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Permalink
https://escholarship.org/uc/item/0c010108

Journal
Journal of the American Chemical Society, 121(26)

ISSN
0002-7863

Authors
Reed, CA
Fackler, NLP
Kim, KC
et al.

Publication Date
1999-07-07

DOI
10.1021/ja981861z

Peer reviewed
Isolation of Protonated Arenes (Wheland Intermediates) with BARf and Carborane Anions. A Novel Crystalline Supercacid

Christopher A. Reed,* Nathanael L. P. Fackler, Kee-Chan Kim, Daniel Stasko, and Daniel R. Evans

Department of Chemistry, University of California, Riverside, California 92521-0403

Peter D. W. Boyd and Clifton E. F. Rickard

Department of Chemistry, The University of Auckland, Private Bag, Auckland, New Zealand

Received May 27, 1998
Revised Manuscript Received March 26, 1999

Protonated arenes are widely accepted intermediates in electrophilic aromatic substitution chemistry. Known as Wheland intermediates, but more correctly ascribed to Pfeiffer and Wizinger, they have been characterized by isolation and spectroscopy at low temperatures in superacid media. However, obtaining an X-ray crystal structure of a protonated arene salt is an unresolved experimental challenge, and thermal instability has prevented their development as useful reagents. In this paper, we show how modern anions lead to readily crystallized salts of remarkable thermal stability. The salt of protonated benzene is a crystalline superacid with distinct advantages over existing superacid media.

The key to the stability of protonated arene salts lies in the choice of counterion. We have had particular success with the carborane CB11H6Cl6â-. One of the most useful members of a newly recognized class of large anions with uncommonly low nucleophilicity and exceptional inertness is also useful although limited by B–C bond cleavage at higher acidities. The strong Lewis acidity of the ionolike silylum species, (Et3Si)Y+(Y=Br, Cl; Y=I), can be converted to strong Brønsted acidity by treatment with anhydrous HCl. The greater bond strength of Si–Cl (ca. 113 kcal molâ‘¹) versus H–Cl (103 kcal molâ‘¹) provides a driving force for this reaction. Added methylated arenes in dry benzene solution are the strongest bases present, and salts of protonated methylated arenes can be isolated upon partial removal of the volatiles, addition of hexanes, and filtration (eq 1).

\[
\text{Et}_3\text{SiY} + \text{HCl} + \text{Arene} \rightarrow \left[\text{H(arene)}\right]^+ \left[\text{Y}^-\right] + \text{Et}_3\text{SiCl}
\]

For hexamethylbenzene, pentamethylbenzene, and mesitylene, respectively, the salts [C6Me6H][CB11H6Cl6], [C6Me6H2][F20- BPh4], and [C6Me6H2][F20- BPh4], have been isolated. Yields of the yellow crystalline products are typically ca. 60%. The UV–vis \(\lambda_{\text{max}}\) of the C6Me6H+ ion in 1 (in dichloromethane) is 398 nm—the same as that of C6Me6â+ and similar to that of C6Me6Clâ+ (410 nm). As a solid, 4 has a shelf life of several months but decomposes upon heating above 50 °C to give C6H15F, B(C6F5)3, and mesitylene. The structures of 1, 2, and 3 have been investigated by X-ray crystallography, but only 2 has an ordered cation.9 As shown in Figure 2, the order arises from a rare10 example of C–H...F–C hydrogen bonding between the H(pentamethylbenzene)â+ cation and surrounding anions. The site of protonation is clearly the unmethylated carbon atom, i.e., the structure is a σ complex. The C–C bond lengths (Figure 3) are consistent with predominant cyclohexadienyl character similar to that of the heptamethylbenzenium12 and the very recently reported chlorohexamethylbenzenium ion.9 The observed structure is in good agreement with that calculated by a variety of methods,13 suggesting that the interaction with the anion is weak. The low temperature 1H NMR (3.1 ppm) of 9 indicates that both C6Me6â+ and 9 are present in the 1H NMR (3.1 ppm) of 9 indicates that both C6Me6â+ and 9 are present in the

(10) Crystal data for [C6Me6H2][F20- BPh4]: \(a = 34.1308(10), b = 34.8106(10), c = 10.8128(4)\) Å; \(\beta = 128.46(8)\) °; \(Z = 16, D_\text{m} = 1.713 \text{g cm}^{-3}\). 298K \(R = 0.0283, R_\text{p} = 0.0693\) and GOF = 1.07. The methylene protons were observable in difference-electron density maps; positions were refined in the final model.
(13) Full geometry optimization of the [C6Me6H2]+ cation used the program Gaussian 94. Calculations at the Hartree–Fock–McLennan–Plesset and density functional (B3LYP) levels using a 6-311+G* basis set gave structures of C6Me6â+ symmetry (neglecting the methyl protons) consistent with the cyclohexadienyl structure: C(1)–C(2) 1.480, 1.473, 1.478 Å, C(3)–C(4) 1.358, 1.386, 1.377 Å, C(3)–C(4) 1.431, 1.428, 1.432 Å, respectively.
α-complexed static structure, unobservable by NMR in the liquid range of CD₂Cl₂. A α-complex is also the lowest energy calculated structure. The CP MAS ¹³C NMR spectrum of 5 at −120 °C shows peaks centered at 184, 176, 136, and 52 ppm confirming the presence of the α-complexed benzienium ion. Coalescence of these peaks to 145 ppm at ≈−60 °C indicates an interesting case of solid-state proton mobility.

It takes several orders of magnitude of acidity above 100% H₂SO₄ to fully protonate benzene, so 5 readily qualifies as a superacid. If kept dry, it is stable for months. This contrasts with all other salts of protonated benzene which are unstable at room temperature. Upon heating slowly in a sealed tube, 5 gradually turns amber (140–250 °C) with loss of benzene and chlorobenzene, becoming a dark brown solid at 350 °C.

The instability of previously isolated arenium ion salts has left the impression that ions such as C₆H₅⁺ are intrinsically unstable. This is better understood by considering the pathways that particular anions allow for decomposition. Salts formed from nonoxidizing haloacids can simply revert to free arene, hydrogen halide and Lewis acid, e.g., crystalline [H(toluenium)⁺][BF₄⁻] decomposes to toluene, HF, and BF₄⁻ upon warming to −50 °C. Salts formed from oxidizing superacids have anions (e.g., HSO₄⁻, SbF₆⁻, SF₆⁻) capable of irreversible oxidative and nucleophilic destruction. These observations highlight an important property of [C₆H₅⁺][CB₁₁H₆Cl₆]⁺. It is a superacid that is nonoxidizing, not a Brønsted/Lewis acid mixture (compare HF/SbF₃), and the anion is much less nucleophilic than those previously used. As a stable, weighable reagent, 5 is capable of delivering protons more cleanly and stoichiometrically than previously possible. It represents a new generation of superacids (of which HN(SO₂CF₃)₂ may be a member) in which oxidation is separated from protonation. Brønsted acidity is separated from Lewis acidity, the anions are as nonnucleophilic as is presently attainable, and protons of superacid strength can be readily delivered to molecules in common organic solvents. This combination of properties gives protonated arenium salts potentially wide application in nearly nucleophile-free environments.

Acknowledgment. This paper is dedicated to Professor Warren R. Roper on his 60th birthday. We are very grateful to Len Mueller for CPMAS spectra. This work was supported by the National Science Foundation and The University of Auckland Research Committee.

Supporting Information Available: Details of the synthetic procedures and characterization of products 1–5 and the X-ray crystal structure determination of 2. This material is available free of charge via the Internet at http://pubs.acs.org.

JA981861Z


