tautomerization, hydrolysis of the nitrile group, and lactonization on acidification.

When the study was extended to 2-methoxyacetophenone, an unexpected rearrangement was observed: some 2-methyoxyacetophenone isomerized to 3-methoxyacetophenone (experiments 4 and 5; reaction 3). Special care was taken to ensure the purity of the starting ketone and the product was isolated as a pure substance: nmr[7b] 2.60 (s, 3 H, acetyl), 3.85 (s, 3 H, methoxyl), 7.0–7.6 (4 H, aromatic). To gain information on the pathway for the rearrangement, 2-methoxyacetophenone was photolyzed in the presence of cyanide in deuterium oxide (experiment 6). Integration of the nmr spectrum of the 3-methoxyacetophenone isolated from this reaction showed that one deuterium had been introduced in the aromatic ring, and the splitting pattern in the aromatic region showed that the deuterium was in the 2 position (see Figure 1).[8] No deuterium was found in the aromatic portion of the recovered 2-methoxyacetophenone, and a control experiment showed that 3-methoxyacetophenone did not undergo hydrogen–deuterium exchange at the ring under these conditions. Accordingly, we conclude that the H–D exchange accompanies the rearrangement. These results rule out a mechanism in which hydrogen and a neighboring acetyl or methoxyl group simply exchange positions and render unlikely a rearrangement proceeding by a benzvalene-type intermediate.[9]

It was then found that photoexcited 3,5-dimethylacetophenone reacts similarly with cyanide ion (experiment 7); the ketone fraction isolated (34%) after irradiation for 23 min in 0.17 *M* sodium cyanide in 11:1 acetonitrile–water was 75% 3,5-dimethylacetophenone and 25% 2,4-dimethylacetophenone: nmr[7b] 2.33 (s, 3 H, methyl), 2.46 (s, 6 H, methyl and acetyl), 6.97 (broad peak with shoulder at 6.91, 2 H, aromatic protons meta to acetyl), and 7.50–7.5 (doublet for 1 H ortho to acetyl). No rearrangement occurred in the absence of cyanide ion. Formation of 2,4-dimethylacetophenone corresponds to migration of acetyl (rather than methyl) in the rearrangement. In support of this pathway, the 2,4-dimethylacetophenone isolated from a reaction conducted in acetonitrile–deuterium oxide had a deuterium atom ortho to the acetyl group.[10] The nmr spectrum of the 3,5-dimethylacetophenone recovered from this experiment showed no incorporation of deuterium in the aromatic nucleus. These results can be accommodated by a mechanism involving attack by cyanide ortho to the acetyl group; however, further data are needed to define the actual pathway.

Only limited work has as yet been done with other nucleophiles. Hydroxide, though less reactive than cyanide, attacks photoexcited 3-methoxyacetophenone in aqueous solution to give a good yield of 3-hydroxyacetophenone (isolated in 66% yield; on the basis of unrecovered 3-methoxyacetophenone the yield is 90%).

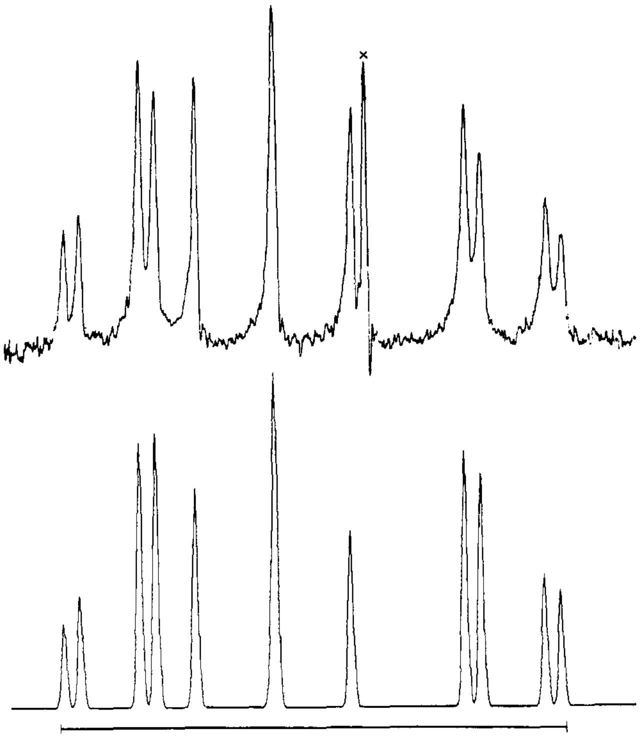

Figure 1. Aromatic hydrogen region of 90-MHz nmr spectrum of 2-deuterio-3-methoxyacetophenone from experiment 6; observed spectrum above, calculated spectrum below.[8] The calibration bar represents 50 Hz. The peak marked × corresponds to $CHCl_3$.

