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Isolation and X-ray Structure of Chloroarenium Cations as Wheland Intermediates in Electrophilic Aromatic Chlorination

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Cationic σ-complexes (or benzenium ions) of aromatic hydrocarbons with various electrophiles are commonly accepted as transient (Wheland) intermediates in electrophilic aromatic substitutions.[1] Olah and co-workers were the first to obtain nearly 30 years ago[2] the direct spectroscopic (NMR) evidence for the existence of the NO_2^+ and Cl^+ complexes in magic acid solutions at −70 °C by using hexamethylbenzene as the prototypical aromatic donor. However, the isolation of these highly labile cations as crystalline salts for definitive structural characterization by X-ray crystallography has remained an experimental challenge. As such, we now report that the low-temperature chlorination of hexamethylbenzene (**1**) with antimony pentachloride in dichloromethane (under an argon atmosphere) leads to a bright yellow solution, which upon the addition of cold (−78 °C) hexane affords a highly unstable precipitate according to the stoichiometry in eq 1.[3]

$$\mathbf{1} + 2\,SbCl_5 \xrightarrow[CH_2Cl_2]{-78\ ^\circ C} \mathbf{1}\text{-}Cl^+\,SbCl_6^- + SbCl_3 \qquad (1)$$

The identity of chlorohexamethylbenzenium cation ($\mathbf{1}-Cl^+$) in eq 1 is confirmed by comparison of the ^1H NMR spectrum with that reported by Olah et al., in which the yellow solution at −80 °C shows the characteristic pattern of four singlets in an intensity ratio of 1:2:2:1 at δ 2.15, 2.67, 3.07, and 3.25 ppm.[2] However the isolated yellow salt is very labile and readily decomposes[4] if simply warmed above −70 °C. After repeated attempts at crystallization (especially by varying the solvent and temperature), we have now successfully isolated the reactive yellow crystals by the slow diffusion of hexane into a dichloromethane solution of **1**-Cl^+ $SbCl_6^-$ at −90 °C. Single-crystal analysis[5] by X-ray crystallography at −150 °C establishes its molecular structure, and the ORTEP diagram in Figure 1 shows the chlorine atom to be bonded to a single carbon atom (C_1). Such an attachment of a positive chlorine (Cl^+) to hexamethylbenzene leads to the rehybridization of C_1 from sp^2 to sp^3 (as judged by the change in bond angles)[6] and to a planar cyclohexadienyl ring system in which the bond lengths and angles are significantly altered as compared to neutral **1**[7] [e.g., C_1-C_2 (1.49 Å) and C_1-C_6 (1.50 Å) approximates a C−C single bond, and C_2-C_3 (1.36 Å) and C_5-C_6 (1.38 Å) shortens to a C−C double bond, whereas C_4-C_3 (1.44 Å) and C_4-C_5 (1.43 Å) corresponds to an elongated C−C aromatic bond].

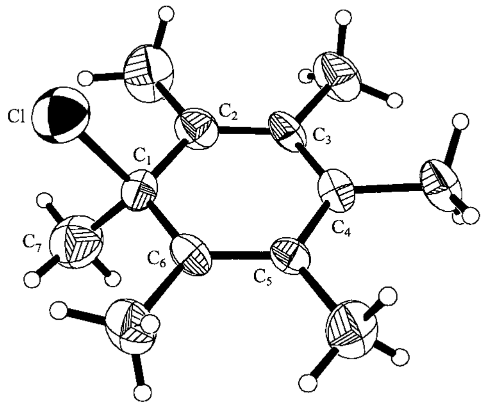

Figure 1. ORTEP diagram showing chlorine attachment to a single carbon center in the chloroarenium cation **1**-Cl^+ from hexamethylbenzene.

It is particularly noteworthy that the pertinent chlorine−carbon bond distance of 1.81 Å is within one standard deviation of that found in the σ-bonding of chlorine to quaternary carbon centers in other (stable) chlorocarbons.[8] We further note that owing to the isosteric nature of chlorine and methyl groups, the chloroarenium cation **1**-Cl^+ is isostructural with the yellow heptamethylbenzenium cation (**1**-CH_3^+),[9] as underscored by comparison of the superimposed structures in Figure 2. [Compare the bond lengths/angles of **1**-Cl^{+6} and **1**-CH_3^{+}.[9]] The strong similarity in the electronic structures of the chloro- and methylarenium cations is also indicated by the UV−vis spectra of **1**-Cl^+ (λ_{max} = 410 nm, log ϵ = 4.01 M^{-1} cm^{-1}) and **1**-CH_3^+ (λ_{max} = 398 nm, ϵ = 3.94 M^{-1} cm^{-1}), as illustrated in Figure 3.

