degradation was checked by degrading the synthesized (see p. 113) phenylcycloheptane-1-$^{14}$C. All the procedures were performed as described above. The results are shown below:

- Phenylcycloheptane $1.85 \times 10^3$ dpm/m mole
- Methylbenzoate $1.8 \times 10^3$ dpm/m mole
- Dimethyladipate $52.2$ dpm/m mole
- Dimethylglutarate $38.7$ dpm/m mole
IV. THE SYNTHESSES

Phenylcycloheptatriene, o-phenyltoluene, phenylcycloheptane-1-$^{14}$C, and glutaric acid-2-$^{14}$C were synthesized for the product identifications and the test runs for the degradations.

Phenylcycloheptatriene was prepared by the reaction of tropylium bromide and phenyllithium. Figure 37 shows the nmr spectrum of this compound. There are absorptions at $\delta = 7.3$ (singlet, phenyl Hs), 6.75 - 6.55 (triplet, C$_{3},4$ Hs), 6.44 - 5.95 (complicated doublet, C$_{2},5$ Hs), 5.50 - 5.17 (quartet, C$_{1},6$ Hs), and a triplet (C$_{7}$ H) around 2.65 with the peak ratio of 5:2:2:2:1. These are in agreement with the data reported by Ter Borg and Kloosterziel$^{75}$ and Tezuka.$^{76}$

Spiro(6,6)tridecahexaene was assumed to be one of our products. Since its synthesis appeared very difficult, its hydrogenated derivative, previously unreported, was prepared. This compound, spiro(6,6)tridecane was synthesized by the routine spiro compound synthesis.$^{77}$

\[
\begin{align*}
\text{I} & \quad \text{II} \\
\text{I} & \quad \text{Wolff-Kishner reductions} \\
+ & \quad \text{t-BuOK} \\
\end{align*}
\]
Figure 37. NMR spectra of 7-phenylcycloheptatriene in carbon tetrachloride.
The base catalyzed condensation of 1,6-hexamethylene dibromide
with cycloheptanone gave about 24% of spiroketone (I), which
was in turn reduced to the corresponding spirane (II). The dis-

cussion of the structures of I and II are presented in the Appendix.

Phenylcycloheptane-1-\textsuperscript{14}C was synthesized from cyclohexanone-
1-\textsuperscript{14}C. This ketone was ring enlarged to cycloheptanone-1-\textsuperscript{14}C by
the reaction with diazomethane.\textsuperscript{78} The Grignard reaction of phenyl-
magnesium bromide with cycloheptanone-1-\textsuperscript{14}C gave 1-phenylcyclo-
heptanol-1-\textsuperscript{14}C. The subsequent dehydration and hydrogenation gave
the desired phenylcycloheptane-1-\textsuperscript{14}C:

\[
\begin{align*}
\text{Ph} & \quad + \text{CH}_2\text{N}_2 \quad \rightarrow \quad \text{Ph} \quad \text{MgBr} \quad \rightarrow \quad \text{Ph} \quad \text{OH} \quad \rightarrow \quad \text{Ph} \\
& \quad \text{PtO}_2 \quad \text{H}_2 \\
\end{align*}
\]

Glutaric acid-2-\textsuperscript{14}C was prepared from diethylmalonate-2-\textsuperscript{14}C by the
following sequence of reactions:

\[
\begin{align*}
\text{COOEt} & \quad \text{CH}_2=\text{CHCN} \quad \rightarrow \quad \text{COOEt} \quad \text{COOEt} \quad \text{conc. HCl} \quad \rightarrow \quad \text{COOH} \\
\text{t-BuO}^- & \quad 1) \quad \text{HCl} \quad \rightarrow \quad \text{CH}_2=\text{CHCN} \quad \text{2) dil. HCl} \quad \rightarrow \quad \text{CH}_2=\text{CHCN}
\end{align*}
\]
Diethylmalonate-2-\(^{14}\)C was cyanoethylated with acrylonitrile. The hydrolysis of the cyano group followed by hydrolysis and decarboxylation gave glutaric acid-2-\(^{14}\)C.

\(\text{o-Phenyltoluene was synthesized starting from o-bromotoluene.}^{79}\)

The Grignard reaction of tolymagnesiumbromide with cyclohexanone gave 1-(o-tolyl)-1-cyclohexanol. The aromatization of this compound with sulfur gave the desired o-phenyltoluene:

\[
\begin{align*}
\text{CH}_3 \quad \text{MgBr} & \quad \begin{array}{c} \text{O} \\ \text{Ph} \end{array} \\
\text{OH} & \text{S} \Rightarrow \end{align*}
\]

\text{Phenylcycloheptatriene:}^{46}

When 25 g of cycloheptatriene was brominated, 73.7 g of dibromotropylium (N\(_0\) 1.5968) was obtained. Heating this dibromo compound at 65 - 70\(^\circ\) under 1 mm yielded 10 g (21.3\% yield) of tropylium bromide, mp 205 - 210\(^\circ\). Tropylium bromide was further reacted with phenyl lithium to give 10 g of crude phenylcycloheptatriene (69\% yield). Vacuum distillation of the crude product at 0.7 mm gave the following fractions:

1. below 25\(^\circ\) 0.9 g  
2. 65 - 87.5\(^\circ\) 2.9 g  
3. 86.5 - 87\(^\circ\) 4.1 g  
4. 87 - 100\(^\circ\) 1.5 g

Fraction 3 crystallized after standing at room temperature overnight. This crystal was filtered and gave a mp 27 - 28\(^\circ\). On
recrystallization from methanol the purified white crystal (3 g) melted at 28 - 29°. The nmr spectrum was shown in Figure 37.

**Spiro(6,6)tridecane(II):**

A mixture of 22.4 g of cycloheptanone, 50 g hexamethylene dibromide, and 50 g potassium t-butoxide in 1 L of benzene was refluxed for 12 hours. After acidification the benzene layer was separated and the benzene distilled. The steam distillation of the residue and the recrystallization (dil. EtOH) of the distilled oil gave 4.6 g of colorless crystalline spiro(6,6)tridecan-1-one (I), mp 58-59°. The yield was 23.7%.

Anal. calcd. for C_{13}H_{22}O: C, 80.41; H, 11.34

Found: C, 80.13; H, 11.33

The nmr spectrum of this spiroketone is shown in Figure 48.

The semicarbazone was prepared in the usual way (except that the heating at 80° was continued for 2 days). About 2 g of colorless crystals, mp 260 - 265°, and 2.5 g of lower-melting crystals, mp 219 - 228°, were obtained. The elemental analysis was made on the latter.

Anal. calcd. for C_{14}H_{25}N_{8}O_{3}: C, 66.93; H, 9.96; N, 16.73

Found: C, 66.95; H, 10.11; N, 17.67

Wolff-Kishner reduction of the lower melting semicarbazone was carried out by heating (215° for 6 hrs) the compound with KOH in diglyme. About 1 g of crude hydrocarbon was obtained from the reaction mixture by extraction with ether. Glc on SB30 (150 - 240°)
showed three major peaks with an approximate ratio of 2:1:0.7. The mp of the first peak was 34 - 36°. The analysis of this compound agreed with C\textsubscript{13}H\textsubscript{24}.

Anal. calcd. for C\textsubscript{13}H\textsubscript{24}: C, 86.66; H, 13.33  
Found: C, 86.3; H, 13.7*

The nmr spectrum (Figure 49) showed 2 proton peaks at \( \tau = 8.58 \) and 8.72 with the ratio of 1:2. The second peak was found to be the starting spiroketone. The third peak was assumed to be 2-(\( \omega \)-hydroxyhexyl)-cycloheptanone, derived from the hydrolysis of the enol ether.

Anal. calcd. for C\textsubscript{13}H\textsubscript{24}O\textsubscript{2}: C, 73.58; H, 11.32  
Found: C, 72.0; H, 12.0*

The higher-melting semicarbazone was reduced in the same manner. The glc showed two major peaks with a ratio of 10:1.5. The retention time, mp, and the nmr spectra corresponded with the first compound obtained in the lower melting semicarbazone. The second peak was identical with 2-(\( \omega \)-hydroxyhexyl)-cycloheptanone.

The deuterium exchange of the spiroketone were carried out with D\textsubscript{2}O-dioxane-NaOD solution in a sealed tube at 90° for 24 hours. The deuterated spiroketones were purified by glc, and the nmr taken (see Appendix).

Phenylcycloheptane-1\textsuperscript{14}C:

Cycloheptanone-1\textsuperscript{14}C was prepared from cyclohexanone-1\textsuperscript{14}C

*Sample too small for more accurate analysis.
(purchased from New England Nuclear Corp.). In a 25 ml flask immersed in an ice water bath was placed 2.5 g of cyclohexanone-1-\(^{14}\)C (1.86 x 10\(^3\) dpm/m mole), 6.25 g of "Diazald" (N-methyl-N-nitroso-p-toluene sulfonamide), 7.5 ml of 95% alcohol, and 0.5 ml water. With slow stirring, a solution of 0.7 g KOH in 2.5 ml of 50% alcohol was added dropwise during 15 minutes. The solution was then stirred for 4 hours. The solution was acidified with HCl and then extracted with ether. Purification with glc (Prepmaster) on CW20M gave 1.6 g (1.87 x 10\(^3\) dpm/m mole) of pure cycloheptanone-1-\(^{14}\)C. The retention time of this compound agreed with that of authentic cycloheptanone.

The solution of 0.1 g cycloheptanone in 1 ml dry ether was added to 0.5 ml of 3 M ether solution of phenylmagnesium bromide in a small test tube. After 30 minutes of stirring, this mixture was hydrolyzed with 1 ml ice water. The resulting phenylcycloheptanol-1-\(^{14}\)C was extracted with ether. The ether extract was dried over anhydrous sodium sulfate and the solvent evaporated.

One ml of 100% formic acid was added to the residue and the mixture shaken for 15 minutes. This mixture was neutralized with NaOH and was then extracted with ether. About 0.2 mg of crude 1-phenylcycloheptene-1-\(^{14}\)C was obtained after removal of the ether. It was then hydrogenated (PtO\(_2\), 2 atm, 2 hrs) in 1 ml of alcohol. The glc (CW20M, Prepmaster) purification of the hydrogenated solution yielded 90 mg of pure phenylcycloheptane-1-\(^{14}\)C. The yield was 52.8%. Specific activity: 1.85 x 10\(^3\) spm/m mole.
Glutaric acid-2-\(^{14}\)C:

Diethyl malonate-2-\(^{14}\)C: Seventy-five grams of malonic acid-2-\(^{14}\)C (sp. act. undetermined) were placed in a 2-liter round-bottomed flask, together with 500 ml absolute alcohol, 800 ml of benzene, and 1.5 ml of conc. \(\text{H}_2\text{SO}_4\). The mixture was refluxed for one day while the water formed was slowly collected in a trap. The solution was then concentrated to 1 liter, washed with 1 liter of water, 1 liter of 1% \(\text{NaHCO}_3\), and again with 1 liter of water. The solution was then dried over \(\text{Na}_2\text{SO}_4\), and distilled. Diethyl malonate-2-\(^{14}\)C, 90.8 g, bp 195\(^\circ\)C, was obtained. The yield was 78.7%. Specific activity was 785.6 ± 8 dpm/\text{mmole}.

Glutaric acid-2-\(^{14}\)C: The cyanoethylation of the 90.8 g of diethyl malonate-2-\(^{14}\)C was carried out as usual. No ethyl-\(\alpha\)-carbethoxy-\(\gamma\)-cyanobutyrate-2-\(^{14}\)C was obtained. Presumably the carboxylic ether had been hydrolyzed to a sodium salt (the reaction mixture was inadvertently heated to 75\(^\circ\)C for about 10 min). The aqueous solution was therefore acidified with concentrated HC1 and evaporated to dryness. The residual solid was extracted with ether and the ether evaporated. About 35 g of a yellow oil was obtained. This oil was then hydrolyzed and decarboxylated as described above. Twenty-five grams of the glutaric acid-2-\(^{14}\)C, mp 94\(^\circ\), was obtained. The yield was 33.4% from diethyl malonate-2-\(^{14}\)C. The specific activity was 754 ± 8 dpm/\text{mmole}. 
To a solution of 4.3 g (25 mmole) of o-bromotoluene and 0.5 ml of methyl iodide (as a "catalyst") in 150 ml of ether, 0.6 g of magnesium turnings were added. With stirring, the solution was warmed to initiate the reaction. After the ether solution started boiling, it was allowed to reflux for one hour. A solution of 4.9 g of cyclohexanone in 100 ml ether was added over a period of 30 minutes and the mixture refluxed for 6 hours. Fifty g of ice were then added and the ether layer separated. Evaporation of the ether gave about 10 g of crude 1-(o-tolyl)-1-cyclohexanol. The aromatization of this product with 20 g of sulfur at 250 - 300° (2 hrs) gave about 4 g of crude o-phenyltoluene.

