

Stable Carbocations. CXXIV.^{1a,b} The Benzenium Ion and Monoalkylbenzenium Ions^{1c}

George A. Olah,* Richard H. Schlosberg, Richard D. Porter, Y. K. Mo, David P. Kelly, and Gheorghe D. Mateescu

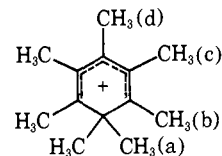
Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received April 10, 1971

Abstract: Benzene and monoalkylbenzenes were protonated in superacid media to form stable, long-lived benzenium ions (cyclohexadienyl cations). These ions were studied by low-temperature pmr and cmr spectroscopy. Protonation of benzene in $\text{HF-SbF}_5\text{-SO}_2\text{ClF-SO}_2\text{F}_2$ solution at low temperature shows a pmr spectrum consistent with the benzenium (C_6H_7^+) ion. Both cmr and pmr spectra are indicative of the anticipated charge distribution in the benzenium and alkylbenzenium ions, with the most stable form of the latter being the 4-alkylbenzenium ions. Indications are that high-temperature line broadening in the case of the monoalkylbenzenium ions is due to intramolecular rearrangement rather than rapid proton exchange with the acidic solvent. Unusual six-bond H-H coupling is observed in most of the 4-alkylbenzenium ions. Cmr parameters are indicative of the expected positive charge distribution at the C_2 , C_4 , and C_6 atoms in the benzenium ring, which is also indicated to be close to planar. Neither a Baker-Nathan nor an inductive order for the 4-methyl-, 4-ethyl-, and 4-isopropylbenzenium ions can be implied from the observed magnetic resonance parameters of these ions. Protolysis of C-C bonds in *tert*-butylbenzene, 2,2-diphenyl-2-propane, 1,1,1-triphenylethane, and tetraphenylmethane to give benzene (which undergoes further reaction) and stable alkyl cations was observed in the superacid media. Isopropylbenzene was observed to undergo competitive $\text{C}_\alpha\text{-H}_\alpha$ protolysis to form the phenyldimethylcarbenium ion. Protonation of neopentyl-, *n*-butyl-, *sec*-butyl-, isobutyl-, and *n*-propylbenzenes was studied at higher temperatures and these alkylbenzenes were shown to undergo protolytic side-chain reactions. Isomerization of the 4-*sec*-butylbenzenium ion to 4-isobutylbenzenium ion was observed. The mechanism of alkylbenzene rearrangements is discussed on the basis of the role of trivalent benzenium ions and tetracoordinated benzenium ions, with intramolecular rearrangements involving three-center bond-to-bond rearrangements of the benzenium ions.

The first direct spectroscopic evidence for the protonation of an aromatic hydrocarbon was reported by Gold and Tye² by observing the electronic spectra of protonated anthracene, and by Reid³ who observed electronic spectra of protonated alkylbenzenes.

McCaulay and Lien⁴ observed protonation of aromatic hydrocarbons in HF-BF_3 (in excess HF as solvent) to form benzenium ions. They observed benzenium ion formation upon introduction of BF_3 into the HF solution containing the aromatics by following decrease in the vapor pressure of the boron trifluoride. Brown, Piersall, and Wallace⁵ also used vapor pressure measurements to substantiate benzenium ion formation in alkylbenzene-aluminum (gallium) halide-hydrogen halide systems. Olah and Kuhn⁶ first achieved the isolation of stable alkylbenzenium ions as tetrafluoroborate salts in 1956-1958. Doering⁷ in 1958 carried out the first investigation of a benzenium ion by nuclear magnetic resonance spectroscopy. The 40-MHz pmr spectrum of a solution of heptamethylbenzenium tetrachloroaluminate consisted of four singlets

at δ 2.55 (6 H, H_a), 3.65 (6 H, H_b), 3.57 (6 H, H_c), and



3.85 (3 H, H_d). In 1960 one of us⁸ reported a detailed nmr investigation of protonated alkylbenzenes. Stable benzenium hexafluoroantimonates were prepared by means of direct protonation of the aromatics with HF-SbF_5 or $\text{Ag}^+\text{SbF}_6^-$ and HCl. The salts were isolated and then redissolved in SO_2 solution. Pmr studies were carried out under relatively acid-free conditions. An absorption in the spectra of the benzenium ion complexes between 4 and 5 ppm was observed, indicative of methylene aliphatic protons. In 1961 MacLean and Mackor⁹ observed the pmr spectra of protonated *m*-xylene, durene, and hexamethylbenzene in hydrogen fluoride solution.

In 1964 Birchall and Gillespie¹⁰ found that the use of HSO_3F at low temperature (-40 to -90°) produced solutions of benzenium ions whose pmr spectra were well resolved. Since that time many studies of protonated arenes have been reported. Recently Arnett and Larsen¹¹ determined calorimetrically heats of formation of protonated methyl-, ethyl-, isopropyl-, and *tert*-butylbenzenes from the parent alkylbenzenes upon

(1) (a) Stable Carbocations. CXXXIII: G. A. Olah, A. M. White and A. T. Ku, *J. Org. Chem.*, **36**, 3585 (1971). (b) For a differentiation of trivalent carbenium ions from tetra- or pentacoordinated carbonium ions and a discussion of the general concept and naming of carbocations, see G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972). Benzenium ion is the correct name of protonated benzene (a trivalent carbocation) and not benzenonium ion as formerly used. (c) Partially reported in preliminary form: G. A. Olah, R. H. Schlosberg, D. P. Kelly, and Gh. D. Mateescu, *ibid.*, **92**, 2546 (1970).

(2) V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172 (1952).

(3) C. Reid, *J. Amer. Chem. Soc.*, **76**, 3264 (1954).

(4) D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951).

(5) H. C. Brown and H. W. Piersall, *ibid.*, **73**, 4681 (1951); **74**, 191 (1952); H. C. Brown and W. J. Wallace, *ibid.*, **75**, 6268 (1953).

(6) G. A. Olah and S. J. Kuhn, *Nature (London)*, **178**, 693 (1956); *J. Amer. Chem. Soc.*, **80**, 6535 (1958).

(7) W. von E. Doering, M. Saunders, H. G. Boynton, J. W. Earhart, E. F. Wadley, W. R. Edwards, and G. Laber, *Tetrahedron*, **4**, 178 (1968).

(8) G. A. Olah, Abstracts, 138th National Meeting of the American Chemical Society, New York, N. Y., 1960, p 3P; G. A. Olah, *J. Amer. Chem. Soc.*, **87**, 1103 (1965).