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Stable Carbocations. CXXXIX.[1] Nitro- and Chlorohexamethylbenzenium Ions and 1-Nitro- and 1-Chloro-2,4,6-trifluoromesitylenium Ions

Sir:

A series of long-lived benzenium ions or σ complexes, considered to be intermediates of electrophilic aromatic substitution reactions, has been directly observed.[2] Some stable long-lived σ complexes have even been isolated as crystalline salts.[3] However, these ions until now were all limited to protonated (generally with superacids) or alkylated benzenium ions, such as the heptamethylbenzenium ion.[4] Long-lived σ-complex intermediates of nitration[5a] or chlorination[5b]

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(8) The integrated intensity observed for resonance of the aromatic protons relative to the methoxyl protons (3.00) is 3.1, and the intensities for the individual protons are 1.03, 1.07, and 1.01 for H_4, H_5, and H_6, respectively. The chemical shifts and coupling constants for the calculated spectrum (Figure 1) are: H_4, 7.11 ppm; H_5, 7.37; H_6, 7.53; J_{4-5}, 8.25 Hz; J_{4-6}, 1.03; J_{5-6}, 7.61. We are grateful to Dr. J. B. Lambert for helpful discussions concerning the spectra.

(9) I. E. Den Besten, L. Kaplan, and K. Wilzbach, *J. Amer. Chem. Soc.*, **90**, 5868 (1968).

(10) The resonance characteristic of the H_6 proton was absent, and a single peak in the aromatic region was found (6.99 ppm, for $H_3 + H_5$). The intensity of this peak relative to that for the 4-methyl group was somewhat low (1.71/3.00 rather than 2/3), suggesting that some deuterium was also incorporated at the 3 and/or 5 positions.

(1) Part CXXXVIII: G. A. Olah, *Angew. Chem.*, in press.

(2) (a) For a review, see D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970; (b) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and Gh. D. Mateescu, *J. Amer. Chem. Soc.*, **94**, 2034 (1972).

(3) G. A. Olah, *ibid.*, **87**, 1103 (1965).

(4) W. v. E. Doering, M. Saunders, H. G. Boyton, H. W. Earhart, E. F. Wadley, W. R. Edwards, and G. Laber, *Tetrahedron*, **4**, 178 (1958).

(5) (a) G. A. Olah, *Accounts Chem. Res.*, **4**, 240 (1971). (b) For a review, see H. P. Braendlin and E. T. McBee in "Friedel-Crafts and Related Reactions," Vol. III, Part II, G. A. Olah, Ed., Wiley-Interscience, New York, N. Y., 1963.

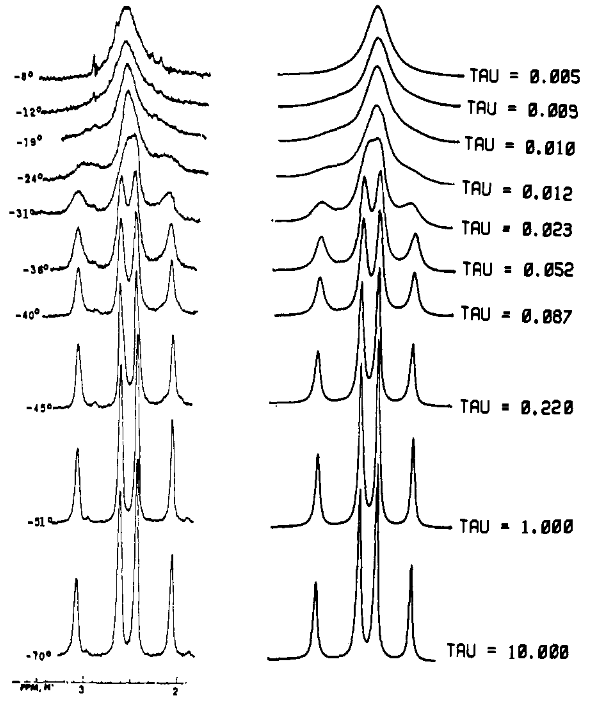
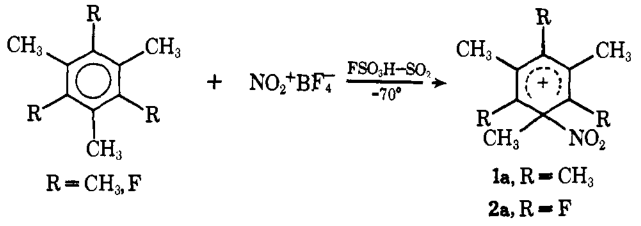