A small amount (about 0.5 g) of pure o-phenyltoluene for this study was obtained by purification with the Prepmaster glc on CW20M (200°).

Anal. calcd. for \( \text{C}_{13}\text{H}_{12} \): C, 94.86; H, 7.14

Found: C, 92.28; H, 7.57

The nmr of this compound is shown in Figure 38.
Figure 38. NMR spectrum of o-phenyltoluene in carbon tetrachloride.
V. RESULTS

Besides the previously reported products\(^1\) (benzene, toluene and cycloheptatriene), styrene, phenylacetylene, benzaldehyde, phenol, tropone, biphenyl, diphenylmethane, and phenylcycloheptatriene were found in the product mixture following the irradiation of solid benzene with \(^{14}\)C\(^+\) ions.

\(\text{C}_3 - \text{C}_7\) normal alkylbenzenes were also identified in the product mixture after hydrogenation. The presence of small amounts of cyclooctane, phenylbarrelane, \(o\)-phenyltoluene and spiro(6,6)tridecane were indicated.

The radiochemical yields of benzene, phenylacetylene, biphenyl and phenylcycloheptatriene were not affected appreciably by the charge state and the energy of incident \(^{14}\)C ions or atoms in the energy range of 15 KeV to 100 eV.\(^4\) The yield of toluene and cycloheptatriene in this energy range decreases slightly as the energy is lowered. The yield of toluene, cycloheptatriene and phenylacetylene decreased drastically below 100 eV. The benzaldehyde and diphenylmethane yields, on the other hand, were found to increase as the energy decreased.

The intramolecular\(^{14}\)C distribution of the major products from a 5000 eV irradiation are shown in Figure 39.
Figure 39. The activity distribution of the major products from 5000 eV irradiation.
The partial (Me vs. ring) degradation of the toluenes obtained from various energy irradiations showed no apparent change in the methyl/ring activity ratio above 31 eV irradiations. However, a drastic increase in the ring activity was observed in 5 eV irradiation. The results are shown in Table XIII.

<table>
<thead>
<tr>
<th>eV</th>
<th>5000</th>
<th>5000</th>
<th>4000</th>
<th>500</th>
<th>100</th>
<th>31</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>90.3</td>
<td>85.2</td>
<td>84.3</td>
<td>81.7</td>
<td>79.9</td>
<td>83.4</td>
<td>28.9</td>
</tr>
<tr>
<td>Ring</td>
<td>11.9</td>
<td>16.0</td>
<td>14.3</td>
<td>15.9</td>
<td>15.1</td>
<td>12.2</td>
<td>65.7</td>
</tr>
</tbody>
</table>

The intramolecular activity distributions of the benzaldehydes from 5000 and 100 eV $^{14}\text{C}^+$, and from 4000 and 15 eV $^{14}\text{CO}^+$ irradiations were essentially identical within experimental error. The benzaldehyde obtained from irradiation of $^{12}\text{C}^+$ produced from 3:2 mixture of $^{12}\text{CO}_2$ and $^{14}\text{CO}_2$, on the other hand, was specifically labeled at carbonyl carbon. These results are summarized in Table XIV.

<table>
<thead>
<tr>
<th>E eV</th>
<th>5000</th>
<th>100</th>
<th>4000</th>
<th>15</th>
<th>4000 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>(a)</td>
<td>(b)</td>
<td>$^{14}\text{C}^+$</td>
<td>$^{14}\text{CO}^+$</td>
<td>$^{12}\text{C}^+ (^{12}\text{CO}_2 ^{14}\text{CO}_2)$</td>
</tr>
<tr>
<td>CHO</td>
<td>64.6</td>
<td>61</td>
<td>68.3</td>
<td>66.5</td>
<td>70.8</td>
</tr>
<tr>
<td>Ring</td>
<td>35.4</td>
<td>39</td>
<td>30.5</td>
<td>32.7</td>
<td>25.6</td>
</tr>
</tbody>
</table>
VI. DISCUSSION

A. The Features of Hot Carbon Atom Chemistry

1. Slowing Down Process

The excess kinetic energy bestowed upon the initially formed carbon atoms by a nuclear reaction must be dissipated by the system down to the range of chemical bond energies (>10 eV) before one can anticipate any "chemical" reaction of that carbon. The present investigations involve energetic carbon-14 ions of below 15000 eV. In our system, no less than in a recoil process, most of this energy must be lost before there is significant probability for a chemical interaction. Rutherford scattering is important for atoms with about 15000 eV energy. At around 5000 - 6000 eV, hard sphere scattering becomes the main energy degradation process. The collisions between atoms of roughly equal mass result in the loss of an average value of one-half the kinetic-energy per collision of the incident atoms. The atoms then reach energies near or at the chemical bond energies (via elastic and inelastic energy degrading collisions) where chemical interactions take place.

As the energy of the carbons reach a few hundred electron volts, their collision cross section becomes so large that the remainder of the energy will be released within a relatively small volume with about 25 to 50 eV being associated with the terminal
hot spot. Since these last few hundred eV are delivered to a small volume in which 5 or 6 terminal collisions take place. These collisions give "local hot spots" that may overlap and provide additional reactive sites for the hot carbon with species in its immediate vicinity during the lifetime of the hot zone.

2. Charge and Excitation State

The charge state of the carbon atom when it reaches the reactive energy in the hot reaction has been treated by Yankwich for ionic crystals. That of carbon in organic matrix was discussed explicitly by Marshall et al. The charge state of the reacting carbon is predicted by the energies at which various charge-transfer processes have their maxima. In general, these maxima are higher for the lower energy process. Therefore, the charge state of the predominant reacting atom should be determined by the lower energy process. The approximate energies for the maximum cross-section for various charge transfer reactions are then calculated from the resonance rule. This rule predicts the maximum cross-section for a process with an energy change, ΔE, will occur when

\[ V_{\text{max}} = \frac{|a| \Delta E}{h} \]

where \( h \) is Plank's constant, \( a \) is an interaction distance, and \( V_{\text{max}} \) is the relative velocity of interacting atoms at the energy of maximum cross-section. Assuming \( a = 7 \times 10^{-8} \) cm, Marshall et al. were able to tabulate maximum cross-section energies for various interactions in carbon-ll-ethylene system. Table XV lists similar calculation for our benzene system.
Table XV. Maximum cross-section energies

| Reaction | $|\Delta E|_{\text{eV}}$ | $E_{\text{max}}$ | $E_{\text{max}}$ |
|---------|-----------------|----------------|-----------------|
| (1) $\text{C}(^{1\text{S}}) + \text{C}_6\text{H}_6 \rightarrow \text{C}^+ + \text{C}_6\text{H}_6 + e^-$ | 8.6 | 1.5 x 10^5 |
| (2) $\text{C}(^{1\text{D}}) + \text{C}_6\text{H}_6 \rightarrow \text{C}^+ + \text{C}_6\text{H}_6 + e^-$ | 10.1 | 2 x 10^5 |
| (3) $\text{C}(^{3\text{P}}) + \text{C}_6\text{H}_6 \rightarrow \text{C}^+ + \text{C}_6\text{H}_6 + e^-$ | 11.3 | 2.6 x 10^5 |
| (4) $\text{C}^+ + \text{C}_6\text{H}_6 \rightarrow \text{C}(^{1\text{S}}) + \text{C}_6\text{H}_6^+$ | 0.6 | 7.2 x 10^2 |
| (5) $\text{C}^+ + \text{C}_6\text{H}_6 \rightarrow \text{C}(^{1\text{D}}) + \text{C}_6\text{H}_6^+$ | 0.9 | 1.65 x 10^3 |
| (6) $\text{C}^+ + \text{C}_6\text{H}_6 \rightarrow \text{C}(^{3\text{P}}) + \text{C}_6\text{H}_6^+$ | 2.1 | 8.1 x 10^3 |
| (7) $\text{C}(^{3\text{P}}) + \text{C}_6\text{H}_6 \rightarrow \text{C}(^{1\text{D}}) + \text{C}_6\text{H}_6^+$ | 1.2 | 2.89 x 10^3 |
| (8) $\text{C}(^{3\text{P}}) + \text{C}_6\text{H}_6 \rightarrow \text{C}(^{1\text{D}}) + \text{C}_6\text{H}_6^+$ | 4.86 | 8.5 x 10^4 |
| (9) $\text{C}(^{1\text{D}}) + \text{C}_6\text{H}_6 \rightarrow \text{C}(^{3\text{P}}) + \text{C}_6\text{H}_6^+$ | 2.46 | 1.2 x 10^4 |
| (10) $\text{C}(^{1\text{S}}) + \text{C}_6\text{H}_6 \rightarrow \text{C}(^{3\text{P}}) + \text{C}_6\text{H}_6^+$ | 1 | 2 x 10^3 |

a. Ionization potential: $\text{C}(^{3\text{P}})$, 11.3 eV; $\text{C}(^{1\text{D}})$, 10.1 eV; $\text{C}(^{1\text{S}})$, 8.6 eV; $\text{C}_6\text{H}_6$, 9.2 eV.

b. $\text{C}_6\text{H}_6^*$: lowest lying excited state
Table XV shows that the ionization process (1, 2, and 3) of neutral carbon has its maximum cross-section at $10^5$ eV, while the cross-sections for neutralization of carbon ions (4, 5, and 6) increase at $10^3 - 10^4$ eV. Therefore, the reionization of the neutral carbon cannot take place at lower energies (below $10^3$ eV), and the reactive species in our system may be expected to be a neutral carbon atom.

The hot carbons-14 produced in $^{14}\text{N}(n,p)^{14}\text{C}$ reactions possess the energy in the range of 45 KeV. During the process of energy degradation, it passes through the energies at which various charge and energy transfer reactions have their maximum cross-sections. The importance of the predominant process may then be predicted. In the present case, however, many experiments were performed at energies at or below energies of maximum cross-section. The neutralization processes (4 - 6) may be important for the 15, 5, and 0.5 KeV irradiations, as was demonstrated in Table VII, where the products are both qualitatively and quantitatively the same for the irradiations of 5 and 0.5 KeV carbon-14 ions and neutral carbon-14. The yields and the products distribution in our 100 eV $^{14}\text{C}^+$ irradiation were also similar to those of higher energy irradiations. This observation may be taken to indicate that the cross-sections for the charge transfer reaction of carbon ion in benzene tail off slowly from their maxima at $10^{3-4}$ eV toward lower energy in such a manner that the predominant reacting species at lower energy is still the neutral carbon.
The ion-molecular reaction between positive ions and hydrocarbons has been extensively studied by the group of Swedish workers. Their investigations, using the double mass spectrometer, at the energy range of 900 eV to 3 eV, indicated that the cross-section for the charge transfer reactions between C⁺ and hydrocarbons with higher ionization potential, such as CH₄ (12.99 eV), CD₄, C₂H₆ (11.65 eV), C₂D₆, and n-C₄H₁₀ (11.8 eV), are relatively low and are considerably lower at lower kinetic energies of the impacting C⁺. On the other hand, for C₂H₄ (10.6 eV) and C₂H₂ (11.4 eV), which have lower ionization potential, the cross-section for the charge transfer reactions are large and are comparable at both ends of the energy range. Benzene has the ionization potential of 9.2 eV; it may therefore be safe to assume, by analogy, that the neutralization of C⁺ in benzene proceeds with large cross-section and that it does not vary appreciably at the energy range of 5 to 900 eV. This conclusion, along with the results discussed in the previous paragraph, predicts that the reacting species in 5 up to 15000 eV irradiations are in fact neutral carbons.