(9) (a) C. MacLean and E. L. Mackor, *Discuss. Faraday Soc.*, **34**, k65 (1962); (b) *Mol. Phys.*, **4**, 241 (1961).

(10) T. Birchall and R. J. Gillespie, *Can J. Chem.*, **42**, 502 (1964).

(11) E. M. Arnett and J. W. Larsen, *J. Amer. Chem. Soc.*, **91**, 1438 (1969).

addition to 11.5 mol % SbF_5 in HSO_3F and found the largest Baker–Nathan order yet reported. These workers observed a difference of $3.75 \text{ kcal mol}^{-1}$, when corrected to the gas phase, between *tert*-butyl- and methylbenzene with values for ethyl- and isopropylbenzene falling between these two. Spectroscopic examination of the mixtures, however, showed dealkylation to have occurred during the course of some of the measurements (particularly *tert*-butylbenzene). Brouwer and Van Doorn¹² measured competitive protonation of the 9 and 10 positions of 9-ethyl-10-methylantracene and found them to be equally reactive, contrary to what might have been expected from Arnett and Larsen's results.

Because of the relationship of electron density to cmr chemical shifts,¹³ we felt that a study of the alkylbenzenium ions by this sensitive method would permit inference of relative monoalkylbenzenium ion stabilities. Our previous observations of polyalkylated benzenium ions have been extended to a more detailed study of the parent benzenium ion and the monoalkylbenzenium ions in the superacid systems $\text{HSO}_3\text{F-SbF}_5$ and HF-SbF_5 . The aromatic compounds were protonated either in $\text{HSO}_3\text{F-SbF}_5$ with excess HSO_3F serving as solvent or in a 1:1 M HF-SbF_5 acid system with a slightly larger than equal volume of SO_2ClF as diluent. The aromatic hydrocarbons protonated were: benzene, toluene, ethylbenzene, the isomeric propyl- and butylbenzenes, neopentylbenzene, 2,2-diphenylpropane, 1,1,1-triphenylethane, and tetraphenylmethane. The pmr spectral parameters for the obtained benzenium ions were established and studied over a range of temperatures.

Carbon-13 magnetic resonance spectroscopic studies were carried out with the use of the indor double resonance method¹⁴ for the benzenium ion itself as well as the *p*-toluenium, *p*-ethylbenzenium, *p*-isopropylbenzenium, and *p*-*n*-propylbenzenium ions. The cmr parameters were compared to the cmr data of Koptyug, *et al.*,¹⁵ for the mesitylenium ion, which was also redetermined in our studies in the $\text{HF-SbF}_5\text{-SO}_2\text{ClF}$ solvent system because of claimed dependence of the cmr chemical shifts on the counterions (Al_2Cl_7^- and Al_2Br_7^-).

Mass spectrometric studies¹⁶ have shown the formation of C_6H_7^+ as a fragmentation ion formed upon the electron bombardment of benzyl alcohol. Although Perkampus and Baumgarten¹⁷ reported solid state infrared and ultraviolet spectra for the ternary system, hydrogen chloride–gallium chloride–benzene, no spectroscopic observation of the C_6H_7^+ ion in solution has previously been made.

Results

A. Monoalkylbenzenium Ions. Pmr Studies. (1) *p*-Toluenium Ion (4-Methylbenzenium Ion). When toluene

(12) D. M. Brouwer and J. A. Van Doorn, *Recl. Trav. Chim. Pays-Bas*, **89**, 88 (1970).

(13) (a) G. Fraenkel, R. E. Carter, A. MacLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, **82**, 5846 (1960); (b) H. Spiessacke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961); (c) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969). This reference contains a general survey of cmr parameters of stable carbocations.

(14) E. B. Baker, *J. Chem. Phys.*, **37**, 911 (1962).

(15) V. Koptyug, A. Rezvukhin, E. Lippmaa, and T. Pehk, *Tetrahedron Lett.*, 4009 (1968).

(16) H. Budkiewicz, C. Djerassi, and D. H. Williams, "Mass Spectroscopy of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 119.

(17) H. H. Perkampus and E. Baumgarten, *Angew. Chem., Int. Ed. Engl.*, **3**, 776 (1964).

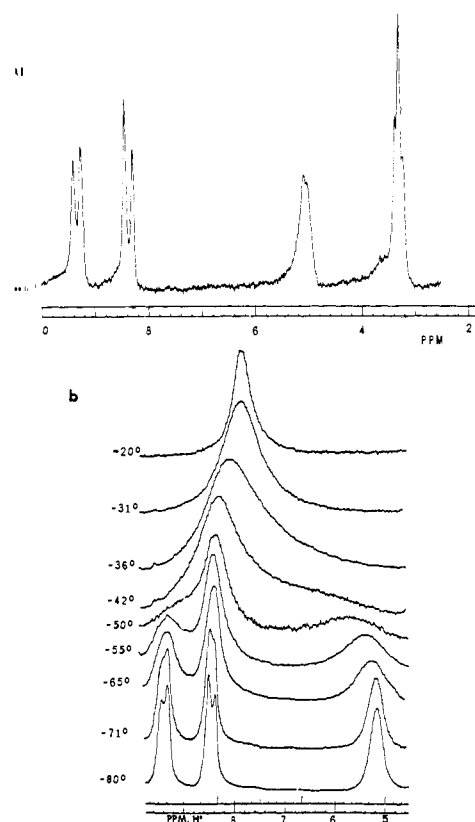


Figure 1. (a) 60-MHz pmr spectrum of *p*-toluenium ion $1\text{-CH}_3\text{a}$ at -97° . (b) Temperature-dependent line broadening at δ 5–10 due to $1\text{-CH}_3\text{a-d}$ equilibrium.

is treated with a 1:1 mol/mol HF-SbF_5 in SO_2ClF (1–2 vol) solution at -78° , a temperature-dependent pmr spectrum is observed consistent with equilibration of ions $1\text{-CH}_3\text{a} \rightleftharpoons 1\text{-CH}_3\text{b} \rightleftharpoons 1\text{-CH}_3\text{c} \rightleftharpoons 1\text{-CH}_3\text{d}$. As the temperature is raised, the ring proton absorptions broaden in a manner characteristic of intramolecular exchange. The order of this line broadening as the temperature is raised is $\text{H}_1 > \text{H}_{2,6} > \text{H}_{3,5}$. Figure 1a shows the complete 60-MHz pmr spectrum of $1\text{-CH}_3\text{a}$ at -97° , while Figure 1b shows the temperature-dependent nature of the intramolecular exchange process. Reaction of toluene with excess $\text{DF-SbF}_5\text{-SO}_2\text{ClF}$ at -30° for 3 hr incorporated only 1.1 atom of deuterium/molecule, thereby demonstrating that intermolecular exchange (with solvent) is slow.¹⁸ (For experimental details of deuteration experiments, see the Experimental Section.) Distribution of the deuterium about the ring, however, was statistical, indicative of a relatively fast intramolecular exchange process. At low temperature (-97°) the 4-methylbenzenium ion is "frozen out" as the most stable ion in the solution showing the methyl absorption to be a well-resolved triplet ($J = 4.4 \text{ Hz}$), which was decoupled to a singlet by irradiation of the methylene absorption. Irradiation of the methyl triplet absorption caused substantial sharpening of the methylene signal, but fine structure was not observed. The large, six-bond coupling is especially noteworthy in that there is no resolvable coupling between the methyl protons and any of the other ring protons, although some peak broadening may indicate small cou-

(18) Such a process is not the rule for all arenium ions. MacLachlan and Mackor (ref 9) observed examples of exchange with solvent and intermolecular (arene \rightleftharpoons arenium) exchange.