The same treatment of the homologous hexaethylbenzene (**2**) with antimony pentachloride at −78 °C affords the characteristic

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(1) (a) Taylor, R. *Electrophilic Aromatic Substitutions*; Wiley: New York, 1990. (b) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992. (c) For a review of arenium structures, see: Koptyug, V. A. Arenium Ions—Structure and Reactivity. In *Comtemporary Problems in Carbonium Ion Reactivity, III*; Rees, C. A., Ed., Springer: New York, 1984. See also: Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133. Reed, C. A.; Fackler, N.; Drovetskaya, T.; Evans, D. 215th National Meeting of the American Chemical Society, 1998; Inorg. Chem. Div., Abstract No. 202.

(2) Olah, G. A.; Lin, H. C.; Mo, Y. K. *J. Am. Chem. Soc.* **1972**, *94*, 3667. See also: Loktev, V. F.; Korchagina, D. V.; Shubin, V. G. *Izv. Nauk SSSR Otd. Khim. Nauk* **1974**, *10*, 2374.

(3) (a) For the stoichiometry of aromatic chlorination with $SbCl_5$, see: Rathore, R.; Kumar, A. S.; Lindeman, S. V.; Kochi, J. K. *J. Org. Chem.* **1998**, *63*, 5847. (b) Compare: Kovacic, P.; Sparks, A. K. *J. Am. Chem. Soc.* **1960**, *82*, 5740. (c) The reduced $SbCl_3$ was isolated as a colorless crystalline complex [**1**, $SbCl_3$] from the reaction of excess **1** with $SbCl_5$ in dichloromethane at −90 °C, and its structure was confirmed by X-ray crystallography, unpublished results.

(4) For reaction pathways leading to the rapid decomposition of chlorohexamethylbenzenium cation, see: Baciocchi, E.; Ciana, A.; Illuminati, G.; Pasini, C. *J. Am. Chem. Soc.* **1965**, *87*, 3953. Kochi, J. K. *Tetrahedron Lett.* **1974**, 4305 and related papers.

(5) (a) Single crystals of **1**-$Cl^+SbCl_6^-$ were obtained by dissolution in cold (−90 °C) dichloromethane followed by careful layering of the 0.01 M yellow solution with cold hexane and allowing the mixture to stand at −95 °C. (b) Crystal data for **1**-Cl^+ $[(C_{12}H_{18}Cl)^+\ SbCl_6^-{\cdot}CH_2Cl_2]$. MW = 617.09, monoclinic, $P2_1/c$, $a = 9.289(2)$ Å, $b = 12.1903(4)$ Å, and $c = 23.4716(8)$ Å, $\beta = 93.792(1)°$, Dc = 1.811 Mg m^{-3}, $V = 2263.70(12)$ Å^3, $Z = 4$. Data collection was carried out at −150 °C on a Siemens SMART diffractometer equipped with a CCD detector, using Mo Kα radiation (λ = 0.71073 Å). The total number of reflections measured were 20184, of which 6585 reflections were symmetrically nonequivalent. The structure was solved by direct methods and refined by full-matrix least-squares procedure. Final residuals were $R1 = 0.067$ and w$R2 = 0.107$ for 6529 reflections with $I > 2\sigma(I_0)$. Crystal data for **2′**-Cl^+ $[(C_{18}H_{30}Cl)^+\ SbCl_6^-{\cdot}2CH_2Cl_2]$. MW = 786.17, triclinic, $P\bar{1}$, $a = 10.4999(2)$ Å, $b = 13.0007(2)$ Å, and $c = 13.2270(1)$ Å, $\alpha = 100.915(1)°$, $\alpha = 109.835(1)°$, and $\beta = 101.549(1)°$, Dc = 1.634 Mg m^{-3}, $V = 1597.90(4)$ Å^3, $Z = 2$. Final residuals were $R1 = 0.041$ and $wR2 = 0.0.88$ for 13689 reflections with $I > 2\sigma(I_0)$.

(6) The pertinent bond angles in **1**-Cl^+ are: $C_2-C_1-C_6 = 116.8°$; $C_2-C_1-Cl = 106.0°$, $C_6-C_1-C_7 = 111.5°$, and $C_7-C_1-Cl = 105.7°$.

(7) X-ray crystallography at −150 °C establishes the aromatic C−C bond lengths in hexamethylbenzene (**1**) to be 1.410 Å (unpublished results).

(8) (a) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A, G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19. (b) Owing to the isosteric nature of chlorine and the methyl group there is a slight disorder (∼20%) in the structure of **1**-Cl^+ that could not be readily resolved. (c) Also note that the hexachloroantimonate anion is strongly coordinated to Cl as judged by the close contact of $Cl-ClSbCl_5$ = 3.11 Å.