The spin state of the carbon atom may also be predicted by resonance rule. The results indicate that highly excited electronic states should not be important. Only low-lying C(3P), C(1D), and C(1S) states would be expected to exist at the energy of chemical interaction.
3. The Formation of Hydrogenated C₁ and C₂ Species

During the slowing down process, the initial kinetically hot
14C⁺ ions will penetrate a certain distance through the solid
matrix, most of the excess energy (e.g., 99.9% for 5000 eV 14C⁺)
must be given up to surrounding molecules by various interactions.
The nature of the interactions may also vary continuously during
its excursion. The net results of these interactions, such as
fragmentations, excitations, charge neutralization, and abstrac-
tions, are the formation of carbon atoms, methyne (CH), methylene
(CH₂), methyl radical (CH₃), and C₂H₄, etc. (not mentioning the
spectrum of fragments and radicals produced by breaking of benzene
route). Although no facet of direct evidence indicating the in-
volvement of these species has been previously available, they have
been widely postulated as the reacting species in the interpretation
of reactions of hot carbons in organic systems.

The formation of CH may involve equations 1 to 5.

\[
\begin{align*}
\text{C}_6\text{H}_5\text{-H} + \text{C}^+ & \rightarrow \text{C-H}^{(2\pi)} + \text{C}_6\text{H}_5^- \quad \Delta H = +22 \text{ Kcal} \\
\text{C}_6\text{H}_5\text{-H} + \text{C}^{(1D)} & \rightarrow \text{C-H}^{(2\pi)} + \text{C}_6\text{H}_5^- \quad \Delta H = -5.6 \text{ Kcal} \\
\text{C}_6\text{H}_5\text{-H} + \text{C}^+ & \rightarrow \text{C-H} + \text{C}_6\text{H}_5^+ \\
\text{C}_6\text{H}_6 + \text{C} & \rightarrow \text{[C}_7\text{H}_6\text{]}^- \rightarrow \text{C-H} + \text{C}_6\text{H}_5^- \\
\text{C}_6\text{H}_6 + \text{C}^+ & \rightarrow \text{[C}_7\text{H}_6\text{]}^+ \rightarrow \text{C-H} + \text{C}_6\text{H}_5^+
\end{align*}
\]
Equations 3 and 5 may represent the hydride transfer reactions. The relative importance of hydride transfer against that of charge transfer reaction has been shown in the ion-molecular reaction studies. Although the population of the ionic species due to the hydride transfer reaction is much larger than that due to the charge exchange reaction for methane, ethane, and n-butane (which have higher ionization potential), the hydride transfer for compounds with low ionization potential (ethylene and acetylene) is practically nil. The ionization potential of benzene is 9.2 eV—much lower than that of ethylene and acetylene. It is therefore probable that the role of hydride transfer reaction is much less important than that of charge exchange reaction.

Since neutral carbon atoms are the most predominant species at the energy of chemical interaction, the abstraction of hydrogen from benzene by carbon atoms may be the main route to the formation of CH. Since the energy of reaction (1) is endothermic, it is evident that the requisite energy must be supplied for the production of CH from ground state carbon atom, C(3P). This can be expected only if the translationally hot C(3P) is involved. Since the bulk of the reacting C atoms are in the ground state (3P), the reaction (1) may very well be the main reaction responsible for the CH formation. The involvement of excited singlet C atoms in the hot reactions was also postulated. Therefore, the reaction (2) may also take place.
An alternative route for CH formation from neutral carbon atoms is shown in equation (4). Temporary incorporation by insertion of hot radiocarbon in the benzene ring may lead to an excited \( \text{C}_7\text{H}_6 \) intermediate. The degradation of this intermediate may then provide CH species (see discussion under "Benzene", on page 141).

The methylene, CH\(_2\), can be formed by both consecutive and concerted hydrogen abstractions by carbon atom. Reaction (6) shows some endothermicity.

\[
2 \text{C}_6\text{H}_5-\text{H} + \text{C}(^3\text{P}) \rightarrow \text{CH}_2(\Sigma_g^-) + 2 \text{C}_6\text{H}_5^- \Delta H = +5 \text{ Kcal} \quad (6)
\]

Therefore, the formation of CH\(_2\) from C\(^3\)P again, requires the excess kinetic energy. On the other hand, the abstraction of hydrogens by C\(^1\)D or by higher electronic state of carbon is exoergic. The collisional deactivation of the translationally hot \( \text{CH}_2 \) formed from the latter process may eventually promote bond rupture rather than deexcitation. In fact, the decomposition of some hot CH\(_2\) to C + H\(_2\) and C-H + H are reported. The possibility of the correlation between the energy content of CH\(_2\) and that of the reacting hot carbon, therefore, becomes difficult.

The originally-proposed insertion-excitation-decomposition route\(^2\) for the formation of hot \( \cdot\text{CH}_3 \) radicals is not likely in the benzene matrix. The sequential picking up of hydrogens by hot carbon atom, reaction (7), is probably the most relevant process.
\[ 3 \text{C}_6\text{H}_5\text{H} + \text{C}{}^3\text{P} \rightarrow \cdot\text{CH}_3 + 3 \text{C}_6\text{H}_5\cdot \quad \Delta H = +1 \text{ Kcal} \] (7)

Usually, only a few per cent (3-8\%) of the total hot reaction products could be accounted for by the formation of these radicals. This is reasonable in view that the chemical reactivities decrease in the order of \( \cdot \text{C} > \cdot \text{CH} > \cdot \text{CH}_2 > \cdot \text{CH}_3 \). Therefore, most of the product-determining reactions could take place before the hot carbon atom could experience as many collisional processes as required for the production of hot methyl radicals. This is in good agreement with the observation that only 0.2\% of methane was found in the reaction of recoiling carbon with benzene.

The most prominent product in most of the hot carbon reactions in aliphatic hydrocarbon substrates is acetylene. The mechanism of formation of this unique product is well established as insertion-excitation-decomposition mechanism. The formation of hot \( \text{CCH}_2, \text{C}_2\text{H}, \text{or C}_2 \) species may follow a similar path. However, the path by means of stripping of \( \text{CH}_x \) by fast carbon from benzene molecule may also be possible. The \( \text{C}_2\text{H}_x \) species has been postulated in the formation of products having two more carbons than the product molecule.
B. Undesired Side Effects in our System

1. The incoming hot ions or atoms, during their slowing down process, may use up most of their excess energy in the fragmenting of benzene molecules. Tracks of fragments and radicals are thus produced along their path. There is certain probability that the primary labeled products and labeled reactive intermediates may interact with these fragments or radicals in the immediate neighborhood. The destruction of the products, or the quenching of labeled intermediate species, may occur both during the irradiation and during the working up process.

During our irradiations, the benzene was constantly added to the target cold finger so that only a fresh surface of solid benzene was bombarded by incoming ions or atoms. The ratio of the incident ions or atoms to benzene molecules was about $10^{-4}$. Therefore, for 10 KeV ion irradiations, the energy dose was 1 eV/molecule (approximately $10^8$ rads). It is possible that this relatively high dosage may cause some damage on the final labeled products. However, as is revealed in Table VII, the data covering the dosage between 0.01 and 1.5 eV/molecule, indicate that these effects are negligible within experimental error. A further support for this conclusion can be obtained from the fact that 31 up to 5000 eV irradiations are essentially equivalent.

2. As the energy of the fast carbons approaches a few hundred eV, a "terminal hot spot" may result. A 300 eV atom may release
its energy, capable of heating about 1000 atoms of the crystal
lattice to above the melting point, in a time of $10^{-13}$ seconds
at the center of the hot zone. The "hot spot" thus formed may
have a radius of about $10\,\AA$ and a lifetime of $10^{-11}$ seconds (the
time required for the temperature to fall below the melting
point). There is a finite chance that the hot atom or hot
products will react with species in its vicinity during the life-
time of the hot zone. The thermal rearrangement or decomposition
of the labeled products within this region are also possible.
Since the intramolecular radioactivity distributions are used as
the criteria for the discussion of the reaction mechanisms, the
effect on the hot products within this hot spot must be considered.
However, as will be discussed later (under "Biphenyl", p. 166 ),
the effect of the hot spot on the products appears not to be impor-
tant in our system.

3. The utilization of $^{14}$CO$_2$ as the $^{14}$C source presents an
unexpected difficulty. Although the irradiations are carried out
at high vacuum ($10^{-5}$ mm Hg), a complete removal of oxygen, or oxygen-
containing fragments, from the target was not attained. This has
resulted in the formation of appreciable amounts of benzaldehyde,
tropolone, and phenol, which are apparently derived from the quench-
ing of the key intermediate (carbenes or radicals) by oxygen or
oxygen derivatives. While the contamination by oxygen sources may
affect the absolute yields of the observed labeled products, the
relative yields of the products should not be changed as long as the steady state concentration of oxygen source can be maintained (for all the irradiations).

C. The Major Labeled Products

1. Acetylene

For a long time, our failure to detect labeled acetylene,\textsuperscript{3,18} which is a main product in all carbon recoil studies on hydrocarbons,\textsuperscript{2} was the only discrepancy between this work and carbon recoil chemistry. The difficulty has lately been solved by our use of a vacuum transfer technique for the product collection.\textsuperscript{90} About 5\% labeled acetylene is formed in our system. This is in good agreement with the value obtained from liquid benzene by Williams and Voigt\textsuperscript{43} (4.68\%) and Rose et al.\textsuperscript{42} (4.75\%, only relative yields are given in this report. This value is obtained by assuming the absolute yield of toluene as 2.3\%).

The insertion-excitation-decomposition has been suggested as the mechanism for the acetylene formation:\textsuperscript{2}

\[
\begin{align*}
\text{C*} + \text{R-CH}_2 & \rightarrow \text{R-C-C*H} \rightarrow \text{R-} + \text{R' + HCC*CH} \\
\text{H} & \\
\text{C*} + \text{R-CH}_2 & \rightarrow \text{R-C-C*H} \rightarrow \text{R-R' + HCC*CH} \\
\text{H} & 
\end{align*}
\]
The spin state of carbon can probably decide whether route (8) or (9) will be followed.\(^2\) The carbon insertion was suggested by Mackay and Wolfgang\(^91\) from the fact that an unusually high yield of acetylene was formed in cyclopropane (65% vs. 20 - 30% for other hydrocarbons) since a simple electronic redistribution is required in the formation of acetylene:

\[
\begin{align*}
1^{11}C + & \quad \begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\end{array} \\
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\end{array} & \quad \begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\end{array} \quad \Rightarrow \quad \begin{array}{c}
\text{H}^{11}C \\
\text{C} \\
\text{C} \\
\end{array} + \text{CH}_2=\text{CH}_2
\end{align*}
\]

(10)

The support for this carbon insertion mechanism was subsequently obtained from several double labeling experiments. Thus, the \(^{11}C\) recoiling in the mixture of (1) \(\text{C}_2\text{D}_6\) and \(\text{C}_2\text{H}_6\), (2) \(\text{CD}_3\text{CH}_3\), (3) \(\text{C}_2\text{D}_4\) and \(\text{C}_2\text{H}_4\),\(^92\) (4) \(\text{CD}_2\text{CH}_2\), and (5) \(\text{C}_6\text{D}_6\) and \(\text{C}_6\text{H}_6\),\(^93\) gave acetylene largely in the form of \(\text{C}_2\text{D}_2\) and \(\text{C}_2\text{H}_2\); the yield of \(\text{CHCD}\) was substantially lower (about 10 percent). The other mechanisms involving \(\text{CH}\) species and the stripping reaction of carbon is unlikely because such processes are expected to produce a much larger amount of \(\text{CHCD}\).

In contrast to aliphatic hydrocarbons whose adduct with carbon can easily fragment to give high yield of acetylene, benzene gives a relatively small amount of acetylene. The formation of acetylene from thermal carbon and benzene, equation (11),\(^42\) is energetically possible:

\[
\text{C} + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_6 - \text{C} \rightarrow \text{HC} \equiv \text{CH} + \text{H}_2\text{CCCHCCH} \quad \Delta H = -34 \text{ Kcal}
\]

(11)
The small exothermicity of the reaction, the facile dissipation of the excitation energy of the adduct into the aromatic system and the extensive internal rearrangement required in the acetylene formation may account for the low yield (5%, compare to 13% from cyclohexane)\textsuperscript{41} of acetylene from benzene.