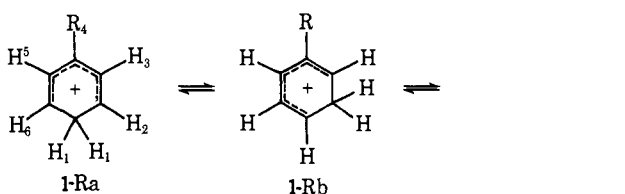
Table I. Pmr Parameters^a for Parent and 4-Alkyl-Substituted Benzenium Ions^b

4-Substituent	Benzenium ring protons			4-Alkyl substituent proton absorptions			
	H _{2,6}	H _{3,5}	CH ₂	H _α	H _β	H _γ	H _δ
H ^c	9.58	8.22	5.69	9.42 ^f			
CH ₃	9.38	8.40 (8.6)	5.05	3.30, t (4.4)			
C ₂ H ₅	9.44	8.47 (9.0)*	5.13	3.60, q	1.73, t (7.5)		
<i>n</i> -C ₃ H ₇	9.30	8.30 (8.5)*	5.02	3.40, t (7.5)*	2.07, m	1.37, t (7.0)*	
<i>i</i> -C ₃ H ₇	9.37	8.39 (9.0)*	5.07	3.70, sp	1.63, d (6.5)*		
<i>n</i> -C ₄ H ₉	9.44	8.44 (8.5)*	5.10	3.48	1.90 ^e	1.90 ^e	1.12 (6.5)*
<i>sec</i> -C ₄ H ₉	9.40	8.40 (8.5)*	5.11	3.48 (6.0)*	2.08, m	1.18, t (7.0)*	
<i>i</i> -C ₄ H ₉	9.37	8.37 (8.5)*	5.08	3.37, d (7.0)*	1.65, d (7.0)*	1.28, d (6.0)*	
<i>tert</i> -C ₄ H ₉ ^d	9.05	8.30	4.92		2.50, t of q		
neo-C ₅ H ₁₁	9.35	8.30 (8.5)*	5.07	3.38	1.68	1.32	

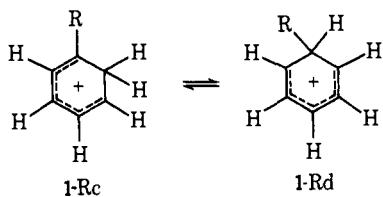
^a Chemical shifts in parts per million relative to external TMS at 60 MHz. Coupling constants (parentheses) in hertz; d, doublet, t, triplet, q, quartet, m, multiplet, sp, septet, t of q, triplet of quartets; the asterisk indicates ± 0.5 Hz, otherwise ± 0.1 Hz. ^b Except where noted solvent system is (1:1 mol/mol) SbF₅-HF in 1.0-2.0 vol of SO₂ClF at -100° . ^c Solvent HF-SbF₅-SO₂ClF-SO₂F₂ at -134° . ^d Solvent 6:1 mol/mol HSO₃F-SbF₅ at -78° . ^e β and γ side-chain protons not resolved. ^f δ_{H_3} .

plings. Long-range coupling (across the cyclohexadienyl ring) is common in many of the studied alkylbenzenium ions; similarly unusual coupling effects have been ob-

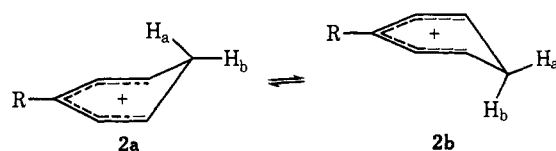
The H₂,H₃ and H₅,H₆ protons appear as an AB-like quartet in this system as well as in the other monoalkylbenzenium ions studied.



R = CH₃, ~
C₂H₅, ~
n-C₃H₇, ~
i-C₃H₇, ~
tert-C₄H₉, ~



R = *n*-C₄H₉, ~
i-C₄H₉, ~
sec-C₄H₉, ~
neo-C₅H₁₁, ~
H



The data show that: (1) the 4-methylbenzenium ion 1-CH₃a is the most stable of the isomeric ions 1-CH₃a-d. (2) Indications are that either the cyclohexadienyl ring is close to planar or equilibration of the type 2a \rightleftharpoons 2b, if present, is rapid even at temperatures as low as -115° . (3) Coupling constants $J_{H_\alpha-H_{1a}} = J_{H_\alpha-H_{1b}} = 4.4$ Hz, in spite of the fact that $J_{H_1-H_2(H_6)} < 0.1$ Hz, $J_{H_1-H_3(H_5)} = 0$, and $J_{H_\alpha-H_{2,3,5,6}} \cong 0$. (4) A rapid intramolecular rearrangement takes place through ions 1-CH₃a \rightleftharpoons 1-CH₃b \rightleftharpoons 1-CH₃c \rightleftharpoons 1-CH₃d²⁰ while exchange with the solvent is minimal.

(2) **4-Ethylbenzenium Ion.** A solution of ethylbenzene in SO₂ClF reacts with an HF-SbF₅-SO₂ClF solution at low temperature to give the equilibrating ions 1-C₂H₅a-d. Pmr spectra at 60 MHz were recorded over the temperature range -40 to -115° . In Figure 2, spectra obtained at (a) -100° , (b) -80° , and (c) -40° are shown. Again, a striking feature is the formation, upon "freezing out" of the 1-C₂H₅a isomer, of a complex multiplet of the side-chain methylene absorption due to H₁-H_α six-bond coupling. Inspection of the H_{3,5} absorptions shows a well-resolved portion of an AA'BB' pattern (an apparent AB pattern) not coupled to the side-chain methylene protons. The clean triplet of the side-chain methyl group at δ 1.98 is further indication that the complexity of the α -CH₂ absorption must arise from coupling with the ring H₁ methylene protons. The ring methylene absorption remains broadened and lacks observable fine structure even at low temperature. The broadness reaches a minimum at -85° and the line width remains constant over a 30° range down to -115° , as was observed for ion 1-CH₃. In some hydroxy and alkoxy arenium ions, analogous vicinal

served in many other stable carbocations.¹⁹ Pmr parameters for 1-CH₃a are given in Table I.