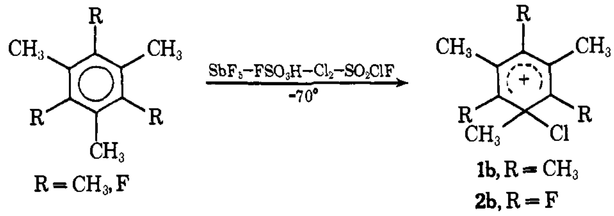
Figure 1. Temperature-dependent pmr spectra (60 MHz) of nitrohexamethylbenzenium ion, **1a** (left), and calculated spectra (right).

reactions were not observed, as proton elimination from these σ complexes is generally so rapid that no physical detection is possible. In early work (preceding the nmr era) we reported an ion complex of benzotrifluoride with nitryl fluoride and boron trifluoride.[6] This complex on reinvestigation is now considered the O-protonated *m*-nitrobenzotrifluoride onium ion formed *via* proton transfer from ring to oxygen. It is inferred that if proton transfer could be avoided, the intermediate ions should be capable of long-lived existence. Therefore, hexasubstituted benzenes, *i.e.*, hexamethylbenzene and trifluoromesitylene, were chosen in our studies because CH_3 and F are poor or not leaving groups in electrophilic aromatic substitution reactions. Nitration[7] and chlorination[8] of substituted benzene is known. We now wish to report the first direct observation of stable, long-lived benzenium ion intermediates formed in both electrophilic nitration and chlorination of hexamethylbenzene and trifluoromesitylene.

When hexamethylbenzene in SO_2 was added, with vigorous stirring, to a solution containing $NO_2^+BF_4^-$–FSO_3H–SO_2 at −70°, the resulting clear solution exhibited a proton magnetic resonance (pmr) spectrum (Figure 1, left, bottom trace) consisting of four singlets, at δ 2.00, 2.40, 2.60, and 3.00 with a peak area ratio 1:2:2:1. This pmr pattern is quite similar to that reported for the hexamethylbenzenium hexafluoroantimonate salt in SO_2,[3] except that there is no aliphatic methine proton peak present and consequently the "aliphatic" methyl group is of a singlet. Thus, we assign the spectrum to the nitrohexamethylbenzenium ion **1a**. The most shielded singlet is assigned to the methyl group attached to the sp^3 carbon atom and the most deshielded is that of the *p*-CH_3. The remaining two singlets can be readily assigned. The fact that a position ortho to the aliphatic carbon is more deshielded than the meta position has been demonstrated by nmr (^1H and ^{13}C) studies in alkylbenzenium ions.[2b] Thus, the lower field singlet (δ 2.60) is assigned to the *o*-CH_3 and the higher field singlet (δ 2.40) to the *m*-CH_3.



The chlorohexamethylbenzenium ion **1b** was obtained by adding a solution of hexamethylbenzene in SO_2ClF to a solution of Cl_2 in "magic acid," SbF_5–HSO_3F–SO_2ClF solution at −70°. The pmr spectrum of ion **1b** again shows four singlets with a ratio of 1:2:2:1 at δ 2.03 (Cl-C-CH_3), 2.54 (*m*-CH_3), 2.96 (*o*-CH_3), and 3.11 (*p*-CH_3).



Protonation of hexamethylbenzene in strong acid media, such as magic acid, is known.[2] Under our experimental conditions, thus, protonation may have occurred. However, in the presence of excess chlorine, only ion **2a** was observed. When chlorine was less than equimolar, both ion **2a** and protonated hexamethylbenzene were observed. In the absence of FSO_3H, that is, in SbF_5–Cl_2–SO_2ClF solution, ion **2a** could not be observed as a stable entity and decomposed.

