These facts, in combination, demonstrate that an electron transfer from a σ bond to π acceptor really occurred. Naturally, observation of these phenomena is not limited to polysilanes. Hexamethyldigermane showed a charge-transfer band maximum at 23,000 cm^{-1} and gave strong photosignals attributable to TCNE radical anions, whereas hexamethyldistannane underwent a spontaneous reaction with TCNE, presumably through a charge-transfer interaction, to give precipitates. Hydrocarbons with strained σ bonds are also expected to behave similarly.

Work on related spectroscopic, photochemical, and epr studies is in progress.

Acknowledgment. The authors are grateful to Professor R. West and Dr. Traven for making their results available prior to publication. The support of this work by the Ministry of Education (Grant-in-aid No. 8304 and No. 68304) is acknowledged.

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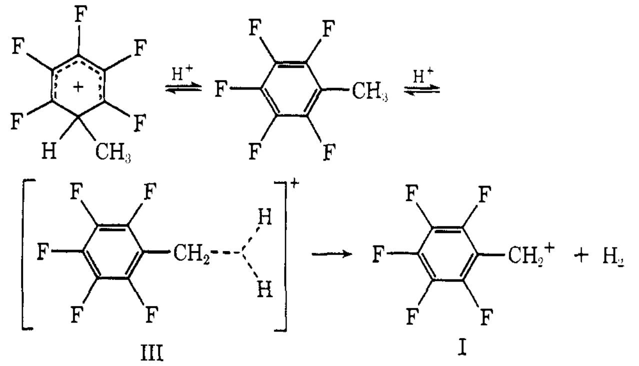
Electrophilic Reactions at Single Bonds. VIII.[1] Side-Chain C–C and C–H σ-Bond Protolysis in Alkylbenzenes, Alkylpolyfluorobenzenes, Alkylbenzoic Acids, and Nitroalkylbenzenes. Competing σ- *vs.* π- and n-Donor Ability

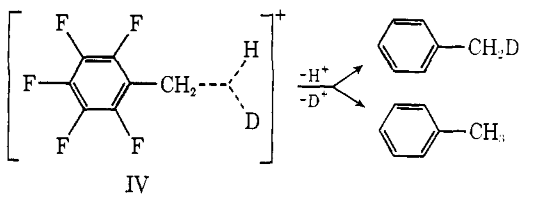
Sir:

Evidence has been presented that alkanes undergo protolytic processes in superacids through the formation of pentacoordinated carbonium ions.[2] We now would like to report the protolytic behavior of some alkylbenzenes in superacids showing competing side-chain σ-bond protolysis with aromatic ring π protonation (as well as side-chain n-protonation in substituted alkylbenzenes).

When pentafluorotoluene is treated with $HF-SbF_5-SO_2ClF$ solution at −80°, the methyl protons display a temperature-dependent pmr singlet absorption at δ 2.60. It becomes broad when the temperature is raised (*e.g.*, −30°) and sharpens when cooled back to −80°. The temperature dependence of the methyl absorption indicates hydrogen exchange with the superacid system. (Radical cation formation[3] would also lead to the broadening, as it shortens the transverse relaxation time, T_2,[4] but the ^{19}F nmr spectrum shows no such behavior.) The solution also shows an additional pmr singlet absorption at δ 9.60 which was found to be identical with that of the pentafluorobenzyl cation I. The ^{19}F nmr spectrum of ion I is also identical with that reported in our previous work.[5] These results show that protonation of the C_α–H bond occurred leading through cleavage of III to I (and H_2). Pentafluorotoluene thus reacts like a substituted methane, *i.e.*, as a σ base. It, of course, is probable that initial protonation takes place on the π-electron system of the ring. The highly deactivated ring, however, is a poor π donor and ring π protonation leading to the benzenium ion II must be considered completely reversible (CH_3^+ and F^+ are both extremely poor leaving groups). Protonation at the nonbonded electron pairs of fluorine, due to the high electronegativity of fluorine, is also reversible. On the other hand, C–H protonation leads through cleavage of III to ion I. As the reaction is carried out at atmospheric pressure with H_2 escaping from the system, formation of I is not reversed.