The triplet nature of the methyl absorption indicates equal coupling of methyl protons to both methylene H₁ protons. The width of the methylene absorption reaches a minimum at -85 to -90° indicating the "freezing out" on the nmr time scale of the intramolecular exchange process 1-CH₃a \rightleftharpoons 1-CH₃b \rightleftharpoons 1-CH₃c \rightleftharpoons 1-CH₃d. The equivalent H_α-H₁ couplings indicate a planar or nearly planar cyclohexadienyl ring or rapid conformational equilibrium if the ring is distorted from planarity (cf. 2). The H₂(H₆) absorption at δ 9.43 indicates vicinal $J_{H_1-H_2(H_6-H_1)}$ coupling of less than 0.1 Hz.

(19) Unusually large coupling constants are observed in many stable carbocations. Examples include large four-bond H-H coupling in the *tert*-amyl cation of 15 Hz (G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Amer. Chem. Soc.*, **86**, 1360 (1964)), seven-bond H-F coupling in the *p*-fluorostyryl cation of 2.7 Hz (G. A. Olah, R. D. Porter, C. L. Jeuell, and A. M. White, *ibid.*, **94**, 2044 (1972)).

(20) Although in these systems there is no direct observation of ion 1-R-d it is reasonable to assume its existence. Examples of C₁-protonated alkylbenzenium ions (with an alkyl group on the aliphatic carbon) are known (ref 8) and are sterically also favored. Recent work in our laboratory has shown a number of additional cases of polysubstituted benzenes being protonated at carbons carrying alkyl substituents: G. A. Olah and S. Kobayashi, manuscript in preparation.

$J_{H_1-H_2}$ coupling constants were observed on the order of 2.0 Hz (equal for both H_1 methylene protons).²¹ Ion $1-C_2H_5^+$ shows (as do the other studied monoalkylbenzenium ions) coupling constants of less than 0.1 Hz. Solutions of ions $1-C_2H_5^+$ were stable for 3 hr at -30° . Keeping the ions for 10 hr at 0° resulted in unidentifiable polymeric materials (probably through dealkylative processes).

(3) 4-Propylbenzenium Ions. The behavior of both *n*-propyl- and isopropylbenzene was studied in superacids. Solutions of the propylbenzenium ions were prepared in the same fashion as those of ions $1-CH_3^+$ and $1-C_2H_5^+$ using $HF-SbF_5$ (1:1 molar) in SO_2ClF . The pmr parameters for the most stable of the isomeric benzenium ions, *i.e.*, the 4-*n*-propylbenzenium ion $1-n-C_3H_7^+$ and 4 isopropylbenzenium ion $1-i-C_3H_7^+$, are given in Table I. The 4-*n*-propylbenzenium ion $1-n-C_3H_7^+$ was studied over the temperature range from -40 to -115° . At -90° , the side-chain α -methylene proton triplet absorption became broadened due to coupling with the methylene H_1 protons of the benzenium ring, as the $1-n-C_3H_7^+ \rightleftharpoons b \rightleftharpoons c \rightleftharpoons d$ equilibrium has been sufficiently retarded at this temperature. When the solution was warmed to $+25^\circ$ and kept there for 1.5 hr, reexamination of the somewhat darkened solution at low temperature (-70°) by pmr showed about 80% of the original ion $1-n-C_3H_7^+$ remained unchanged. The phenyldimethylcarbenium ion **3** was observed as a new singlet absorption at δ 3.22 as well as the characteristic aromatic absorptions in the δ 8–9 region. The assignment of these absorptions to ion **3** was made by comparison to known spectra of the ion **3** prepared from *tert*-cumyl precursors and reported previously. A singlet at δ 8.12 is due to a small amount of $C_6H_7^+$ (benzenium ion) formed as a cleavage product. The secondary dimethyl carbenium ion anticipated from the C_4-C_α bond cleavage which resulted in the formation of the benzenium ion was not observed. The concentration of the $C_6H_7^+$ ion in the observed solution was low and the identification of the equivalent low concentration of isopropyl cation would be difficult. Unidentified small broad absorptions at δ 7.11 and 4.90 were also observed.

The isopropylbenzenium ion $1-i-C_3H_7^+$, prepared as above, contains a small amount (5–10% by pmr peak area comparisons) of the ion **3**. At -100° , the "frozen out" 4-isopropylbenzenium ion $1-i-C_3H_7^+$ shows substantial broadening of the α -methine proton septet absorption due again to the six-bond coupling with the H_1 benzenium ring methylene protons. Warming the solution to -30° for 3 hr shows no apparent change in the ratio of ion $1-i-C_3H_7^+$ to **3**, but keeping the solution for 10 hr at 0° results in an apparent polycondensation reaction. Reaction of isopropylbenzene with 1:1 molar $HF-SbF_5$ acid (neat) was also carried out at room temperature. After 5–10 min, the reaction mixture was cooled and diluted with SO_2ClF . The pmr spectrum showed no isopropylbenzenium ion $1-i-C_3H_7^+$ to be present, the solution being comprised almost entirely (80%) of the benzenium $C_6H_7^+$ ion and *tert*-butyl $C_4H_9^+$ ion. Presumably such a process of *tert*-butyl ion formation occurs through a rather complex route of dealkylations and cleavages. These reactions are well known in superacids.²²

(21) G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, in press.

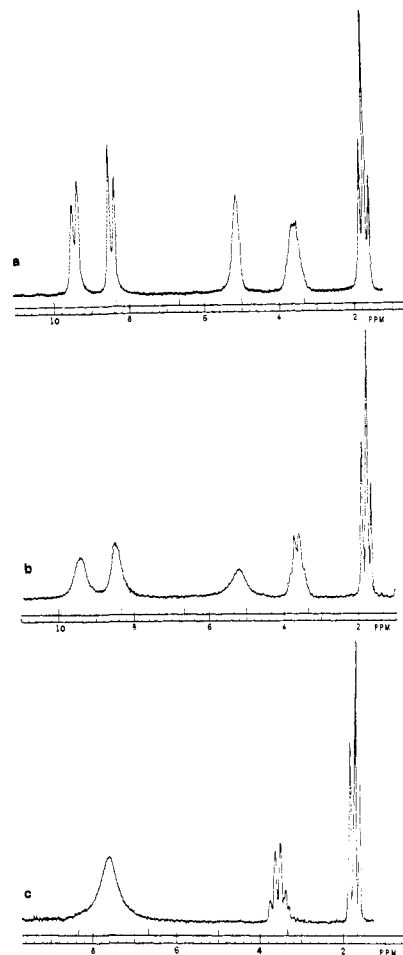


Figure 2. 60-MHz pmr spectrum of the ethylbenzenium ion $1-C_2H_5^+$ at: (a) -100° ; (b) -80° ; (c) -40° .