Williams and Voigt have recently suggested the following reaction routes for acetylene formation from benzene:\textsuperscript{43}

\begin{align*}
\text{(12)} & \quad \text{[C--H]} \rightarrow \text{HC}=\text{CH} \\
\text{(13)} & \quad \text{[C--H]} \rightarrow \text{HC}=\text{CH} \\
\text{(14)} & \quad \text{HC}=\text{CH}
\end{align*}

\begin{itemize}
  \item Here, the intermediates in brackets are assumed to be highly activated species. Reaction (14) agrees with the double labeling (equal amounts of C\textsubscript{6}H\textsubscript{6} and C\textsubscript{6}D\textsubscript{6}) experiment.\textsuperscript{93} Reactions (12) and (13), however, involve a subsequent hydrogen abstraction step which should give CH=CD and HC=CH + DC=CD in the same probability. Since only 8.8% of the acetylene was in the form of HC=CD, equations (12) and (13) can account for only 18% of the total acetylene production.
  \item A most interesting and, perhaps, important feature of these mechanisms is that the hydrogens or radiocarbon in the C\textsubscript{7} cyclic intermediates must be well scrambled and that equations (12) and (13) are but of minor importance.
\end{itemize}
Alternatively, the C≡CH species produced in (12) and (13) may undergo several reactions (low energy processes, such as insertion in C-C and C-H bonds of benzene) other than hydrogen abstraction, rendering the yield of acetylene from this species very low.

2. Benzene

The hot nature of the labeled benzene (re-entry product) formation from carbon recoiling in benzene was extensively studied by Suryanarayana and Wolf. The addition of the radical scavenger 1,1-diphenyl-2-picrylhydrazyl (DPPH) significantly reduced the yield of benzene-\( ^{11}\)C; the change from liquid to solid phase also showed the same effect. It was therefore suggested that some of the labeled benzene was produced by the thermal reaction of a recoil fragment with some radicals generated in the system.

The re-entry products of many organic amines have been reported. If a mechanism such as the originally suggested "billiard ball" replacement is followed, a statistical product distribution between the labeled parent and its carbon analog should be observed. (The replacement of a carbon or a nitrogen atom by recoiling radio-carbon should take place with almost equal probability.)

The investigation of the statistical nature of the re-entry products by the determination of the yields may present some ambiguities since the determinations of absolute yields are difficult. An alternative, and possibly the more reliable, way for the study of this problem is the determination of the intramolecular
radioactivity distribution. For example, the labeled toluene from the reaction of toluene with radiocarbon should have 6/7 of its activity in the benzene ring if a statistic replacement of \(^{12}\text{C}\) by \(^{14}\text{C}\) (or \(^{13}\text{C}\)) has taken place. Such investigations for the aromatic compounds are collected in Table XVI.

Except for the toluene, the results contradicting the random replacement reaction are well demonstrated. The main features of the investigations tabulated in Table XVI are:

1. The distribution of radiocarbon favors positions with higher electron density in the parent molecule.
2. The incorporation of radiocarbon in the angular positions of the polynuclear hydrocarbons is very small. There is no apparent reason for this.
3. A change of phase or in irradiation time does not affect the observed radioactivity distribution.

It is therefore suggested that thermal carbon could be responsible for the re-entry product formation. Therefore, the nature of the chemical bonding and the thermodynamic factors of the involved intermediate species will control the product formation.

The yields of benzene-\(^{14}\text{C}\) are essentially constant for the \(^{14}\text{C}^+\) with energy range between 5 to 15000 eV (see Table VII and Figure 40). The energy of the reacting carbon, therefore, is below 5 eV. Although the exact energy cannot be estimated in the present work, it appears sure that low energy instead of high energy species are involved. The reaction can then be visualized
Table XVI. The intramolecular activity distribution of the re-entry products (parent molecules)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Positions</th>
<th>Theoretical (%)</th>
<th>Exptl. (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃-C₆H₅</td>
<td>Me</td>
<td>14.3</td>
<td>11</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>C₆H₅</td>
<td>85.7</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>t-Stilbene</td>
<td>CH</td>
<td>7.1</td>
<td>12.5</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>C₆H₅</td>
<td>42.9</td>
<td>37.5</td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>α</td>
<td>10</td>
<td>16</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>β</td>
<td>10</td>
<td>8.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9, 10</td>
<td>10</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>α</td>
<td>7.15</td>
<td>43</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>C₆H₄</td>
<td>42.8</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Anthracene</td>
<td>C₉ = C₁₀</td>
<td>7.15</td>
<td>43.3</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>C₁₋₄ = C₅₋₈</td>
<td>28.6</td>
<td>6.7</td>
<td></td>
</tr>
</tbody>
</table>

by assuming the formation of an excited intermediate species resulting from the interaction of a carbon atom and substrate molecule. Then, a swift reshuffling of the atoms followed by a reverse
reaction will probably introduce radiocarbon into the parent molecule.

Williams and Voigt have suggested mechanisms for the formation of labeled benzene as follows:

\[
\begin{align*}
\text{C} + {^\*}C &\rightarrow \text{[1]} \rightarrow \text{[2]} \rightarrow \text{[3]} \rightarrow \text{[4]} \rightarrow \text{[5]}\quad (15) \\
&\quad (16) \\
\text{C} + {^\*}CH &\rightarrow \text{[6]} \rightarrow \text{[7]} \rightarrow \text{[8]} \rightarrow \text{[9]} \rightarrow \text{[10]}\quad (17)
\end{align*}
\]

These hypotheses were supported by the yields of the labeled parent compounds from the \(^{11}\text{C}\) recoiling in benzene, toluene, and p-xylene (3.54, 2.70, and 2.40% in the unscavenged systems, and 2.85, 2.31, and 2.06% with DDPH). These data have been interpreted as showing that the methyl groups on the aromatic nucleus exert a steric shielding. Thus, the yields of the labeled toluene and xylene were expected to be 5/6 and 4/6, respectively of that of the benzenes. A remarkable agreement with the experimental data was demonstrated.

These data may, however, be interpreted in an alternative way if a bicyclo(1.1.0)-butane structure is present in the C7 intermediate.
The formation of the intermediates IV-VIII may involve the benzyldiene (III) and its methyl derivatives resulting from the C-H bond insertion by carbon atom, the intramolecular C=C bond insertion by the carbene III and its methyl analog, then, give structures IV-VIII. An essential feature of this suggestion is that the oncoming radiocarbon is made equivalent to one of the ring carbon during the formation of the reactive intermediate. Subsequent reverse reaction (the decomposition by removing a carbon atom) leads to the reformation of both labeled and unlabeled parent molecule in the same proportion. The structures IV-VIII are probably over-emphasized; these intermediates may, alternatively, be represented by partial bond structures IXa, b:

(IX)\textsubscript{a} \quad (IX)\textsubscript{b}
In fact, the replacement of $^{12}\text{C}$ by $^{14}\text{C}$ can be envisioned as a one-step process (by analogy to $S_{N2}$ reaction) involving the approach of a radiocarbon from one side of the benzene molecule:

\[
\begin{align*}
^{*}\text{C} + & \quad \longrightarrow \quad \left\{ \quad \right\} \quad \longrightarrow \quad ^{*} & + ^{12}\text{C} \\
\end{align*}
\]

(21)

Attack by a $^{14}\text{C}$ atom and expulsion of a $^{12}\text{C}$ atom are then a synchronous process.

The intramolecular activity distributions of the re-entry product of aromatic hydrocarbons can now be rationalized: the low energy, or thermal, carbon, by virtue of its high electrophylcity, tends to attack the position with higher electron density; thus, for the naphthalene,

\[
\begin{align*}
\text{Xa} & & \text{Xb} & & \text{Xc} \\
\end{align*}
\]

the population of structure Xa may be expected to be higher than that of Xb and Xc. Furthermore, the formation of naphthalene from Xc should be difficult since more elaborate bond breaking
and reformation are required. The observed high activity in C\textsubscript{1} position of naphthalene, and of C\textsubscript{9,10} of phenanthrene and anthracene, and the extremely low activity in angular carbons, are in good agreement with this hypothesis.

The kinetically hot carbon atom may participate in the above reaction. An inelastic collision between hot carbon and benzene may lead to the formation of vibrationally and, also, electronically excited species. It is not unlikely that an electronically excited IX may give rise to a labeled benzene in its higher electronic states. Since benzene is known to isomerize to benzvalene(XI), fulvene(XII) and Dewar benzene(XIII) by the vacuum ultraviolet photolysis,\textsuperscript{95} it was hoped that these compounds would be found in our product mixture. These possibilities were searched for by the hydrogenation of aliquots of target material, but without success. None of the expected labeled n-hexane, cyclohexane, and methylcyclopentane was detectable.

3. Toluene

The detailed study of the toluene-\textsuperscript{11}C formation from carbon recoiling in benzene was reported by Suryanarayana and Wolf.\textsuperscript{58}
The yields of labeled toluene were not depressed either by the addition of radical scavenger (DPPH) or the change in phase (liquid to solid). The toluene-^{11}C was thus said to be a hot reaction product.

The hot reaction products with one more carbon than parent molecule (for example, toluene from benzene, ethyl benzene from toluene, etc.), are classified as the synthesis products. The formation of these products has been widely investigated. Hot methylene was suggested as being responsible for the synthesis product formation by Wolf et al. \cite{36}

The photolysis of 1^{4}\text{CH}_2\text{NH}_2 in benzene solution was reported by Lemmon and Strohmeier \cite{96}, the toluene-^{14}C formed here was specifically methyl labeled (99.8\%). In contrast, only 85 - 88\% activity \cite{36,39} was found in the methyl carbon of the toluene obtained from recoiling carbon and benzene. The results obtained from 5000 eV ^{14}\text{C}^+ beam showed a similar activity distribution \cite{3,18} (Table XIII).

The total activity distribution of toluene-^{14}C obtained from our 5000 and 4000 eV irradiations, along with that of Visser et al.'s \cite{39} are listed in Table XVII.

The essential equivalence of the toluene activity distribution indicates the same kinds of reactions are occurring in both hot carbon ion beam experiments and the recoiling carbon. Columns 2, 3, and 4 represent results obtained by three different degradation routes. Slightly high values for the C$_2$ positions were
Table XVII. The activity distribution in toluene-$^{14}$C from benzene

<table>
<thead>
<tr>
<th>Sources</th>
<th>5000 eV $^{14}$C$^+$</th>
<th>4000 eV $^{14}$C$^+$</th>
<th>$^{14}$N(n,p) $^{14}$C reaction in benzene $^{38}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positions $^a$</td>
<td>+ benzene (%)</td>
<td>+ benzene (%)</td>
<td>(%)</td>
</tr>
<tr>
<td>-CH$_3$</td>
<td>85.2</td>
<td>84.3</td>
<td>85.7</td>
</tr>
<tr>
<td>C$_1$</td>
<td>7.4</td>
<td>7.9</td>
<td>7.65</td>
</tr>
<tr>
<td>2 C$_2$</td>
<td>5.1</td>
<td>4.6</td>
<td>3.68</td>
</tr>
<tr>
<td>2 C$_3$</td>
<td>2.4</td>
<td>1.1</td>
<td>2.00</td>
</tr>
<tr>
<td>C$_4$</td>
<td>1.1</td>
<td>0.6</td>
<td>0.99</td>
</tr>
</tbody>
</table>

$a$) The carbon positions are numbered as CH$_3$- obtain$^r$ in our degradations, yet the agreement of the values, in general, is remarkable. The C$_3$ and C$_4$ activities in column 3 are low compared to columns 2 and 4; the cause of this deviation is not understood.

The mechanism for the scrambling of activity in the ring of toluene-$^{14}$C was first suggested to involve either tropylium ion or an excited norcaradiene intermediate.$^{38}$

\[ 	ext{XIV} \quad \text{XV} \]
The initial formation of hot $^*\text{CH}_2$ from the incoming hot C was assumed. The tropylium ion (XIV) could be formed from the excited $\text{C}_7\text{H}_8$ intermediate resulting from the interaction of the hot methylene with benzene. A toluene with radioactivity distributed equally in all positions should be expected from this route. The results shown in Table XVII serve to eliminate the possibility that the route involving structure XIV or any symmetric intermediate is the sole mechanism of the toluene formation. The insertion of hot $^*\text{CH}_2$ into a C-C bond of benzene, on the other hand, may lead to an excited norcaradiene (XV) specifically labeled at the 7 position. However, the excited norcaradiene may, due to its excess energy brought in by $^*\text{CH}_2$, rearrange and eventually scramble the activity among the carbons in its structure. The toluene labeled in a certain pattern may then be formed from the rearrangement of norcaradiene (Eq. 22).