We also found that pentafluorotoluene underwent hydrogen–deuterium exchange in $DF-SbF_5-SO_2ClF$ solution at −20°. The intensity of the methyl pmr absorption of pentafluorotoluene was gradually reduced and the peak split into a broad multiplet. Meanwhile, the intensity of acid pmr absorption was increased (some protic acid impurity giving rise to a low intensity peak at δ 10.2 was originally present in $DF-SbF_5$). Pentafluorotoluene, recovered on quenching of the solution with ice-water, showed extensive hydrogen–deuterium exchange (15% d_1 and 2% d_2) as analyzed by mass spectrometry. We suggest that the exchange reaction involves a three-center bound carbonium ion transition state IV similar to III.



Hydrogen abstraction through a linear transition state giving I and through its reaction with formed HD deuterated pentafluorotoluene could not explain, due to the very low concentration of HD in the system, the exchange results. These data explain the temperature-dependent pmr spectra of pentafluorotoluene in $HF-SbF_5-SO_2ClF$ solution.

In the case of secondary alkylbenzenes, such as isopropylbenzene and *sec*-butylbenzene, containing a tertiary benzylic C–H bond, side-chain C–H bond protolysis takes place in competition with ring protonation even without the presence of ring deactivating substitutents. Thus, isopropylbenzene when treated with $HF-SbF_5-SO_2ClF$ solution at 0° gave 90% isopropylbenzenium ion V and 10% dimethylphenylcarbenium ion VI. The latter was observed as a singlet absorption at δ 4.1 and the characteristic aromatic ab-

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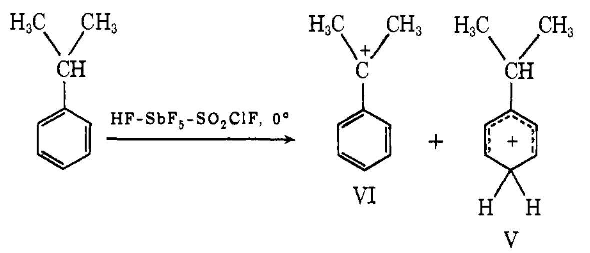
[1] Part VII: G. A. Olah, P. W. Westerman, Y. K. Mo, and G. Klopman, *J. Amer. Chem. Soc.*, **94**, 7859 (1972).

[2] G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *ibid.*, **93**, 1251 (1971), and references given therein.

[3] N. M. Bazhm, Yu. V. Pozdnyakovish, F. D. Shteingarts, and G. A. Yakabson, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, **No. 10**, 2300 (1969).

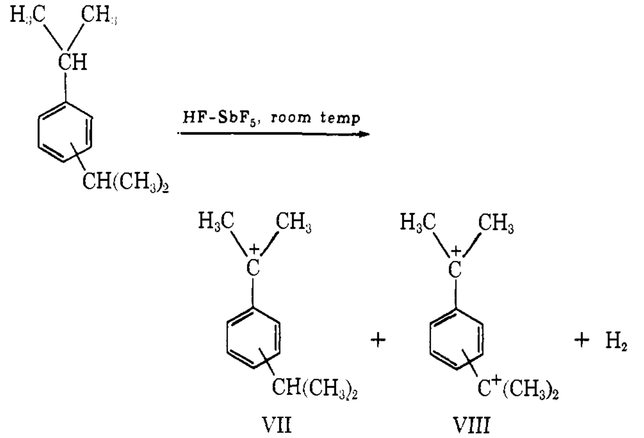
[4] J. W. Emsley, J. Feeny, and L. H. Sutcliffe, "High Resolution Nmr Spectroscopy," Vol. II, Pergamon Press, Oxford, 1966, p 8.

[5] G. A. Olah and M. B. Commisarow, *J. Amer. Chem. Soc.*, **89**, 1027 (1967).