(4) 4-Butylbenzenium Ions. With the exception of *tert*-butylbenzenium ion $1-tert-C_4H_9^+$, all the butylbenzenium ions were easily prepared by reaction of the parent butylbenzenes with $HF-SbF_5$ (1:1 molar) in SO_2ClF as previously described. All pmr parameters of the butylbenzenium ions are summarized in Table I. In the case of the *tert*-butylbenzenium ion, *tert*-butylbenzene was protonated in 6:1 molar HSO_3F-SbF_5 solution at -78° . Under these conditions there is no evidence for dealkylation. Warming of the solution, however, results in immediate cleavage of the *tert*-butyl group. Attempted protonation in 1:1 HSO_3F-SbF_5 in SO_2ClF solvent as well as 1:1 $HF-SbF_5$ in SO_2ClF resulted in immediate cleavage resulting in the expected 1:1 ion ratio of *tert*-butyl cation and benzenium ion ($C_6H_7^+$) with no other products evident.

Reaction of *n*-butylbenzene with neat $HF-SbF_5$ or by low-temperature conditions in SO_2ClF gives ion $1-n-C_4H_9^+$ which is stable at 0° for 12 hr and at $+25^\circ$ for 2 hr. The side-chain β - and γ -methylene protons were not resolved, but rather made up a complex multiplet. The six-bond H_1 ring methylene to H_α side-chain methylene coupling of the $1-n-C_4H_9^+$ "frozen out" ion at low temperature (*cf.* ions $1-CH_3^+$, $1-C_2H_5^+$, $1-n-C_3H_7^+$, and $1-i-C_3H_7^+$) is observed whereas other

(22) (a) G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 4739 (1967); (b) G. A. Olah, G. Klopman, and R. H. Schlosberg, *ibid.*, **91**, 3261 (1969).

H_{α} - H_{ring} couplings are not observed. The intramolecular shift $1-n-C_4H_9a-d$ of the arene ring-protonation site is observed in all the butylbenzenes and they are frozen out in all cases below -90° as the stable 4-butylbenzenium ions.

Both isobutyl- ($1-i-C_4H_9a$) and *sec*-butyl- ($1-sec-C_4H_9a$) benzenium ions showed only slight coupling from the α -substituent protons to the methylene ring protons at -100° , although all other low-temperature spectral properties of these ions are as expected. The behavior of these arenium ions at higher temperatures depends on conditions, although in all cases, gas evolution is observed. Isobutylbenzene, when allowed to react for 10 min at room temperature with neat HF-SbF₅, showed, upon dilution with SO₂ClF and subsequent pmr examination at -40° , that 50% of the originally formed 4-isobutylbenzenium ion $1-i-C_4H_9a$ remains. The remainder of the solution was comprised of about 30% phenylethylmethyl carbenium ion **4** (which was identified by comparison to the known ion **4**, generated from 2-phenyl-2-butyl precursors and reported previously²³), the remaining 70% being a mixture of *tert*-butyl cation $t-C_4H_9^+$ and benzenium ion (in the expected 9:7 peak area ratio). Presumably, C-H protolysis would result in formation of hydrogen gas^{22b} (mechanism shown in Discussion). Preparation of the ion at low temperature followed by gradual warming (3 hr at -30° , 2 hr at 0° , then 1.5 hr at $+25^\circ$) showed about 50% of ion $1-i-C_4H_9$ remaining, about 30% of ion **4**, and the remainder not identifiable. No benzenium and *tert*-butyl ions were formed. Similarly, no aralkyl carbenium ions (stryryl,²⁴ *tert*-cumyl (**5**),²⁵ dimethylbenzylcarbenium,²³ isopropylphenylcarbenium ions²³) or any isomeric 4-alkylbenzenium ions (with C₁-C₄ alkyl substituents) were observed.

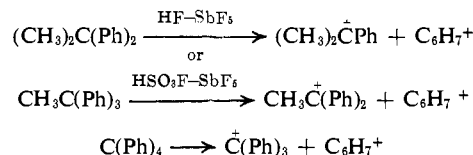
The $1-sec-C_4H_9$ ion, when prepared from *sec*-butylbenzene in HF-SbF₅ at room temperature, shows 50% of unchanged ion $1-sec-C_4H_9$ remaining and some cleavage to *tert*-butyl ($C_4H_9^+$) and benzenium ($C_6H_7^+$) ions (9:7 ratio of proton absorptions, as expected). Some isomeric $1-i-C_4H_9$ ion (10-20%) is also observed. Careful preparation of the ion at -78° and warming immediately to 0° for 2.0 hr result in a mixture of 50% $1-sec-C_4H_9$, the remainder being *tert*-butyl and benzenium ions. Slow warming (3 hr at -30° , 2 hr at 0° , 1.5 hr at $+25^\circ$) shows about 80% isomerization to ion $1-i-C_4H_9$, the remainder being 10% $1-sec-C_4H_9$ and 10% unidentified products.

(5) 4-Neopentylbenzenium Ion. The 4-neopentylbenzenium ion $1-neo-C_5H_{11}$ was formed in the same fashion as other monoalkylbenzenium ions. Stable solutions of the ion were prepared either by reaction with 1:1 molar HF-SbF₅ in SO₂ClF or with a 7:1 molar mixture of HSO₃F-SbF₅. The pmr spectral parameters for the ion $1-neo-C_5H_{11a}$ are given in Table I. The ion was examined over the temperature range -30 to -115° . Over this range the intramolecular $1-neo-C_5H_{11a} \rightleftharpoons b \rightleftharpoons c \rightleftharpoons d$ equilibrium process was observed by line broadening as in the case of other 4-alkylbenzenium ions. Coupling between the α -methylene protons in the $1-neo-$

C_5H_{11a} isomer and the H₁ methylene ring protons is not observed.