(9) (a) Borodkin, G. I.; Nagi, S. M.; Gatilov, Y. V.; Shakirov, M. M.; Rybalvo, T. V.; Shubin, V. G. *Zh. Org. Khim* **1992**, *28*, 1806 and references therein. (b) Compare also: Doering, W. von E.; Saunders, M.; Boyton, H. G.; Earhart, H. W.; Wadley, E. F.; Edwards, W. R.; Laber, G. *Tetrahedron* **1958**, *4*, 178. (c) The equivalent bond lengths/angles in **1**-CH_3^+ are: C_1-C_2 (1.47 Å), C_2-C_3 (1.36 Å), C_3-C_4 (1.46 Å), C_4-C_5 (1.44 Å), C_5-C_6 (1.34 Å), C_1-C_6 (1.45 Å), C_1-CH_3 (1.59 Å), $C_7-C_1-C_8$ = 110°.

10.1021/ja983314j CCC: $15.00

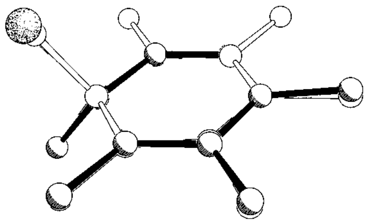


Figure 2. Isostructural comparison of the chloro- and methylarenium cations as shown by the superposition of **1**-Cl$^+$ and **1**-CH$_3$$^+$.

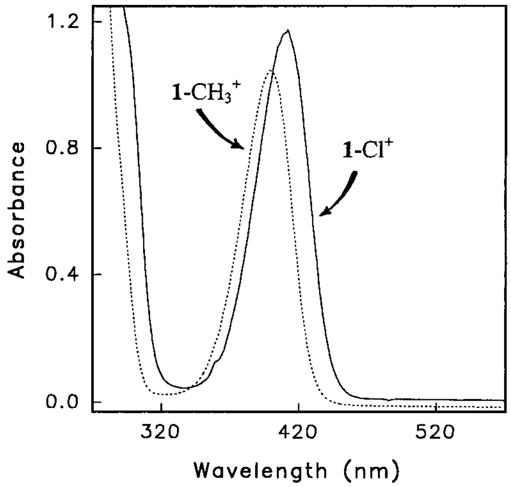


Figure 3. UV−vis spectra of the chloroarenium cation **1**-Cl$^+$ and the methylarenium analogue **1**-CH$_3$$^+$ in dichloromethane solution.

yellow solution (λ_{max} = 420 nm)[10] that also yields pale yellow microcrystals by the workup procedure at −90 °C (vide supra). However, all attempts at low-temperature recrystallization and X-ray crystallographic analysis at −150 °C reveal the isomeric cation **2′**-Cl$^+$ shown in Figure 4,[11] in which the *gem*-diethyl group is clearly a result of the rapid isomerization of the first-formed chloroarenium cation, i.e.

$$\mathbf{2} \quad + \quad \mathrm{SbCl_5} \longrightarrow \mathbf{2}\text{-Cl}^+ \xrightarrow[\text{o}]{} \mathbf{2'}\text{-Cl}^+ \qquad (2)$$

The facility of the 1,2-ethyl shift in eq 2 (relative to that pertaining to eq 1) is qualitatively in accord with the significantly enhanced migratory aptitude of the ethyl (relative to the methyl) group in Wagner−Meerwein rearrangements.[12]

The spectral observation (and isolation) of chloroarene cations is only feasible with the fully substituted hexaalkylbenzenes such as **1**-Cl$^+$ and **2**-Cl$^+$, since the analogous exposure of partially methylated benzene donors to antimony pentachloride leads only to the corresponding chlorobenzenes. For example, the treatment of 0.1 M SbCl$_5$ with 1 equiv of mesitylene **3** (or pentamethylbenzene **4**) at −50 °C affords a yellow solution that takes on a pale-brown coloration with stirring for 15 min. However, rapid quenching at this temperature leads to a nearly quantitative yield of only chloromesitylene (86%) or chloropentamethylbenzene (93%). We conjecture that chloroarenium cations analogous to **1**-Cl$^+$ and **2**-Cl$^+$ are also generated from **3** and **4**, but their detection is not possible owing to their deprotonation that is faster than Cl$^+$ transfer,[2] i.e.