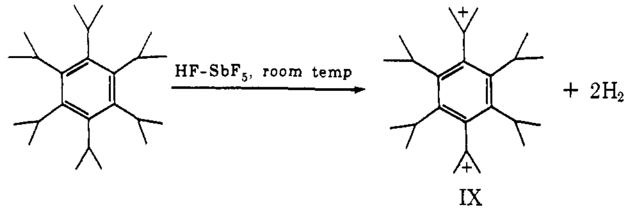


sorptions pattern in the δ 8–9 region.[6] Similarly, the pmr spectrum of isopropylbenzenium ion has been reported[7] and the formation of this species could be readily identified. Furthermore, no significant disproportionation or isomerization of isopropylbenzene was found under these experimental conditions.

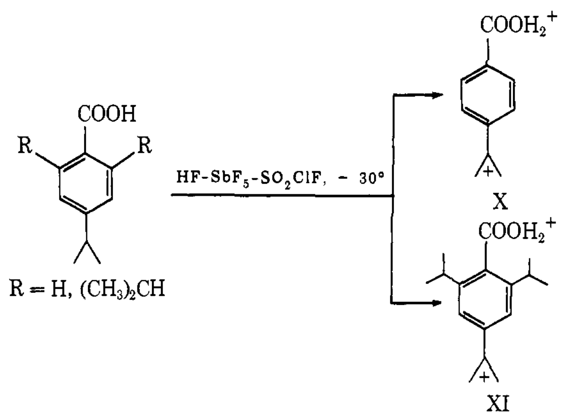
When isomeric diisopropylbenzenes were treated with HF–SbF$_5$, besides products of disproportionation, the mono- and dications VII and VIII were formed, respectively, with evolution of hydrogen, as indicated by the pmr parameters of the observed ions (VII, $\mathrm{C^+CH_3}$ δ 4.2, $\mathrm{CH_3}$ 2.0, CH 2.95, ArH ~3.2; VIII, $\mathrm{C^+CH_3}$ ~4.5, ArH ~8.6).



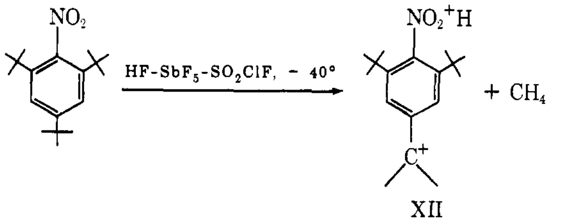
In the case of the protolysis of hexaisopropylbenzene in fluoroantimonic acid, besides depropylation, formation of dication IX is observed as the result of successive C$_\alpha$–H bond cleavage. The pmr spectrum of dication IX shows a doublet at δ 1.90 ($(\mathrm{CH_3})_2\mathrm{CH}$, J = 6 Hz), a multiplet at 3.8 (methine proton), and a singlet at 4.33 ($(\mathrm{CH_3})_2\mathrm{C^+}$). Quenching dication IX with ice-water gave mainly the corresponding diol (identified by ir, nmr, and mass spectrometry).



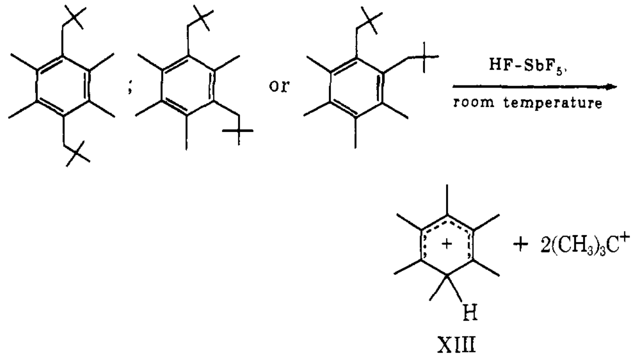
p-Isopropylbenzoic acid and 2,4,6-triisopropylbenzoic acid when treated with HF–SbF$_5$–SO$_2$ClF solution showed formation of dications X and XI, respectively. Ring protonation in these systems is very limited (if at all) and besides protonation of the carboxylic group, the tertiary benzylic C–H bond undergoes protolytic cleavage. (The pmr parameters are: X, $\mathrm{CO_2H^+}$ δ 13.2, $\mathrm{C^+CH_3}$ 4.5, ArH 8.8; XI, $\mathrm{CO_2H^+}$ δ 13.2, $\mathrm{C^+CH_3}$ 4.5, $\mathrm{CH_3}$ 2.15 (1.95), CH ~3.1, ArH 8.6.)