Warming of solutions of the ion to -30° for 3 hr in sealed nmr tubes produced no detectable changes in the pmr spectrum, but after warming to 0° and maintaining at that temperature for 10 hr, the solution contained not only ion $1-neo-C_5H_{11}$ but the secondary phenylisopropylcarbenium ion **5**. There are as well unidentified smaller absorptions in the spectrum. The solution darkened during the reaction indicating some polymer formation. As the pmr spectrum of ion **5** was known from our previous work²³ the assignment could be made from comparison. Preparation of $1-neo-C_5H_{11}$ in neat HF-SbF₅ at room temperature results in 50% decomposition to *tert*-amyl ($C_5H_{11}^+$) and benzenium ions ($C_6H_7^+$).

(6) Attempted Preparation of Phenylalkylbenzenium Ions Leading to Protolytic Cleavage. In attempting to prepare phenylalkylbenzenium ions from 2,2-diphenylpropane, 1,1,1-triphenylethane, and tetraphenylmethane in superacid media, we observed with all conditions only protolytic cleavage to take place giving methylphenyl (diphenyl) carbenium ions and the $C_6H_7^+$ benzenium ion. It is also interesting to note that tri-



phenylmethane under the same conditions forms the benzhydryl cation and $C_6H_7^+$ and not, *via* hydride abstraction, the trityl cation.

B. Cmr Studies of Monoalkylbenzenium Ions. Carbon-13 nmr data were obtained at -90° in HF-SbF₅-SO₂ClF solutions for the benzenium ring carbons of the 4-alkylbenzenium ions $1-CH_3a$, $1-C_2H_5a$, $1-n-C_3H_7a$, and $1-i-C_3H_7a$. The carbon-13 chemical shifts were obtained *via* the indor method by observing enhancement of the ¹²C-H ring proton absorption due to decoupling of the corresponding ¹³C-H satellites. In all cases sharp singlet enhancements were observed for C_{1,2,3,5, and 6} carbons. The C₄ carbon cmr shift was obtained for ions $1-CH_3a$, $1-C_2H_5a$, and $1-n-C_3H_7a$ by monitoring the heteronuclear decoupling frequencies of the α protons in the side chain and in ion $1-i-C_3H_7a$ by monitoring that of the H_{3,5} protons to obtain a singlet. The indor method used in these studies has been previously described.^{13c, 24, 26}

Cmr parameters obtained are tabulated in Table II. All values have a precision of ± 0.2 ppm, except where noted. Shown for comparison are cmr shifts of the 2,4,6-trimethylbenzenium ion **6** as determined by Koptuyg, Rezvukhin, Lippmaa, and Pehk¹⁵ in two acid systems (HCl-AlCl₃ and HBr-AlBr₃). For better comparison, and because Koptuyg had observed a small effect of the counterion on cmr shifts, we redetermined the values for **6** in the superacid systems employed in the present study.

The monoalkylbenzenium ions show cmr shift differences of significance only at the alkyl-substituted C₄ carbon. The C_{2,6} and C_{3,5} carbons although substantially expected gross charge distributions remain es-

(23) G. A. Olah, C. U. Pittman, Jr., E. Namanworth, and M. B. Comisarow, *J. Amer. Chem. Soc.*, **88**, 5571 (1966).

(24) G. A. Olah, R. D. Porter, and D. P. Kelly, *ibid.*, **93**, 464 (1971).

(25) G. A. Olah, M. B. Comisarow, and C. J. Kim, *ibid.*, **91**, 1458 (1969).

(26) A. M. White and G. A. Olah, *ibid.*, **91**, 2943 (1969).

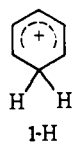
Table II. Benzenium Ring Carbon Cmr Shifts^a of 4-Alkylbenzenium Ions and Mesitylenium Ion (Mes)

4 substituent	C ₄	C ₃ ,C ₅	C ₂ ,C ₆	C ₁ (methylene)
CH ₃	-7.3	55.2	13.4	145.1
CH ₃ CH ₂	-16	56.2	13.3	145.4
CH ₃ CH ₂ CH ₂	-10.5	55.7	13.1	144.8
(CH ₃) ₂ CH	-18 ^b	59.6	14.7	146.5
Mes	-2.3	58.7	-2.3	140.4
Mes ^{c,d}	-0.5	57.5	-0.5	138.2
Mes ^e	-0.5	58.3	-0.5	139.2

^a Parts per million relative to ¹³CS₂; HF-SbF₅-SO₂ClF solvent at -90°. ^b ±2.0 ppm. ^c Reference 15. ^d Counterion Al₂Br₇⁻. ^e Counterion Al₂Cl₇⁻.

essentially unaffected by change in the alkyl substituent at C₄ in the case of the four monoalkylbenzenium ions examined. As was shown by Koptug for ion 6, the cmr chemical shift of C_{3,5} indicates little change in electron density at these carbons upon protonation of the parent alkylbenzenes while C₁ is changed in basic character from aromatic sp² to aliphatic sp³. Methyl substitution at C₂ and C₆ (ion 6) causes substantial deshielding of these carbons, apparently at the expense of C₄ (compared to C₄ in ion 1-CH₃a).

C. The Benzenium Ion (1-H). The parent ben-



zenium ion was prepared by careful addition of benzene in SO₂ClF to a rapidly stirred mixture of HF-SbF₅ (1:1 molar) in SO₂ClF at -78°. The pmr spectrum of the supernatant solution at -80° shows a single sharp absorption at δ 8.09 with large (3.3%) ¹³C-H satellites of J_{13C-H} = 26 Hz. This spectrum is assigned to a degenerate set of time-averaged C₆H₇⁺ benzenium ions 1-Ha-d. Using the mixed solvent system SO₂ClF-SO₂F₂ to lower the freezing point and viscosity of the solution, the pmr spectrum could be obtained at -129° at which temperature it was partially resolved into the static (only slowly equilibrating) benzenium ion (Figure 3). The methylene protons H₁ gave a broad absorption at δ 5.69, H₃ and H₅ were at δ 8.22, H₂ and H₆ were at δ 9.58, while H₄ appeared as a shoulder on the H₂,H₄ absorption at δ 9.42. Rewarming the solution demonstrated the reversibility of this process. The size of each of the ¹³C-H satellites (3.3% of the main ¹²C-H peak) is characteristic of a degenerate set of ions with all J_{13C-H} couplings time averaged.²⁷ The indor technique was used to obtain the averaged cmr shift of the equilibrating ion 1-H at -78° of δ_{13CS₂} +48 ppm which is the average of the cmr shifts of all six carbons. The values of the cmr shift and coupling constant are in agreement with those anticipated for such a degenerate ion. Coupling constants were estimated from a single resonance form of 1-H. This resonance structure contains four olefinic carbons (C_{2,3,5,6}) which would be expected to exhibit coupling of J_{13C-H} = 167 Hz, one secondary carbenium carbon C₄ (for which the iso-

(27) Such a phenomenon was observed for the cyclopentyl cation; see ref 13c.