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A more elaborate mechanism was recently suggested by us. \(^9\)

Again, the hot \(^*\)CH\(_2\) was postulated.

This mechanism differs from that of Suryanarayana and Wolf's in two features: First, the insertion of hot methylene was assumed to occur at both C-H and C-C bonds. Second, detailed mechanisms of the insertion reaction, hydrogen migration, and rearrangement of excited norcaradiene (XV) were suggested. Here, most of the activity in the methyl group of toluene was attributed to C-H bond insertion by a hot methylene (Eq. 23). Meanwhile, the C-C bond insertion of hot \(^*\)CH\(_2\) gave, instead of norcaradiene (XV) directly,
a biradical (XVI). The scrambling of the activity in the benzene ring could then take place via the formation of norcaradiene and the subsequent rearrangements (Eq. 24).

Although the hot methylene formation in hot atom chemistry is generally well accepted, the first direct evidence for its formation is still to be seen. A synthesis product from a hot carbon reaction, consisting of one CH$_2$ more than the parent molecule, can basically be considered as resulting from three possible routes:

\[
C + RH \rightarrow CH + RH \rightarrow CH_2 + RH \rightarrow RCH_3 \quad (25)
\]

\[
C + RH \rightarrow CH + RH \rightarrow RCH_2 + RH \rightarrow RCH_3 \quad (26)
\]

\[
C + RH \rightarrow RCH + 2RH \rightarrow RCH_3 \quad (27)
\]

The possibility of the participation of methyl radical is not considered here for the reason previously mentioned. The argument about the relative importance of equations (25), (26), and (27) is intriguing, although the energy and momentum considerations tend to favor (25). There is as yet no chemical means to indicate at what stage the hydrogen pick-up process takes place. However, several interesting features concerning this matter may be obtained from the literature and from the present work:

a. One of the supports for the CH$_2$ formation in carbon recoiling was that the xylenes-$^{14}$C and ethylbenzene-$^{14}$C obtained
from toluene showed a statistical distribution, the relative yields for o-, m-, and p-xylene and ethylbenzene, 2.1, 2.3, 1, and 3.1 respectively, were taken as indicating a random attack behavior of the methylene. This is to be contrasted with the recent results reported by Williams and Voigt, in which a detail of carbon-11 recoils in benzene, toluene, and p-xylene was studied. A non-statistical rather than statistical nature for the formation of the synthesis products was well demonstrated (a similar result was also obtained for the interaction of recoiling carbon-11 with p-xylene).

The reaction of singlet methylene (from photolysis of ketene) with toluene was reported by Terao and Shida, using both pyrex and quartz cells. A high-pressure mercury arc was used as the light source. The results indicated that a ratio other than statistical was obtainable for the reactions of methylene in liquid toluene.

Table XVIII shows the yields of xylenes and ethylbenzene from the reactions of toluene with recoiling carbons, photolytically produced methylene, and methyl radicals. Williams and Voigt's result indicated, besides non-statistical nature, the product distribution was not identical with that obtained from singlet methylene and from methyl radical.

The yield of ethylbenzene was among the highest (4.8) in the products. While the random mode of attack predicts the value of 3, this is indicative of the participation of a species other than methylene, which prefers to attack the methyl group. The
yield of o-xylene (despite the possible steric effect) was slightly higher than (or at least comparable to) that of m-xylene. This is in agreement with the observation that the yield of α-methylnaphthalene was twice as much as the β-derivative from naphthalene.\textsuperscript{94} the preference of attack at an electron-rich center is indicated.

b. The gas phase photo-isomerization of cycloheptatriene to toluene has been reported by Srinivasan.\textsuperscript{99} It was established that the isomerization to toluene occurred not from an electronically excited cycloheptatriene, but from a vibrationally excited ground state molecule formed by the internal conversion of the electronic energy. The cycloheptatriene at a higher electronic state, however, would convert itself to a bicycloheptadiene.

These results were in agreement with results obtained from the photolysis of cycloheptatriene in the liquid phase in which the

Table XVIII. Relative yields of xylenes from toluene

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Statistical insertion</th>
<th>( \cdot \text{CH}_3\text{+Tol} )\textsuperscript{98}</th>
<th>( \cdot \text{CH}_2\text{+Tol} )\textsuperscript{97}</th>
<th>( \text{C+Tol} ) Williams\textsuperscript{37}</th>
<th>( \text{C+Tol} ) et al's\textsuperscript{43}</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-Xylene</td>
<td>2</td>
<td>3.3</td>
<td>trace</td>
<td>0.8</td>
<td>2.1</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>2</td>
<td>1.6</td>
<td>1.55</td>
<td>1.84</td>
<td>2.3</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>3</td>
<td>1.6</td>
<td>1.1</td>
<td>1.2</td>
<td>3.1</td>
</tr>
</tbody>
</table>
products consisted mostly of bicycloheptadiene and very little toluene. The toluene-$^{14}$C formed in the photolysis of diazomethane-$^{14}$C in benzene was exclusively labeled at the methyl position. The rearrangement of cycloheptatriene to toluene, as was indicated by Eq. (22) and (24), is not the predominant cause for the scrambling of radiocarbon into the aromatic ring.

c. While the ratio of cycloheptatriene and toluene produced from the reaction of photochemically produced CH$_2$ and benzene is 3.5, the ratio of these two compounds in carbon-11 recoiling and our $^{14}$C$^+$ irradiations are 2.3, 1.2, and 2.3, respectively. The indication is that a species other than that of the CH$_2$ produced photochemically is involved in the hot atom chemistry.

d. An important conclusion can be derived from the activities in the C$_1$ and C$_2$ positions of toluene. Eight and five percent of the total activity in toluene was found in C$_1$ and C$_2$, respectively (Table XVII). The norcaradiene (XV) was the key intermediate for the scrambling of activity in the benzene ring in both mechanisms described above (Eq. 22 and 24). The formation of toluenes labeled at different positions can then be represented by the following equations:
Obviously, structure XV \(_a\) is the only source of C\(_1\)-labeled toluene. Since XV \(_a\) is a symmetrical molecule, the probabilities for the production of C\(_1\)- and C\(_2\)-labeled toluenes should be equal. C\(_2\)-labeled toluene can also be formed from XV \(_b\). Therefore, the ratio of C\(_1\)/C\(_2\) activity should always be less than one. The observed C\(_1)/C_2\) ratios are 1.5, and 1.7 for our degradation, and 2.1 for Visser et al.'s. These are much larger than the expected value of less than one. One may then be tempted to assume a kinetic isotope effect. The calculated upper limit for \(^{14}\text{C}\) isotope effect\(^{102}\) is 1.5, yet the largest effect actually observed is 1.14\(^{103}\).

The reaction scheme involving norcaradiene as a main intermediate should therefore be questioned.
e. The mechanisms involving equations (22) and (24) require the formation of hot methylenes because the isomerization of norcaradiene structures must be energized by the excess energy brought in by this species. The formation of hot :CH₂ is possible in the case of high-energy carbon irradiation. As the energy of the carbon is lowered, the population of hot :CH₂ should be reduced accordingly. Since the excess energy of :CH₂ is no longer available in the lower energy irradiations, the extent of the isomerization of norcaradiene and, therefore, the activity in the aromatic ring should be expected to decrease.

Our results obtained from the partial degradations of toluene from various energy irradiations, however, showed an opposite trend (Figure 40). The ring/methyl activity ratio for irradiations above 31 ev ¹⁴C⁺ were practically constant; however, a dramatic increase in the ring activity was found at 5 eV. The irrelevancy of the excess kinetic energy in the incorporation of radiocarbon in the toluene ring can therefore be concluded.

f. While the toluene yield decreases slightly as the energy is lowered from 15 to 0.1 KeV, and does so drastically below 0.1 KeV, the ring/methyl activity ratio is constant above 31 eV (Figure 40). It is likely that the methylene-¹⁴C, if there is any formed, should give activity only on the methyl group (see b.). Some reactive species such as C and CH should then be responsible for the activity incorporation in the ring (see e.). If this is the case, the decrease in the yield at the lower energy
Figure 40. The yields of benzene, toluene, cycloheptatriene, and phenylacetylene, and the $C_6H_5/CH_3$ activity ratio of toluene.
irradiation must mean the decrease in the formation of :CH$_2$ and therefore affect the activity ratio. A reverse effect was observed in our system. The involvement of :CH$_2$, therefore, cannot apply. This observation can, however, be visualized by assuming the insertion reactions carbon with different energy of electronic state ($^3$P, $^1$D, and $^1$S, see p. 169).

Finally, Skell and Engel$^{104}$ indicated that synthesis products are obtainable from the reaction of thermal C($^1$S) with alkanes. The C-H bond insertion, followed by hydrogen abstractions by the resulting carbene was suggested as the sole reaction mechanism. The absence of :CH$_2$ formation was clearly demonstrated by attempted trapping with olefinic compound. The hypothesis of :CH$_2$ formation in favor of C-H insertion of carbon in hot atom chemistry should therefore be made only with reservations.

Although all the facts a – g tend to indicate the relative unimportance of reaction (25), the possibility of its minor role in the formation of methyl labeled toluene cannot be excluded.

Reaction (26) is unique, because the addition of CH into the benzene molecule may lead to the formation of the cycloheptatrienyl radical (XVII). This is a symmetrical and resonance-stabilized (RE=31 Kcal/mole)$^{105}$ species. A randomly labeled

XVII
-157-
toluene should be expected if XVII is formed in the reaction. A careful examination of activity distribution reveals that the activity in C4 and C3 positions of toluene are equally distributed. One may, therefore, conclude that some of the toluene is formed from reaction (26).

By a process of elimination, reaction (27) can be considered as the most important process leading to the ring labeling in toluene.

Two basic mechanisms have previously been postulated for the reaction of hot carbon with ethylene.31 First, the carbon is able to attack the carbon-carbon double bond to give cyclopropylidene. Such an intermediate seems to collapse swiftly to a hot allene which, in turn, rearranges to methylnacetylene, or is collisionally deactivated to allene. Second, the insertion of carbon may take place at a C-H bond to give an intermediate carbene which can then rearrange to methylnacetylene and allene, fragment to acetylene, and form a C5 compound by inserting into a second molecule of ethylene. The support for these hypotheses is substantial.31

Our activity distribution can similarly be interpreted by the basic reaction schemes (31) through (33) shown on the following page. The insertion of carbon into a C-H bond gives C7-labeled benzylidene (III). Subsequent hydrogen abstraction by III gives toluene specifically labeled on methyl group (reaction 31). The carbenes (III) and (XVIII) (resulting from C=C insertion
of carbon), on the other hand, may intramolecularly insert into a C-C double bond producing the tricyclic compound IV. The structure IV is postulated here to account for the $C_1$ and $C_2$ activities which are, otherwise, difficult to explain (see p. 152, d.). There are three different bonds, a, b, and c, in the bicyclobutane ring of IV. The simultaneous or stepwise ruptures of a and b, and a and c on $C_1$ respectively give $C_1^-$ and $C_2^-$-labeled carbene III. We shall
assume that the rate of ab and ac ruptures are in such a manner that the ratio of $C_1$ and $C_2$ labeled III equal the $C_1/C_2$ ratio observed in toluene molecule. This is possible since b and c are physically different. One other feature of the bond rupture of IV must be considered. $C_1$ and $C_7$ are equivalent in IV; thus the bond breaking of ab and ac on $C_7$ which gives methyl labeled III may take place with the same rate. The net result of these isomerizations is the formation of IIIa with radioactivity equally distributed in methyl and $C_1 + C_2$ of toluene (with $C_1/C_2$ equivalent to that of toluene obtained from high energy irradiations). Similarly labeled toluene can then be formed by the hydrogen abstractions by IIIa (reaction 32).