In the case of 2,4,6-tri-*tert*-butylnitrobenzene, besides the usual protolytic dealkylation giving the *tert*-butyl cation, dication XII ($\mathrm{NO_2H^+}$ δ 14.5, $\mathrm{C^+CH_3}$ 4.2, $(\mathrm{CH_3})_3\mathrm{C}$ 2.15 (1.90), ArH 8.2) and methane (analyzed by mass spectrometry) were formed, indicating protolytic side-chain C–C bond cleavage.



Isomeric (ortho, meta, and para) dineopentyltetramethylbenzenes when treated with neat HF–SbF$_5$ at room temperature gave hexamethylbenzenium ion XIII and 2 mol of *tert*-butyl cation, exclusively. These results indicate side-chain C–C bond protolysis in these systems. In contrast, when neopentylbenzene was treated with HF–SbF$_5$–SO$_2$ClF at 0° for 10 hr, the solution (after cooling at −78°) contained 70% 4-neopentylbenzenium ion XIV (ring π-protonation product) and 30% phenylisopropylcarbenium ion XV[8] (with some unidentified polymeric products) due to side-chain C–C bond protolysis. The difference in protolytic behavior between neopentylbenzene and isomeric dineopentyltetramethylbenzene is due either to greater difficulty in ring protonation of the latter, due to steric effects, or to a diprotolytic process,



The observed protolytic behavior of alkylbenzenes, pentafluorotoluene, alkylbenzoic acids, and nitroalkylbenzenes in superacid media reflects the competing

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[6] G. A. Olah, *J. Amer. Chem. Soc.*, **86**, 932 (1964); D. G. Farnum, *ibid.*, **86**, 934 (1964).

[7] G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and Gh. D. Mateescu, *ibid.*, **94**, 2034 (1972).

[8] G. A. Olah, C. U. Pittman, Jr., E. Namanworth, and M. B. Comisarow, *ibid.*, **88**, 5571 (1966).

π and n *vs.* σ electron-donor ability. The latter becomes more predominant when strongly electron-withdrawing groups or steric crowding decrease the otherwise dominant π-aromatic donor ability and allow the σ-donor single bonds to compete. Thus, protolytic cleavage of alkylbenzenes and substituted alkylbenzenes depends on the nature and availability of π-, σ-, and n-donor sites and the acid system used.

Acknowledgment. The support of our work by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. Professor E. M. Arnett is thanked for samples of hexaisopropylbenzene and Professor M. S. Newman for samples of dineopentyltetramethylbenzenes.

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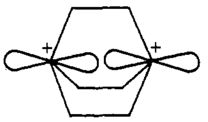
Received February 9, 1973

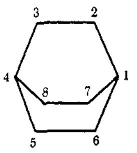
1,4-Bicyclo[2.2.2]octyl Dication, a Novel Pseudoaromatic System[1]

Sir:

We have succeeded in preparing the 1,4-bicyclo-[2.2.2]octyl dication **1** under stable ion conditions.



1



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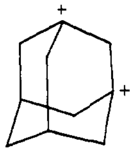
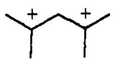


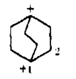
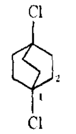
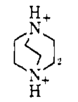
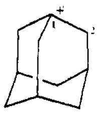
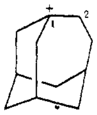
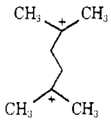
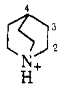
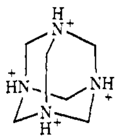
3
not observed



4
not observed

The close approach of charged atoms and of "vacant" orbitals makes this novel and unexpectedly stable dication an intriguing subject for study. The $C_1 \cdots C_4$ nonbonded separation in bicyclo[2.2.2]octane (**2**) is only 2.6 Å; the $C_1^+ \cdots C_4^+$ distance in dication **1** would be expected to be even shorter. Although a number of 1,4 dications are known,[2] none have positive centers held this closely together. Furthermore, alkyl-substituted 1,3 dications, which would have $C^+ \cdots C^+$ separations comparable to **1**, have resisted attempts at preparation both in cage[3] (**3**) and in acyclic (**4**) systems.[3]