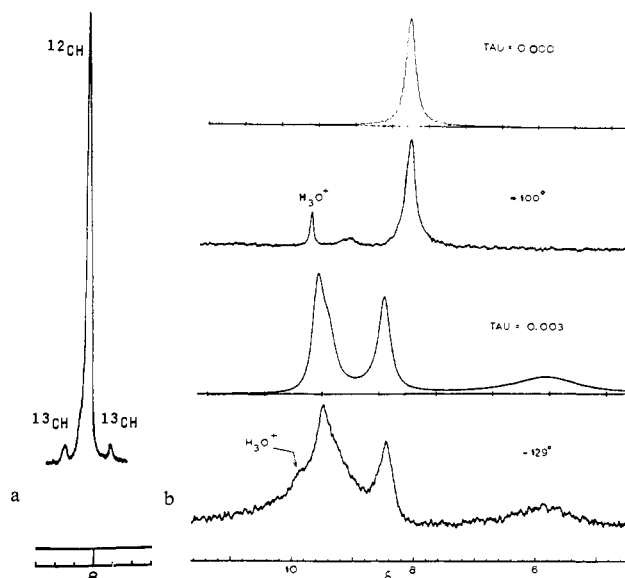
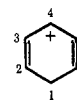


Figure 3. 100-MHz pmr spectrum of benzene in HF-SbF₅-SO₂-ClF-SO₂F₂: (a) at -80°; (b) comparison of spectra at -100 and -129° with computer-simulated spectra.

propyl cation could serve as model (J_{13C-H} = 169 Hz), and two sp³-type cyclohexane methylene ¹³C-H₆ couplings (one carbon, two protons) (J_{13C-H} = 123 Hz).



Equilibration of the seven protons over the six carbons gives time-averaged couplings. The averaged coupling constant can be calculated as

$$J_{13C-H} = \frac{(4 \times 167) + (2 \times 123) + (1 \times 169)}{6 \times 7} = 26 \text{ Hz}$$

which is in good agreement with the observed value. The assumptions made by employing the single resonance form model are: (1) the model ion is not 1-H, therefore the assumptions of the J_{13C-H} for C_{2,4,6}-bound couplings are undoubtedly in error. All experience with sp² carbon bound only to carbon and hydrogen indicates the direct J_{13C-H} coupling constants of such carbons to be similar.^{14a} The other resonance forms of the ion result in the same numerical calculation. (2) The calculation assumes all but direct J_{13C-H} values to be zero. The magnitude of ¹³C-H couplings is known to diminish rapidly with distance^{14a,28} and the error arising from this assumption is probably small relative even to the accuracy of the estimated values for the direct coupling constants.

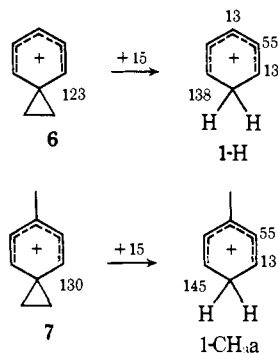
The best models for the cmr chemical shifts of 1-H are the recently reported ethylenebenzenium ions,²⁹ which have been unequivocally characterized. It appears that the benzenium carbons C₂ and C₆ achieve an identical cmr shift regardless of substituents at C₄. From ion 6 it is known that chemical shifts of C₂, C₄, and C₆ are identical. We therefore assume that "re-

(28) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon, London, 1966, p 1024 ff. Typically, H-C-¹³C coupling constants are 3-7 Hz.

(29) G. A. Olah and R. D. Porter, *J. Amer. Chem. Soc.*, **93**, 6877 (1971).

removal" of methyl substituents (*i.e.*, conversion of ion 6 to ion 1-H) should have the same effect at all three carbons. Therefore using as models the 4-methylbenzenium ion 1-CH_{3a}, the ethylenebenzenium ion 7,²⁹ and the ethylene-*p*-toluenium ion 8,²⁹ the anticipated cmr shifts for the C₆H₇⁺ benzenium ion can be estimated (Scheme I). The values for C₂, C₄, and C₆ are taken as

Scheme I



the $\delta +13$ value obtained for the similar ring C₂-C₆ carbons in the studied monoalkylbenzenium ions. The value of $\delta +55$ for C₃ and C₅ is taken from the same series of ions (for ions 1-R, $\delta_{C_{3,5}} = +55$ to $+60$), a lower value being used because presumably it is less shielded due to increasing demand for positive charge delocalization. The C₁ "aliphatic" methylene cmr shift is estimated by correcting the spiro carbon cmr shift for the ethylenebenzenium ion (spiro[2.5]octadienyl cation) 7 ($\delta +123$) by 15 ppm to $\delta +138$. This correction is equal to the difference between the spiro carbon cmr shift in the ion 8 ($\delta +130$) and that for the methylene carbon of the analogous ion 1-CH_{3a} ($\delta +145$) itself. Assuming these values are time averaged, the calculated cmr shift is $[(13 \times 3) + (55 \times 2) + (138 \times 1)]/6 = +48$ ppm, matching the observed value exactly.

The temperature dependence of the spectrum was compared with calculated spectra based on a series of varying rate constants and activation parameters of the hydrogen migration. The line shapes for various rate constants were calculated and recorded by means of a multiple-site exchange program³⁰ The axial (C_{2v}) symmetry of the ion allowed us to treat this case as a four-site problem. Fitting the data to the Arrhenius equation gave an activation energy E_a of 10 ± 1 kcal mol⁻¹ and a preexponential factor A of $10^{15.9 \pm 1.6}$.

The deuterated analogous ion 1-H is shown to undergo slow exchange with solvent HF-SbF₅-SO₂ClF-SO₂F₂ at -134° , which is much accelerated at higher temperatures.

When sulfur dioxide is added to the solution of the benzenium ion at -78° , an immediate reaction occurs to form the protonated benzenesulfonic acid,³¹ as evidenced by a two-proton pmr singlet at $\delta 9.54$ (S-OH) and a five-proton aromatic absorption at $\delta 7.96$.

Discussion

A. Structure of Monoalkylbenzenium Ions and of the Parent Benzenium Ion. The obtained experimental

(30) The Fortran IV program was written by C. S. Johnson, Jr. (*Advan. Magn. Resonance*, **1**, 33 (1965)) and adapted for use on the Univac 1108 computer by Mr. W. Heyd of this department.

(31) M. Brookhart, F. A. L. Anet, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 5657 (1966).