Similar to the nitro- and chlorohexamethylbenzenium ions, 1-nitro-2,4,6-trifluoromesitylenium ion, **2a**, and the 1-chloro-2,4,6-trifluoromesitylenium ion, **2b**, were also observed under similar conditions. The pmr spectrum of ion **2a** shows two singlets at δ 2.26 (3 H) and 2.33 (6 H) and that of **2b** at δ 2.60 (3 H) and 2.65 (6 H). The pmr data are consistent with the benzenium ion structures.

The ^{19}F nmr spectra of ions **1b** and **2b** are even more significant in confirming the structures. In ion **1b**, the *p*-F shows a triplet at ϕ −16.20 (J_{FF} = 83 Hz) and the two *o*-F, a doublet at ϕ 42.97 (J_{FF} = 83 Hz). Ion **2b** again shows a triplet at ϕ −19.18 (J_{FF} = 83 Hz) for the *p*-F and a doublet at ϕ 43.08 (J_{FF} = 83 Hz) for the two *o*-F. The unusually large long-range fluorine–fluorine couplings are good evidence in supporting the structure of the ions, because this type of long-range fluorine–fluorine coupling is known in protonated 2,4,6-trifluoromesitylene.[9]

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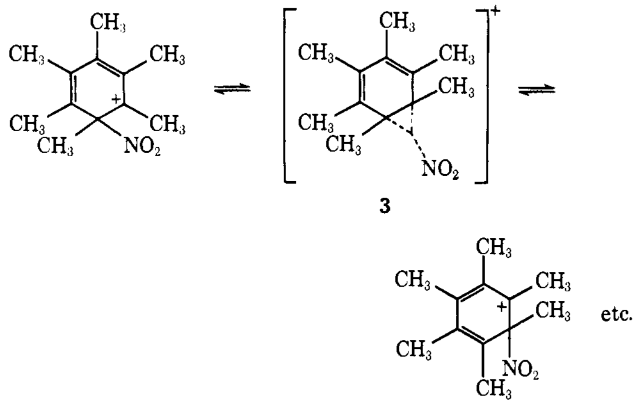
(6) G. A. Olah and S. J. Kuhn, *J. Amer. Chem. Soc.*, **80**, 6541 (1958).

(7) H. Suzuki, *Bull Chem. Soc. Jap.*, **43**, 879 (1970), and reference therein.

(8) E. Baciocchi, A. Ciana, G. Illuminati, and C. Pasini, *J. Amer. Chem. Soc.*, **87**, 3953 (1965).

(9) G. A. Olah and T. E. Kiovsky, *ibid.*, **90**, 2583 (1968).

Temperature-dependent pmr spectra of ion **1a** were also observed (Figure 1, left). This behavior indicates that the nitro group (NO_2^+) is not fixed and can undergo a degenerate migration or exchange process. On the right-hand side of Figure 1, we also show the theoretical, computed spectra with various exchange rates.[10] Matching of the line shapes allows the activation energy to be determined as $E_a = 16.8 \pm 1.5$ kcal/mol. The nitrohexamethylbenzenium ion **1a** is slightly decomposing to yet unidentified products at higher temperature (> −8°). It is assumed that excess nitronium ion (NO_2^+) could attack the C–H bond of the methyl groups and give benzylic products. The exchange process was further studied by quenching experiments. When benzene or mesitylene was added to the solution of ion **1a**, nitrobenzene or nitromesitylene was formed.[11] With hexamethylbenzene in slight excess, no formation of nitrobenzene or nitromesitylene was observed, even when the temperature was raised to −20°. If benzene or mesitylene was mixed with hexamethylbenzene in SO_2 before the addition of the nitronium ion solution, formation of nitrobenzene or nitromesitylene was detected. These experimental results strongly support the intramolecular nature of the exchange process. The migration of NO_2^+ is assumed to proceed *via* 1,2-nitro shifts involving three-center-bond benzonium ion transition states **3**.[12]



No temperature-dependent nmr spectra of ion **2a** were observed in the temperature range from −70 to −20°. This may be due to the *vic*-fluorine substituent causing a high enough activation energy barrier as to prohibit the nitro group to migrate. The pmr spectra of chlorohexamethylbenzenium ion **1b** and 1-chloro-2,4,6-trifluoromesitylenium ion **2b** were also temperature independent ranging from −70 to −20°. It must be assumed that the leaving ability of "Cl^+" is less than that of NO_2^+, indicating increased barrier for chlorine migration in these chlorinated ions. Such relative migrating ability ($NO_2^+ > Cl^+$) was also observed recently by Perrin.[13] Whereas alkenechloronium ions are well known[14] and even observed as stable species, cycloalkene (polyene) chloronium ions were until now never observed.[15] Higher strain in the latter seems to make them thermodynamically less favorable.