Table I. Proton (δ_H) and Carbon-13 ($\delta_{^{13}C}$) Parameters of the 1,4-Bicyclo[2.2.2]octyl Dication and Model Ions[a]

Dication	δ_H	$\delta_{^{13}C}$[b]
 **1**	3.45, s[c]	-114.1 (C_1) $+149.3$ (C_2)
 **5**	2.72, s[d]	$+128.6$ (C_1)[d] $+154.2$ (C_2)
	4.14, s[e] 7.38 (NH)	$+147.3$ (C_2)[e]
	4.19 (H_2)	-106.0 (C_1)[f] $+128.0$ (C_2)
	3.90 (H_2)	-110.9 (C_1)[f]
	4.20 (H_2)	-129.5 (C_1)[g]
 **8**	5.04 (CH_2) 4.24 (CH_3)	-137.8 (C^+) $+140.6$ (CH_2) $+146.2$ (CH_3)
	3.50 (H_2)[e] 2.20 (H_3, H_4) 7.73 (NH)	$+144.2$ (C_2)[e] $+169.7$ (C_3) $+173.4$ (C_4)
	5.85, s[e] 8.40 (NH)	$+121.1$[e]

[a] δ_H and $\delta_{^{13}C}$ are in parts per million from external Me_4Si and CS_2, respectively. [b] Obtained by Fourier transform ^{13}C nmr method unless otherise indicated. [c] s, singlet. [d] In $CDCl_3$. [e] In FSO_3H-SO_2, $-60°$. [f] G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, **95**, 194 (1973). [g] Obtained by the indor ^{13}C nmr method: G. A. Olah, G. Liang, J. R. Wiseman, and J. A. Chong, *J. Amer. Chem. Soc.*, **94**, 4927 (1972).

The 1,4-bicyclo[2.2.2]octyl dication **1** formed from 1,4-dichlorobicyclo[2.2.2]octane (**5**)[4] in SbF_5-SO_2ClF (SO_2) at $-78°$. Ion **1** was found to decompose gradually at temperatures above $-60°$. The dicarbenium ion nature of **1** is deduced from the following evidence. (1) The unrearranged dimethyl ether[5] is isolated on quenching the solution of ion **1** in MeOH-MeONa at $-78°$. (2) The pmr spectrum (60 MHz) of ion **1** at $-90°$ consists of a singlet at δ 3.45 (capillary Me_4Si). The Fourier transform (FT) ^{13}C nmr spectrum[6] of ion **1** shows two carbon resonances at $\delta_{^{13}C}$ -114.1 and $+149.3$ (*vs.* CS_2) assigned to the two equivalent bridgehead carbenium carbons and the six equivalent methy-

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(1) (a) Stable Carbocations. CLXII. (b) Taken in part from the Ph.D. Thesis of G. Liang, Case Western Reserve University, Cleveland, Ohio, 1973.

(2) J. M. Bollinger, C. A. Cupas, K. J. Friday, M. L. Woolfe, and G. A. Olah, *J. Amer. Chem. Soc.*, **89**, 156 (1967).

(3) Unpublished observations of G. A. Olah, *et al.*

(4) 1,4-Dichlorobicyclo[2.2.2]octane was provided by Dr. J. C. Kauer. See J. C. Kauer, U. S. Patent 3,255,254 (June 7, 1966); *cf. Chem. Abstr.*, **65**, 15249*g* (1966).

(5) When the solution of **1** was added to NaOMe-MeOH at $-78°$, 1,4-dimethoxybicyclo[2.2.2]octane was obtained in 45% yield (in addition to some unidentifiable materials): pmr ($CDCl_3$, capillary Me_4Si) δ 2.60 (s, CH_2) and 3.05 (s, CH_2O) in a ratio of 2:1.

(6) Carbon-13 nuclear magnetic resonance spectra were obtained by the Fourier transform method using a Varian XL-100 nmr spectrometer equipped with a variable temperature probe. Carbon shifts are reported in parts per million from capillary CS_2.