Table XIII shows that the ring activity of toluene from 5 eV irradiation is twice as much as that of the methyl group. This is not feasible if III and IV are the only intermediates involved. An intermediate which incorporates more activity in the aromatic ring is mandatory. Cycloheptatrienylidene XIX and the aromatic tropenyl radical, XVII, seems to best fit this requirement (the extensive rearrangement of the hot norcaradiene and cycloheptatriene may lead to the labeling of 6/7 activity in the ring; such a possibility may be eliminated by the reason stated on p. 152-154, e.). XIX can be formed from the C=C insertion of carbon atom. The isomerization of this species is unknown. However, with the help of excess energy introduced into the molecule, the randomization of the molecule is not unlikely. The formation
of XVII may involve the hydrogen abstraction of norcaradienyli-
dene XVIII and/or cycloheptatrienylidene XIX. Another possible
route for XVII is, as was mentioned previously, the interaction
of CH with benzene. The relative importance of these two routes
is difficult to estimate, although for simplicity, the former
is preferred.

While C-H and C=C bond insertions are postulated and sub-
stantiated by Wolfgang, little attention has been paid to the
possibility of product formation via the hydrogen abstraction
by the carbenes produced from the interaction of carbon with
the organic substrate. The evidence that a substantial hydrogen
abstraction by intermediate carbene does take place can be ob-
tained from the study of the reaction of the carbon atoms with
alkanes reported by Skell and Engell. Thus, the reaction of
carbon vapor with isobutane gave 32% (based on the total C
species to which the substrate was exposed) of isopentane, and
the reaction of n-butane similarly gave 21% n-pentane and 23%
isopentane. The absence of CH₂ formation here was firmly es-
tablished with added olefin (no corresponding cyclopropane
was found). Further, 52% of dimethylcyclopropane and 9%
ethylcyclopropane, resulting from an intramolecular C-H bond
insertion of initially formed carbenes, were obtained from iso-
butane and n-butane, respectively. A similar insertion is pos-
tulated here for the formation of IV.

The activity distribution of toluene from high energy irra-
diation can be explained by the reactions (31), (32), and (33).
The participation of 73% of reaction (31), 20% of reaction (32), and 7% of reaction (33) may then account for the observed activity distribution. However, because of the excess kinetic energy of the carbon atom, some methylene gives, as in the case of photolysis, toluene exclusively labeled at the methyl group. While the estimated minimum role of reaction (31) is about 20% (calculated from activity distribution in benzaldehyde), its upper limit contribution cannot be predicted.

The second part of reaction (31), and the formation of methylene, are endothermic processes. The probability of these reactions would certainly be suppressed at the low end of the energy scale. In fact, the yield of toluene was drastically reduced when the energy of incident $^{14}$C$^+$ ion was below 100 eV (see Figure 40).

The data on the 5 eV irradiation (see Table XIII) appears to indicate that reactions (32) and (33) are enhanced at low kinetic energies of the incoming carbon. Thus, at 5 eV irradiation, the ring/methyl activity distribution ratio increases drastically.

The intermediates III, IV, and XVII are most probably formed from carbon atoms of different energy and spin states. The assumption of these states must be made in order to account for the many observations obtained in this work.
4. Cycloheptatriene

Many aspects of this compound's production from benzene and $^{14}\text{C}^+$ ions are described by Pohlit. Its mechanism of formation is assumed to be due to the reaction of \(\text{CH}_2\) and benzene.

While the complete degradation has not been done, the result from the partial degradation (see Figure 39) shows a near random distribution. A process including the formation of nor-caradienyldiene (XVIII), cycloheptatrienyldiene (XIX), and cycloheptatrienyl radical (XVII), followed by hydrogen abstraction, is possible. Some support for this possibility can be found in Williams and Voigt's paper, in which the yield of cycloheptatriene was reduced by 1/3 by the addition of radical scavenger (DPPH).

5. Phenylcycloheptatriene and Diphenylmethane

The formation of these two compounds can best be understood by the insertion reaction of the carbenes III, XVIII, and XIX: phenylcycloheptatriene can be formed by the insertion of III into a C=C \(\pi\) bond, XVIII and XIX into a C-H bond of a benzene molecule, whereas diphenylmethane can be formed by the CH insertion of III. Another possible route for the diphenylmethane is the isomerization of phenylcycloheptatriene (or phenynorcaradiene). Such a process is unlikely since the intramolecular activity distributions of these two compounds are distinctly different.
A photolytically produced phenylcarbene (III) is known to be able to attack the C-C bond of benzene (producing phenylcycloheptatriene) but no diphenylmethane was found in this system. Similarly, the cycloheptatrienyldiene XIX is inert toward addition to an olefinic double bond. Therefore, the insertion into a C-H bond by a thermal III, and the reaction of thermal XIX with benzene, cannot be expected in our system. The assumption of the hot III and XIX is then necessary.

The intramolecular $^{14}$C distribution of phenylcycloheptatriene-$^{14}$C from 5000 eV $^{14}$C+ irradiation is shown in Figure 39. This is tentatively explained by the reactions of the carbenes III, IIIa and/or IIIb, and a hot XIX.

We can, for example, estimate the ratio of participating III, IIIa, and XIX. Since cycloheptatrienyldiene XIX may be the intermediate leading to cycloheptatriene, the cycloheptatriene ring in phenylcycloheptatriene may be assumed to have an activity distribution similar to that of cycloheptatriene. If the activity due to XIX is subtracted, a phenylcycloheptatriene with phenyl/C$_7$ ratio of 16/43 can be obtained. This ratio can further be explained by III and IIIa,b. The relative abundance for III, IIIa and XIX, so estimated, for the phenylcycloheptatriene formation is III:IIIa:XIX = 37:32:37.

There are two alternative ways for the incorporation of $^{14}$C in the phenyl ring: (1) The intermediate formation of spiro(6.6)-tridecahexaene, XXI, from the reaction of XIX with benzene, and a subsequent rearrangement to phenylcycloheptatriene may give the
phenyl labeled compound. (2) The C=C insertion of benzylidene IIIb resulting from the isomerization of XIX. The first possibility was checked by the isolation of its hydrogenated product, spiro(6,6)tridecane, II. The result indicated an upper yield limit of 0.01%. Since the yield of phenylcycloheptatriene is 6%, this route is less appealing. The second route is essentially indistinguishable with that involving IIIa. Whether IIIa or IIIb is responsible for the process could probably be decided by the complete degradation of the phenylcycloheptatriene.

The $^{14}$C distribution in diphenylmethane is relatively simple. The activity in aromatic rings could be accounted for by IIIa or IIIb, and that in the methylene carbon by III.

6. Phenylacetylene and Styrene

$C_{2}H_{x}$ ($x = 0, 1, \text{or 2}$) has been postulated for the phenylacetylene formation.$^{43,90}$ The formation of C-CH via insertion-excitation-decomposition mode was described on p. 137 (Eqs. 12, 13). An alternative mechanism of $C_{2}H_{x}$ formation by the stripping reaction of the fast carbon was also suggested.$^{90}$ Phenylacetylene could then be formed from the subsequent reaction of this $C_{2}H_{x}$
with benzene. The support for this mechanism is substantial, since more than 96% of the activity was found in the acetylene part.

The 2 to 1 ratio in the activity of \( \alpha \) and \( \beta \) of carbons of phenylacetylene is of particular interest. The intermediacy of \( C_2 \) is unlikely since such a species would lead to random distribution. \( C-CH \) is the most likely candidate. The \( \alpha \) and \( \beta \) activity ratio can then be taken as: (1) the ratio of reactions 13 and 12, or (2) the formation of hot \( *C-CH \) species causing a partial scrambling of the activity.

A decomposition stabilization of a metastable \( C_{13} \) compound may, similarly, yield phenylacetylene. This process is supported by the formation of n-alkylbenzenes (see alkylbenzenes). Figure 40 shows that the yield of phenylacetylene and phenylcycloheptatriene is constant in the energy range of 0.1 to 15 KeV (while others change slightly with the change in energy). The possibility of phenylacetylene's formation by the fragmentation of phenylcycloheptatriene, or its precursor, is indicated.

The yield of styrene is quite low (about 0.5%). While no degradation was done for this compound, the mechanism of its formation would be expected to be similar to that of phenylacetylene.

7. Biphenyl

Biphenyl could be produced from the reaction of phenyl radical\(^{107}\) and benzyne\(^{108}\) with benzene.
Benzobarrelene (XXII) and benzocyclooctatetraene (XXIII) are also formed along with biphenyl in the reaction of benzyne with benzene. These compounds (XXII and XXIII) are not found in our target material. Therefore, benzyne appears not to be formed in our irradiations.

The finding of the labeled phenol, on the other hand, may be taken as evidence of the existence of the phenyl radical. This radical is known to be highly reactive (much more reactive than alkylradicals). Its e.s.r. spectrum at 77°C consists of nine hyperfine lines that can be attributed to major hyperfine coupling between the two ortho protons and a smaller coupling due to the two meta protons. At higher temperature (about -50°C), only a singlet spectrum is obtainable. The delocalization of the electron and, as a consequence, the scrambling of activity in the labeled phenyl radical is then expected at high temperature. Figure 39 shows that the 14C in biphenyl is concentrated (81.3%) at the C1 carbons. It appears, therefore, that 14C scrambling by the rearrangement of the phenyl radical hardly occurs in our irradiation. As little restriction to the isomerization of phenyl radical should be expected in the previously mentioned hypothetical "hot spot", the lack of delocalization of 14C in biphenyl is an indication for the absence of such a "hot spot" at the point where the biphenyl precursor is formed.
8. Benzaldehyde, Tropone, and Phenol

These compounds most likely resulted from a quenching reaction by oxygen or an oxygen-containing species on one of the intermediates: benzyldiene (III), cycloheptatrienylidene (XIX), and phenyl radical. C\textsubscript{7}H\textsubscript{6} intermediates such as III, XXIV, XXV, and XVIII\textsuperscript{42} have been suggested for recoil carbon reactions in benzene. No direct evidence of the involvement of such species has been given. Our results here may serve as the first instance in which the participating intermediates are clearly trapped.

The possible sources of the oxygen are discussed by Pohlit.\textsuperscript{44} However, there is as yet no definite answer to this problem.

The yield of benzaldehyde, as well as that of other major products, is not affected when O\textsubscript{2} is introduced simultaneously with the input benzene. This is to be contrasted with \textsuperscript{11}C recoils in ethylene\textsuperscript{31} where the addition of oxygen eliminates the production of a C\textsubscript{5} compound. It is probable that intermediates which cannot react effectively with triplet oxygen are formed.

The carbonyl-ring activity distribution of benzaldehydes obtained from various irradiations are listed in Table XIV. For both
14C+ and 14CO+ beams the activity distributions are similar for irradiations at energies between 5000 and 15 eV. Support for this result is provided by the fact that the kinds and yields of the major products are the same for 14C+ and 14CO+ at the same energy. The indication is that, for the 14CO+ irradiations, the incident 14CO+ ions break down before the actual chemical events take place. The possible spin states of III and XIX will be briefly discussed below.

9. n-Alkylbenzenes

n-Propyl-, n-butyl-, n-pentyl-, n-hexyl-, and n-heptyl-benzenes are tentatively identified from the hydrogenated sample. The yields are between 0.5 and 0.9% (see Table VI). These products are apparently formed from the benzene derivatives carrying unsaturated straight chain groups.

As for the phenylacetylene and styrene, two possible mechanisms can be predicted for the formation of these unsaturated phenyl derivatives: (1) that they are formed from the reaction of benzene with the labeled unsaturated straight-chain fragments resulting from the random fragmentation caused by the fast carbon, and (2) that they are formed as a result of decomposition of a C13 metastable intermediate.

Unsaturated non-aromatic hydrocarbons are certainly formed in our system. The reported compounds are allene, propyne, 1,2-butadiene, 1,3-butadiene, isobutene, and 1-butyne. If the precursors to these C3 - C4 compounds react with benzene, the
precursors to n-propyl- and n-butylbenzene should be formed. Since n-penty-, n-hexyl-, and n-heptylbenzenes are formed in our hydrogenation reaction and their yields are higher than that of their n-propyl- and n-butylbenzene counterparts, unsaturated C₅ - C₇ chain compounds must also be formed. We therefore carefully sought for the presence of unsaturated C₅ - C₇ compounds. The results, unfortunately, were negative. Mechanism (2) is therefore favored over (1). It is believed that insight into this problem could be achieved by degradations of these alkylbenzenes.