We consider present studies of significance, because they represent the first observation of an intermediate σ complex in electrophilic aromatic substitution reactions (nitration and chlorination) other than protonation and alkylation. Furthermore, they help to understand the strong complexing ability of polyalkylbenzenes with electrophiles.

Acknowledgment. Support of our work by the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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(10) The theoretical spectra for various rate constants were calculated by use of a multiple site exchange program originally obtained from Dr. T. Gerig and was adapted to the Univac 1108 computer by Dr. W. E. Heyd. The methyl exchange process of the heptamethylbenzenium ion was previously studied by a more elaborate line-shape method by Professor M. Saunders, as reported in "Magnetic Resonance in Biological Systems," A. Ehrenberg, B. G. Malmstrom, and T. Vanngard, Ed., Pergamon Press, New York and London, 1967, pp 85–99, who pioneered the study of exchange processes and wrote the original programs.

(11) The resultant solution was quenched with ice and washed with $NaHCO_3$ solution. The nitro products were then extracted with ether and analyzed by gas chromatography.

(12) For the concept of three-center-bond carbonium ions, see G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).

(13) C. L. Perrin, *J. Org. Chem.*, **36**, 420 (1971).

(14) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 4744 (1967); **90**, 2587 (1968).

(15) G. A. Olah, G. Liang, and Y. K. Mo, *ibid.*, **94**, 3544 (1972).

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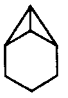
Transition Metal Catalyzed Valence Isomerizations of Tricyclo[4.1.0.0^{2,7}]heptane. Evidence for an Organometallic Intermediate[1]

Sir:

It has recently been suggested that the transition metal catalyzed rearrangement of bicyclobutanes, like **1**, proceeds *via* a stepwise process involving intermediates **2** and **3**[2] with the presence of **2** being established by trapping with methanol. In the course of studies in these laboratories related to these processes,[3] we have found that by using a high catalyst concentration, an organometallic intermediate can be detected by nmr spectroscopy.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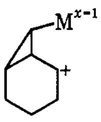

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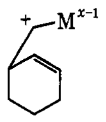

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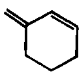
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With a catalytic amount of $PdCl_2(C_6H_5CN)_2$, **1** rearranges to the diene **4** in deuteriochloroform solutions.[4] Using a 1:1 molar ratio of **1** and the catalyst

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(1) This work was supported by the National Science Foundation, Grant No. GP-8700.

(2) (a) P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, **93**, 4597 (1971); (b) M. Sakai and S. Masamune, *ibid.*, **93**, 4610 (1971); (c) M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *ibid.*, 4611 (1971).

(3) (a) W. G. Dauben, C. H. Schallhorn, and D. L. Whalen, *ibid.*, **93**, 1446 (1971); (b) W. G. Dauben and A. J. Kielbania, *ibid.*, **93**, 7345 (1971).

(4) Reactions were carried out in base-washed nmr tubes in $CDCl_3$. Molar ratio of **1** to catalyst was approximately 30:1. Products were identified by comparison of spectral properties and vpc retention times with the known compounds. We have found that the following catalysts also bring about a rearrangement of **1** to **4**: $PdCl_2[(C_6H_5)_3P]_2$; $PdCl_2[(C_6H_5)_3As]_2$; $PdCl_2[(C_6H_5)_3Sb]_2$; $PdCl_2[P(OCH_3)_3]_2$; $PdCl_2[P(OC_6H_5)_3]_2$; $PtCl_2[(C_6H_5)_3P]_2$; $PtCl_2[(C_5H_5)_3Sb]_2$; $PtCl_2(pyr)_2$; $[Rh(nor)Cl]_2$; $Rh[(C_6H_5)_3P]_3Cl$, $RhCO[(C_6H_5)_3P]_2X$, X = Cl, Br, I. Pyridine is (pyr) and norbornadiene is (nor).