Title
Rearrangements of azidoquinones. IX. Pyrolysis of 2,3-diazido-1,4-naphthoquinone-dibenzenesulfonimide

Permalink
https://escholarship.org/uc/item/0529f30p

Journal
Tetrahedron Letters, 12(39)

ISSN
0040-4039

Authors
Moore, HW
Lee, MS

Publication Date
1971

DOI
10.1016/S0040-4039(01)97252-1

License
CC BY 4.0

Peer reviewed
REARRANGEMENTS OF AZIDOQUINONES. IX. PYROLYSIS OF 2,3-DIAZIDO-1,4-NAPHTHOQUINONE-DIBENZENESULFONIMIDE

Harold W. Moore and Mei-Sie Lee

Department of Chemistry
University of California
Irvine, California 92664

(Received in USA 2 June 1971; received in UK for publication 1 September 1971)

Azidoquinones have been shown to be very versatile synthetic intermediates. γ-κyaio-
alkylidine-Δα,β-butenolides, 1 2-cyano-1,3-cyclopentencdioncs, 2 cyanoketenes, 3 azapinc-
diones, 4 aminoquinones 5 and acylcyanides 6 can be prepared from azidoquinones by employing
the appropriate reaction conditions. The synthetic utility of this class of compounds suggested
an investigation of certain azidoquinone derivatives to see if analogous transformations could
be accomplished. Reported here is a study of the thermal decomposition of 2,3-diazido-1,4-
naphthoquinone-dibenzenesulfonimide, 2. This vicinal diazide cleaves pyrolytically in reflux-
ing benzene to give phthaloyl cyanide-dibenzenesulfonimide, 3. Compound 3 undergoes subse-
quent hydrolytic ring closure upon reaction with alcohols to 1,3-substituted isoindolines and
phthalimidine-benzenesulfonimides.

The purple crystalline diazide, 2, was prepared in nearly quantitative yield from 2,3-
dichloro-1,4-naphthoquinone-dibenzenesulfonimide, 7 4, upon reaction with excess sodium
azide. A solution of 2.1 mol of 4 in 40 ml of acetone was reacted with 6.1 mol of sodium
azide in 5 ml of water at 0-5°. The reaction solution immediately turned from yellow to purple
upon addition of the azide. Water (20 ml) was added to the reaction solution which induced the
precipitation of the diazide, 2.

Phthaloyl cyanide-dibenzenesulfonimide, 3, was obtained by refluxing a suspension of
725 mg (1.4 mol) of 2 in 7 ml of anhydrous benzene for 6 hrs. A small amount (40 mg) of
an unidentified insoluble precipitate was collected by filtration and the solvent removed in
vacuo to give 3 as a brownish oil. The structure of 3 is in complete agreement with its spec-
tral data (Table I) and its chemical properties. The thermal cleavage, 2→3, has good
precedent; 2,3-diazido-1,4-naphthoquinone loses nitrogen in refluxing toluene and forms
phthaloyl cyanide, 6 and 9-diazidobenzene thermally fragments to cis-1,4-dicyanobutadiene. 8

3645
The α-cyanobenzencesulfonimide moieties in 3 are very reactive toward hydroxylic reagents. Compound 3 reacts readily with water to give the substituted N-benzenesulfonyllactam, 5, in 85% yield. The formation of 5 is envisaged as arising via the isoindoline, 4, which then eliminates hydrogen cyanide. Hydrolysis of the lactam 5 with 5% NaOH converted it to benzenesulfonamide, 8, and N-benzenesulfonylphthalimide, 7, which were identified by comparison (ir and mixed mp) with authentic samples.
The hydrolytic ring closure of \( \mathcal{Z} \) could also be accomplished with alcohols. Methanol and isopropanol react with \( \mathcal{Z} \) to give respectively the 1,3-substituted isoindolines, \( \mathcal{Y} \) and \( \mathcal{Z} \). These compounds are heat labile and lose hydrogen cyanide upon attempted recrystallization from acetone-diethyl ether to give respectively the substituted N-benzenesulfonylphthalimidine-benzenesulfonimides, \( \mathcal{T} \) and \( \mathcal{T} \). The spectral data (Table I) for compounds \( \mathcal{T} - \mathcal{T} \) are in complete accord with their proposed structures. Of particular utility in the structural assignments is the nmr spectrum of \( \mathcal{I} \) which shows nonequivalent methyl absorptions (\( \delta \), 1.38 and 1.10) for the isopropyl group. This is consistent with structure \( \mathcal{I} \) which has the isopropoxide moiety directly substituted to an asymmetric center.

\[
\mathcal{Z} + \text{ROH} \quad \rightarrow \quad \mathcal{Y}, R = -\text{CH}_3 \\
\mathcal{Z}, R = -\text{CH}(_3)\text{CH}_3 \\
\mathcal{T}, R = -\text{CH}(_3)\text{CH}_3
\]

**TABLE I**

<table>
<thead>
<tr>
<th>Spectral Data of New Compounds</th>
<th>( \mathcal{T} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compound</strong></td>
<td><strong>Yield</strong></td>
</tr>
<tr>
<td>( \mathcal{Z} )</td>
<td>&gt;95%</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>( \mathcal{Y} )</td>
<td>85%</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>( \mathcal{Y} )</td>
<td>72%</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>( \mathcal{Y} )</td>
<td>74%</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>( \mathcal{Y} )</td>
<td>166-68</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Adams and coworkers\textsuperscript{10} have published an extensive investigation concerning the synthesis and chemistry of variously substituted quinonedimides. The availability of the corresponding azidoquinonedimides via standard routes gives a class of previously unexplored azides. The chemistry of these compounds as compared to that of the corresponding azidoquinones is currently under study.

ACKNOWLEDGEMENT

The authors are grateful to the National Science Foundation (GP 19268) for financial support of this project.

REFERENCES

10. Combustion analysis for the new compounds 2, 10 and 11 are all in complete accord with their proposed formulations.