10. Barrelanes

We originally thought that the Diels-Alder addition of acetylenic compounds to benzene and the subsequent decomposition of the highly strained adducts, barrelenes (XXVI), might contribute to the formation of benzene and toluene. Similarly, phenylacetylene might react with benzene to give phenylbarrelene. These possibilities were checked by the search for their hydrogenated products, barrelanes. The results indicate that the occurrence of these reactions is, at most, negligible (Table VI).

D. Electronic States of the Precursors

Atomic carbon has been known to have a triplet ground state (³P) with two low-lying, long-lived, metastable singlet states: the ¹D(T-1/2 ≈ 15 sec) and ¹S(T-1/2 ≈ 2 sec) lying ~1.3 eV and ~2.7 eV above the ground state.
The reactions of $^1$S, $^1$D, and $^3$P carbon with both alkanes and alkenes were reported by Skell and Engell.\textsuperscript{21,104,111} They found that the C($^1$S) is capable of inserting into the C-H bond of alkanes. The carbene formed can, in turn, undergo intramolecular insertions and hydrogen abstractions leading to cycloalkanes and alkanes (with one more carbon than the parent molecule). No such insertion is observed for C($^1$D) and C($^3$P). The reactions of carbon atoms with olefins are unique. Only spiropentanes, resulting from consecutive π-bond additions of carbon, and initially formed cyclopropylidene, are formed from C($^1$D) and C($^3$P). None of the spiropentane is obtainable from the reaction of C($^1$S) with olefin; the sole observable products here are the allenes.

Marshall, Mackay, and Wolfgang,\textsuperscript{31} on the other hand, postulated the C-H insertions of C($^3$P) for the reaction of hot $^{11}$C atom with ethylene leading to acetylene. The experimental support for this is convincing. The formation of the other major product, allene, is accounted for by the π-bond insertion of C($^1$D). This is to be contrasted with Skell's results.

The results of these two groups of workers differ in several aspects: (1) Thermal $^1$D and $^3$P do not insert into C-H, while $^3$P does react in carbon recoiling. (2) Thermal C($^1$S), but not C($^1$D), gives allenes from olefins. However, C($^1$D) in carbon recoiling is assumed to give allene. (3) No spiropentane is formed in carbon recoil systems. These differences are, in fact, to be expected, since a large excess of kinetic energy is available in recoil.
chemistry. The C-H insertion of hot C(3P) is a likely process. Similarly, the cyclopropylidene formed from hot 1D and 3P is probably so excited that it bypasses this configuration and collapses directly to the allene.

For the interpretation of all the facts observed in this work, the insertion of the hot C(3P) and C(1D) as well as C(1S) is postulated.

The C-H and C=C insertions of the hot C(3P), C(1D) and C(1S) lead to the intermediate carbenes with corresponding spin states (shown on the following page).

Table VII shows that the addition of O₂ during the irradiation does not affect the kind and yield of the products. The singlet and/or excited nature of all the intermediates is indicated.

The excited triplet phenylcarbene (III, Me labeled) derived from C-H insertion of hot C(3P) can: (a) dispose of its spin by bond rupture to give acetylene, and C≡CH which in turn reacts with benzene to give phenylacetylene, (b) abstract two hydrogens to form toluene-7-¹⁴C, and (c) insert into C=C of benzene to form CHT-7-¹⁴C.

The C=C bond insertion of C(3P) gives excited triplet norcaradienylidene XVIII, and/or cycloheptatrienyldiene XIX, which: (a) may decompose to acetylene and C≡CH, and (b) abstracts hydrogen to give cycloheptatriene-7-¹⁴C (this is supported by the fact that slightly higher activity was found in C₁,₆,₇ of cycloheptatriene, the other CHT from a similar reaction of singlet carbons is expected to isomerize to near randomness due to the higher internal energy of the carbon involved).
A C-H insertion of hot $^{1}D$ gives hot singlet III, similar
reactions of singlet III then provide methylene labeled diphenyl-
methane, $\phi$CHT-$^{14}$C, and toluene-$^{14}$C. Meanwhile, singlet III is
capable of undergoing intramolecular C=C insertion, giving IV, which during its energy degradation isomerized to III \(_a\) (see p. 172). Such a species (III \(_a\) or IV) cannot be obtained from triplet III since the spin disposal is difficult in this case. The insertion and hydrogen abstraction of III \(_a\) eventually leads to the formation of phenylcycloheptatriene (activity in \(C_7 = \text{aromatic } C_1 + C_2\)) and toluene (activity in \(C_7 = C_1 + C_2\)).

The C=C addition of the hot C(\(^1\)D), on the other hand, gives excited norcaradienylidene, XVIII and/or XIX. XVIII affords IV upon an intramolecular C-H insertion. The energy imposed on XVIII and XIX are probably so great that their isomerization to XIX \(_a\) and subsequent randomization of the activity may take place before they abstract hydrogen to give cycloheptatriene with near random activity distribution. The insertion of XIX \(_a\) into the C-H bond of benzene then gives \(\phi\)CHT, whose activity in the CHT ring resembles that of CHT. XIX \(_a\) may also rearrange to phenylcarbene III \(_b\) with radioactivity randomly distributed in the molecule. Similarly distributed toluene may result after hydrogen pick up. While this route may contribute some of the toluene formation at high energy, less of it should be expected from low energy irradiation.

Finally, the C-H insertion of C(\(^1\)S) may give rise to extremely excited phenylcarbene, III \(_e\). A facile hydrogen abstraction and C-H insertion of III \(_e\) should be expected (giving toluene-7-\(^{14}\)C and methylene labeled \(\phi_2\)CH\(_2\)). The intramolecular insertion
of III, leading to IV may not be feasible due to the former's excess energy.

The C=C insertion of C(1S), on the other hand, gives XIX, which promptly rearranges via XIX_a to phenylcarbene, III_b, with a random activity distribution. The formation of randomly distributed toluene, φCHT (activity in CHT ring), and CHT from III_b and XIX_a are as described.

Several features of the above postulates are derivable from Figures 40 and 41, as follows:

1) The radiochemical yields of toluene and cycloheptatriene decrease gradually as the energies of the incident ions are lowered from 15 KeV to 0.1 KeV. The yields of benzaldehyde and diphenylmethane, however, show a reverse relationship. This is difficult to understand because kinetic theory predicts that the kinds and yields of products are independent of the initial energy of the irradiating carbon as long as it is larger than 100 eV. Nevertheless, these observations can be explained by the change in the ratio of the populations of 3P, 1D, 1S states. This is to be expected since the nature and the number of collisions of the incoming carbon should vary as its kinetic energy changes. Thus, the relative abundance of 1D and 1S should be higher at lower energies than at higher energies, but the reverse is true for 3P. This is consistent with the finding that more 3P is present in an inert-gas moderated carbon recoiling system.
Figure 41. The yields of benzaldehyde, diphenylmethane, and phenylcycloheptatriene, and the CHO/C₆H₅ activity ratio of benzaldehyde.
The apparent slight decrease in the yield of toluene and cycloheptatriene, as one goes down to 100 eV, may then be accounted for by the diminution of $^3P$ carbon. The increase in the yields of benzaldehyde and diphenylmethane, on the other hand, may reflect the abundance of $^1D$ and $^1S$.

The benzaldehyde and diphenylmethane line drawn in Figure 41 may need some comment. At first glance, the drawing of those lines may seem arbitrary since the points are well scattered. Their slope is actually determined by the benzaldehyde/benzene and diphenylmethane/benzene yield ratios vs energy plots where a good straight line can be drawn. An example of such plots for benzaldehyde/benzene is shown in Figure 41. Benzene is chosen as internal standard in the hope of minimizing the experimental error because its yields are essentially constant in the energy range studied (Figure 40).

(2) Toluene is probably formed by hydrogen abstraction of both singlet and triplet III, $^{III}_a$, $^{III}_b$, and $^{III}_c$. The yield and $C_6H_5/CH_3$ activity-ratio plots of toluene can now be rationalized. As the energy is lowered from 15 KeV toward 100 eV, the abundance of triplet III decreases. The methyl activity in toluene should fall accordingly. Figure 40 indicates this is not so; the $C_6H_5/CH_3$ activity is constant in this energy range. Therefore, this effect must be balanced out by the change in ratio of the singlet species III and $^{III}_a$ (since excess energy is required for the isomerization of III to $^{III}_a$, the ratio of these species should approach infinity.
as the energy is lowered). In this manner, the constant ring/methyl ratio may be retained as the triplet III decreases.

Figure 41 shows that aldehyde activity of benzaldehyde increases slightly as the energy of $^{14}C^+$ ions fall. This seems to agree with the above prediction. As the energy falls below 100 eV, the hydrogen abstraction of phenylcarbenes becomes difficult. Since the ratio of III (the main source of the methyl label, and a non-contributor to ring label) and III $^{a-c}$ (the sources of toluene's ring label) remains the same, the ring/methyl activity of the product toluene should not be affected by the retarded hydrogen pick-up process. The increase in ring activity below 30 eV indicates either: (i) the C-H insertion of $^3P$ and $^1D$ does not occur, or (ii) even if such insertions do occur, the resulting carbenes do not possess sufficient energy for the hydrogen abstraction.

The formation of toluene at 5 eV may then be accounted for by the reaction of $^{1}S$ carbon.

(3) A straight line is obtained for the energy-yield relationship for benzaldehyde. The yields increase as the energy of the $^{14}C^+$ ions approaches the lower energy end. The supposition that spin states, rather than energy, are important in this product formation is indicated. The precursors for benzaldehyde are probably $^{1}S$ and $^1D$. This is consistent with the observation that the introduction of $O_2$ does not affect their yield.

The slope for the benzaldehyde yield-energy curve is larger than that of diphenylmethane (especially when one considers the
 CHO/\phi H ratio). The same slope should be expected if the same species is involved. It can, therefore, be concluded that both \(^1\)S and \(^1\)D are responsible for the benzaldehyde formation and the \(^1\)S is the predominant reacting species for diphenylmethane.

(4) Assuming the diphenylmethane is formed solely from \(^1\)S, and the rate of reaction of diphenylmethane does not vary appreciably in the energy range studied, the relative abundance of \(^1\)S at 5000 and 5 eV irradiations can be calculated. The value obtained is 1 to 1.8.

Alternatively, about 7% (corresponding to 0.09% of the incident ions) of the observed toluene from 5000 eV irradiation can be accounted for by \(\text{III}_b\) (from \(^1\)S). If the ring activity of toluene from the 5 eV irradiation is assumed to be due to \(\text{III}_b\), the relative abundance, 1, and 1.7, for \(^1\)S at 5000 and 5 eV can be estimated. The agreement with that calculated from diphenylmethane is quite good. This is a support for the prediction (see [2]) that the toluene obtained from 5 eV irradiation is probably formed from \(^1\)S.

(5) The yields of phenylcycloheptatriene at all energies are equivalent within experimental error. The constancy of the yields is due probably to the counterbalancing effect of the reactions involving \(^3\)P, \(^1\)D, and \(^1\)S carbons.

(6) The plot of the sum of toluene, cycloheptatriene, benzaldehyde, and diphenylmethane yields shows a straight line with
zero slope. The importance of the inter-relationship between all the reactions involved in the system is therefore demonstrated.

(7) If the intermediate leading to benzaldehyde is a singlet, the role of triplet carbon in the toluene formation at 5000 eV irradiation can be estimated by comparing the activity distribution. Approximately 60% of the total toluene is attributable to C(3P).

E. The Role of Excess Kinetic Energy

The foregoing discussions seem to indicate that hot singlet and triplet III, IIIa-c, XIX and XIXa play important roles in the product distribution. That the kinetic energy is important in the toluene formation from triplet III can be seen from the drastic increase in ring activity below 30 eV irradiation. The intermediate IV is formed at higher energies, but IV is shown to be absent at 5 eV for the toluene formation (if the argument presented in (4) is valid). The role of singlet III in the toluene formation at both ends of the energy scale is hard to predict.