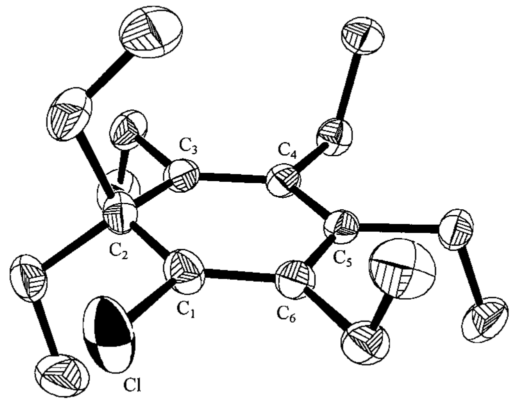
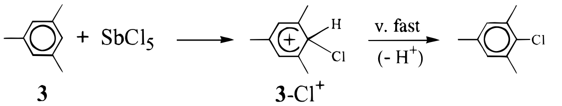


Figure 4. The *gem*-diethyl groups in the arenium cation **2′**-Cl$^+$ resulting from the spontaneous Wagner−Meerwein rearrangement of the chloroarenium cation **2**-Cl$^+$ during hexaethylbenzene chlorination.



3 **3**-Cl$^+$ (3)

If so, we believe the chloroarenium cation **1**-Cl$^+$ in Figure 1 serves as a excellent prototype for the Wheland intermediate in electrophilic aromatic chlorination.[13] Indeed, the structural and electronic (near) identity of the chloro- and methylarenium cations in Figures 2 and 3 points to a series of 1-X-cyclohexadienylium structures for the Wheland intermediate that are not strongly affected by the electrophilic (X = Cl, CH$_3$) substituent.[15] With this conclusion in mind, we hope to direct our attention to the highly elusive nitroarenium cations.

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Supporting Information Available: Crystallographic data for **1**-Cl$^+$ [(C$_{12}$H$_{18}$Cl)$^+$ SbCl$_6$$^-$·CH$_2Cl_2$] and **2′**-Cl$^+$ [(C$_{18}$H$_{30}$Cl)$^+$ SbCl$_6$$^-$·2CH$_2Cl_2$] including positional parameters, thermal parameters, and interatomic distances and angles (10 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[10] Identified as **2**-Cl$^+$ by its diagnostic ^{1}H NMR spectrum with δ 0.29 (br t, 6H), 1.17 (t, 6H), 1.35 (t, 3H), 1.39 (t, 3H), 2.62 (q, 4H), 2.74 (br q, 2H), 2.95 (br q, 2H), 3.07 (q, 4H) and ^{13}C NMR spectrum with δ 12.64, 14.37 (2C), 15.22, 21.95, 23.74, 28.62, 29.65, 71.40, 147.71, 148.01, 189.02, 197.25, 207.27 ppm.

[11] As an arenium cation, the relevant bond lengths/angles in **2′**-Cl$^+$ are essentially the same as those in **1**-Cl$^+$, i.e., C$_1$−C$_2$ (1.489 Å), C$_2$−C$_3$ (1.497 Å), C$_3$−C$_4$ (1.386 Å), C$_4$−C$_5$ (1.426 Å), C$_5$−C$_6$ (1.435 Å), C$_1$−C$_6$ (1.373 Å), C$_1$−Cl (1.721 Å), C$_{21}$−C$_2$−C$_{23}$ = 107.0°, C$_1$−C$_2$−C$_{21}$ = 110.5°, C$_3$−C$_2$−C$_{23}$ = 107.1°, and C$_1$−C$_2$−C$_3$ = 113.6°.

[12] For example, the relative intramolecular migratory aptitude for Et/Me = 30 obtains in the arenium cations from phenanthrene derivatives. See: Korchagina, D. V.; Derendyaev, B. G.; Shubin, V. G.; Koptyug, V. A. *Zh. Org. Khim.* **1976**, *12*, 384. Also see: Koptyug, V. A. *Top. Curr. Chem.* **1984**, *122*, 119. Shubin, V. G.; Borodkin, G. I. In *Stable Carbocation Chemistry*; Surya Prakash, G. K., Schleyer, P. v. R., Eds.; Wiley and Sons: New York, 1997, and references therein.

[13] In this regard, the chloroarenium cation **1**-Cl$^+$ is a better model for the Wheland intermediate in electrophilic aromatic chlorination than the related chloroarenium cation derived from the tris-annelated benzene donor TMT (dodecahydrotrimethanotriphenylene).[14] Indeed the latter (TMT-Cl$^+$) shows an unusually red-shifted absorption band at λ_{max} = 510 nm and a rather long C$_1$−Cl distance of 1.86 Å arising from steric effects of tris-annelation in the nonplanar cyclohexadienylium moiety. We believe that the latter is also responsible for the greater reactivity of TMT-Cl$^+$ (compared to **1**-Cl$^+$) in electrophilic (transfer) chlorination.

[14] Rathore, R.; Loyd, S. H.; Kochi, J. K. *J. Am. Chem. Soc.* **1994**, *116*, 8414.

[15] Especially in view of the fact that chlorine and carbon (CH$_3$) have substantially different electronegativities of 2.83 and 2.50, respectively.