The role of C(1S) seems to increase at lower energies. Thus, most of the toluene, diphenylmethane, and benzaldehyde, at low energy irradiation, probably resulted from this species. There is as yet no indication that this is so. The degradation of benzaldehyde at low energy should clear up the matter. The CHO/C₆H₅
ratio, after a gradual rise as the energy is lowered, should be expected to fall at even lower energy. While the data for the irradiation at energy below 5 eV is not available presently, the question of whether or not the kinetic energy is able to change the reaction mode of C(1S) cannot be answered from the present work. However, in view of the reported toluene and cycloheptatriene formation from the reaction of thermal carbon and benzene, and the observed C-H insertion of C(1S), it is likely that the intrinsic chemical potential of C(1S) is, itself, sufficient to overcome the threshold energy for C-H insertion in benzene. The addition of excess kinetic energy, therefore, does not alter its course of reaction.

It is obvious that the validity of our suggestions can be determined by the further study of the reaction products; for example, the degradations of benzaldehyde, tropone, diphenylmethane, and phenylcycloheptatriene from lower energy irradiations must be performed in order to determine the quantitative natures of the intermediates involved.

The toluene produced by the reaction of thermal 14C with benzene is of particular interest. Since the hot and thermal C(1S) seem to react similarly, one should expect that the toluene formed in the thermal 14C(1S) reaction should have an activity distribution the same as that from our 5 eV irradiation. Such information could be obtained from experiments of the sort reported by Skell and Engel.
VII. SUMMARY AND CONCLUSION

The study of hot-atom chemistry with nucleogenic carbon is handicapped by many difficulties such as serious radiation damage, the effects of nitrogen sources on the product formations (for $^{14}$C recoils), short half-life of the radiocarbon (for $^{11}$C beams) and the difficulty of determining the threshold energies for the reactions of particular interest. The ion accelerator eliminated most of these difficulties by giving us a beam of monoenergetic $^{14}$C$^+$ ions in the energy range of 15 KeV to 5 eV. It thus has given us some idea of the chemical fates of these carbons with benzene.

In the present research we have found, in addition to the products previously observed in the carbon hot-atom chemistry of benzene (acetylene, benzene, toluene, cycloheptatriene, styrene, and diphenylmethane), the following: phenylacetylene, biphenyl, phenylcycloheptatriene, benzaldehyde, tropone, and phenol for the first time. The latter three compounds resulted from the unintended presence of an (as yet) unknown oxygen source. In the hydrogenated product mixture, we also established the formation of n-C$_3$ - C$_7$ alkylbenzenes, and traces of phenylbarrelane, spiro-(6,6)tridecane, cyclooctane, and o-phenyltoluene. The formation of benzene derivatives carrying unsaturated C$_3$ - C$_7$ straight
chains were, therefore, indicated, as were minor amounts of phenyl-barrelene, spiro(6,6)tridecahexaene, cyclooctatetraene, and o-phenyltoluene. About 28% of the irradiating $^{14}\text{C}^+$ ions should be accounted for by the sum of identified compounds.

The radiochemical yields of the eight major compounds: benzene, toluene, cycloheptatriene, phenylacetylene, benzaldehyde, biphenyl, diphenylmethane, and phenylcycloheptatriene were determined for the irradiations with the energy of the $^{14}\text{C}^+$ ions ranging from 15 KeV to 5 eV.

Toluenes obtained from 5000 and 4000 eV $^{14}\text{C}^+$ irradiations were totally degraded by two different routes. The activity distributions thus obtained were essentially equivalent to that for toluene obtained from the $^{14}\text{N}(n,p)^{14}\text{C}$ reaction in benzene. It appears, therefore, that our reactions are the same as those involved in the $^{14}\text{C}$ recoiling in benzene.

Toluene and benzaldehyde from various energy irradiations were partially degraded. The ring/methyl activity ratios of toluenes were not altered in the energy range from 5000 to 31 eV, while a drastic increase in the ring/methyl activity ratio was observed at 5 eV. The $-\text{CHO}/\text{C}_6\text{H}_5$ activity ratio of the benzaldehyde, on the other hand, showed a slight increase towards the lower energy end.

The partial degradation of the other major compounds were also performed. These were indispensable for the mechanistic interpretation of the over-all picture of the reactions involved in our system.
For the purpose of identifying the products, and for testing the suitability of the degradations, phenylcycloheptatriene, o-phenyltoluene, spiro(6.6)tridecane, glutaric acid-2-\(^{14}\)C, and phenylcycloheptane-1-\(^{14}\)C were synthesized.

The possible mechanisms of the reactions leading to the product formation were discussed. It was suggested that the hot C\(^{3}\)P, C\(^{1}\)D, and C\(^{1}\)S were involved. The insertions of these species into the C-H and C-C bond of benzene might lead to the formation of excited phenylcarbene, cycloheptatrienyldiene and/or norcaradienyldiene. These might fragment, abstract hydrogens, and insert into another molecule of benzene both before and after scrambling the activity by rearrangement. These suggestions were in full agreement with the radioactivity distributions of the products and the energy dependence of the yields of the products. The existence of the proposed intermediates was substantiated by the isolation of benzaldehyde, tropone, and phenol. All the results obtained in this work indicate that the relative abundance of C\(^{3}\)P, C\(^{1}\)D, and C\(^{1}\)S played a key role in the product distribution and the labeling pattern of the products.

The formation of \(\cdot\)CH\(_2\) has long been accepted as the major reactive intermediate leading to toluene and cycloheptatriene. We do not now regard this as the major intermediate, at least for the toluene formation, since such a role for \(\cdot\)CH\(_2\) conflicts with many of our observations. Hydrogen abstraction by phenylcarbene was, instead, tentatively suggested as the main reaction
leading to toluene formation. Evidence for this is presented in this work.

Thermal C\(^{3P}\) and C\(^{1D}\) are incapable of inserting into C-H bonds, but such insertions do clearly take place in hot-atom reactions. It is therefore concluded that the hot and thermal reactions are distinctly different for C\(^{3P}\) and C\(^{1D}\). The intrinsic reactivity of C\(^{1S}\) may, on the other hand, be so high that both hot and thermal species react similarly.
VIII. APPENDIX

THE SPIRO(6,6)TRIDECANE

The mass spectrum of spiro(6,6)trideca-1-one (I) and spiro-(6,6)tridecane are shown in Figure 42. The m/e of molecular ions in the mass spectrum as well as the elementary analysis of I and II are in complete agreement with the molecular formula C_{13}H_{22}O and C_{13}H_{24}.

(I) was synthesized from the base catalyzed condensation of cycloheptanone with 1,6-dibromohexane (see Experimental). It was possible that 3 isomeric compounds would be formed:

XXVII could not be reduced to C_{13}H_{24} by Wolff-Kishner reduction. Apparently, we have to choose between I and XXVIII. Examination of the fragmentation pattern in mass spectrometry could be the solution to our problem. However, without the knowledge of the fragmentation pattern of the spiro compound this could not be attempted.
Figure 42. Mass spectrum of I and II.
A benzylidene derivative formation\textsuperscript{112} was taken as the indication of the existence of the -CH$_2$-C- group in a spiroketone molecule. Our attempt in making this derivative was not successful. It was probable that the steric hindrance of our spiroketone inhibited the approach of attacking benzaldehyde molecule.

Figure 43 shows the IR spectrum of II. Chiurdoglu et al.\textsuperscript{113} and Dixon et al.\textsuperscript{114} have studied the IR spectra of various spiro compounds and reported that the absorption at 1387 - 1364 cm$^{-1}$ (doublet) which was contributed by the gem-dimethyl and isopropyl grouping might be the characteristics of the spiro system. Our spectrum shows an ill-resolved doublet in this region. This, in connection with absorption at 1228, 1206, and 1180 cm$^{-1}$, which were also observed in gem-dimethyl compounds, was taken as an indication for the presence of a quaternary carbon. The bicyclic structure (XXVIII) was therefore excluded.

The confirmative evidence of structure I as well as II was obtained from the NMR spectrum of these compounds. The spectrum of spiro(5.5)undecan-1-one (XXIX), spiro(4.7)dodecan-6-one (XXX), spiro(5.6)dodecan-1-one (XXXI), and spiro(6.7)tetradecan-8-one (XXXII)* were studied for comparison. The α,α-dideutero derivative of I, XXIX-XXXII, were also prepared and the nmr taken.

Figures 44a,b through 47a,b show the nmr spectra of XXIXa,b, through XXXIIa,b, and Figures 48a,b, 49 and 50 show those of Ia,b, II, and 2-methylcyclohexanone, respectively.

*These four compounds were kindly provided by Professor Krapcho of the University of Vermont.
Figure 43. The IR spectrum of spiro(6,6)tridecane.
Figure 44a. NMR spectrum of spiro(5,5)undeca-1-one.
Figure 44b. NMR spectrum of 2,2-dideuterospiro(5,5)undeca-1-one.
Figure 45a. NMR spectrum of spiro(5,6)dodeca-1-one.
Figure 45b. NMR spectrum of 2,2-dideuterospiro(5,6)dodeca-1-one.
Figure 46a. NMR spectrum of spiro(4,7)dodeca-6-one.
Figure 46b. NMR spectrum of 7,7-dideuterospiro(4,7)dodeca-6-one.
Figure 47a. NMR spectrum of spiro(6,7)tetradeca-8-one.
Figure 47b. NMR spectrum of 9,9-dideuterospiro(6,7)tetradeca-8-one.
Figure 48a. NMR spectrum of spiro(6,6)trideca-1-one.
Figure 50. NMR spectrum of 2-methylcyclohexanone.
Table XIX summarizes all the data and the assignment of the peaks. The protons in XXIX_{a,b} and XXX_{a,b} were assigned according to De Johgh and Wynberg. The proton resonance of XXXI_{a,b}, XXXII_{a,b} and I_{a,b} required alternative peak assignment as shown in the table. The region at $\sigma = 2.1 - 2.4$ was assigned to $\alpha$-keto hydrogens, and $\sigma = 1.5 - 2.1, \sigma = 1 - 1.5$ to $\beta$-hydrogens within the same ring of the ketone group and the rest of methylenes respectively. The 2-methylcyclohexanone was chosen to check this assignment. Although this compound was purified repeatedly on glc, a clear-cut spectrum was not obtained. However, as shown in the table, the fact that the
Table XIX. NMR spectrum of spiro compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\sigma$ ppm</th>
<th>Peak ratio</th>
<th>Number of H</th>
<th>Position of H</th>
</tr>
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<td>Peak ratio</td>
<td>Number of H</td>
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resonance between $\sigma = 1.6 - 2.21$ and $1.1 - 1.6$ ppm had the ratio of approximately 2:1 assured that the interpretation was not incorrect. It appeared that in the case of the spiro compound containing cyclohexanone (XXIX and XXX), the $\beta$-methylene hydrogen in both rings showed the same chemical shift. While for the compounds containing cycloheptanone and cyclooctanone (XXXI and XXXII), the $\beta$-methylene hydrogens in the ring containing the keto group appeared at the lower field than that of the other ring. This difference was attributed to the effect of the conformation of the molecules.

The deuterium exchanges were performed in the hope that some informative changes in the splitting pattern might be observed. It could not be used to differentiate tertiary from secondary hydrogen (e.g., XXVIII from I) since bicyclo(5.2.1)decan-10-one underwent deuterium exchange readily.\textsuperscript{116} Figures 44 through 50 show the disappearance of the $\alpha$-hydrogen peaks in all cases.

The splitting pattern for $\beta$-hydrogen peaks stayed similar both before and after the exchange. One would expect more changes to take place if a bicyclic structure was involved. Therefore, it might be taken as evidence for the spiro structure.

While spiro(5.5)undecane\textsuperscript{115} showed only one resonance at $\sigma = 1.35$ ppm, the spirane($\Pi$) in this experiment showed two peaks at $\sigma = 1.42$ and $1.28$ ppm, with the ratio of 1:2. These were, in complete agreement with structure $\Pi$, assigned as the signal for
hydrogens on carbons α to the quaternary carbon and the rest of the carbons, respectively. The peak width of the latter (10 cps) was broader than that of the former (7 cps). This line broadening might be the reflection of less equivalence of the outer protons.
IX. REFERENCES


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