(nmr) data of monoalkylbenzenium ions can be characterized in the following way. (1) They are equilibrating ions with the most stable form being the 4-alkylbenzenium ions 1-Ra. (2) The intramolecular hydrogen shift about the ring is a facile process, and temperature-dependence studies show the line broadening from "frozen out" 1-Ra ions to occur over almost exactly the same range for all the monoalkylbenzenium ions studied. There is therefore little reason to expect the alkylbenzenium ions to differ appreciably from one another in energy required for the exchange process. (3) Hydrogen (deuterium) exchange with the HF-SbF₅ solvent systems is slow relative to intramolecular exchange processes. Intermolecular exchange with solvent is apparently significantly more rapid for 1-H ions than for the monoalkylbenzenium ions. (4) The unusually large six-bond H-H coupling observed for 1-CH_{3a} indicates all 1-Ra ions to be either: (a) close to planar, (b) undergoing rapid conformational equilibrium, or (c) distorted (as in 2a) with coincidental equivalence of the $J_{H_{1a}-H_\alpha}$ and $J_{H_{1b}-H_\alpha}$ values. *Ab initio* calculations on the ethyl cation³² indicate slight (a few degrees) distortion from planarity of the carbenium carbon center. Extension to the alkylbenzenium ions suggests that the benzenium ring cannot be completely planar by virtue of the alkyl substituent (rapid C₁-C_α rotation would, however, time average such a distortion). Interruption of the sequence of sp²-type carbons in the arenium ring by the "aliphatic" sp³-type methylene group should result in distortion of the planar arrangement as the series of 120° C-C-C internal bond angles is changed. In addition there is undoubtedly the tendency for the positively charged π-dienyl system to involve the C₁-H₁ bonding electron pair in at least partial delocalization, thereby tending to align a C₁H₁ bond with the π system. These latter considerations would, however, probably not raise the barrier to inversion sufficiently to permit observation of the "frozen out" conformers 2a and b if they were sufficiently distorted from planarity to be observed in such a state. (5) Cmr data compare favorably with those reported by Koptug, *et al.*, for ion 6.¹⁵ The C₁ cmr shift is clearly that of an sp³ and not an sp² carbon.^{13c,28} Positive charge as indicated by cmr shifts is predominantly on C₂, C₄, and C₆ with C₃ and C₅ showing little deshielding (therefore little change in charge density) in going from the neutral arene to the corresponding arenium ion.

These results are in qualitative agreement with molecular orbital calculations as well as an X-ray crystallographic study.^{33,34} The significance of the absolute numerical values of these parameters is discussed in B.

The estimated cmr shifts of the benzenium ion 1-H imply it to be analogous to the other alkylbenzenium ions as a degenerate equilibrating set of 1-Ha-d ions. The barriers for the intramolecular proton exchange

(32) J. E. Williams, V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **92**, 2141 (1970).

(33) (a) L. W. Pickett, N. Muller, and R. S. Mulliken, *J. Chem. Phys.*, **21**, 1400 (1953); (b) N. Muller, L. W. Pickett, and R. S. Mulliken, *J. Amer. Chem. Soc.*, **76**, 4770 (1954); (c) T. Morita, *Bull. Chem. Soc. Jap.*, **33**, 1486 (1960); (d) J. P. Colpa, C. MacLean, and E. L. Mackor, *Tetrahedron, Suppl.*, **19**(2), 65 (1963); (e) I. Hanazaki and S. Nagakura, *Tech. Rep. Inst. Solid State Phys., Ser. A.*, **140** (1964); (f) E. Helgstrand, *Acta Chem. Scand.*, **24**, 3687 (1970); (g) W. Jakubetz and P. Schuster, *Angew. Chem.*, **83**, 499 (1971); (h) W. J. Hehre and J. P. Pople, *J. Amer. Chem. Soc.*, in press.

(34) N. C. Baenziger and A. D. Nelson, *ibid.*, **90**, 6602 (1968).

process in the monoalkylbenzenium ions must be somewhat higher than those calculated for the 1-Ha-d equilibrium (10 ± 1 kcal mol⁻¹). Even approximate calculations of such barriers for the 1-Ra-d ions present great difficulties at this time due to lack of symmetry in 1-Rb,c,d species as well as their unknown nmr parameters.

B. Stabilization of 4-Alkylbenzenium Ions by Alkyl Groups. Carbon-13 magnetic resonance parameters measured for the 4-alkylbenzenium ions (Table II) showed significant differences in cmr shifts only at the substituted (C₄) carbons. These measurements showed the deshielding trend expected from decreasing hyperconjugative stabilization as positive charge is less efficiently delocalized onto the α substituent (*i.e.*, deshielding at C₄ follows the order isopropyl > ethyl > methyl). No significant cmr shift differences were observed at C₂ (C₆) as might have been expected from enhanced positive charge stabilization of the entire cyclohexadienyl system. Significant differences would also have been anticipated in the facility of intramolecular proton shift in the 1-*i*-C₃H₇a \rightleftharpoons 1-*i*-C₃H₇b \rightleftharpoons 1-*i*-C₃H₇c \rightleftharpoons 1-*i*-C₃H₇d equilibrium from those of the analogous 1-CH₃a-d systems. Such differences should be evident in temperature-dependent line broadening, but were not observed, indicating that stability ratios of 1-CH₃a to 1-CH₃b, 1-C₂H₅a to 1-C₂H₅b, 1-*n*-C₃H₇a to 1-*n*-C₃H₇b, and 1-*i*-C₃H₇a to 1-*i*-C₃H₇b are similar. Alkyl group stabilization of the cyclohexadienyl system *via* hyperconjugation would have been expected to evidence itself most strongly in 1-Ra and 1-Rc ions with little differences seen in 1-Rb species.

The direct bonding of the alkyl substituent to only a single carbon (C₄) showing significant differences in cmr shift presents difficulties in assigning the source of deshielding. That is, are the observed cmr shift differences genuinely related to charge density changes at that carbon or are the controlling factors differences in shielding effects caused by alkyl substituents? Ideally carbons C₂(C₆) and perhaps C₁ could be effectively used to answer this question because of their distance from the C₄ substituent. As noted, however, the cmr shifts observed for these carbons were not detectably sensitive to the effect of substituents on C₄ to enable a conclusion to be formed. In these systems, cmr shifts and line broadening data are not sensitive enough to detect existence of anticipated hyperconjugative or inductive stabilization. The data obtained by the cmr method most closely support the results of Brouwer and Van Doorn¹² in that stabilities conferred upon benzenium ions do not appear to vary significantly as the C₄ alkyl substituent is varied.

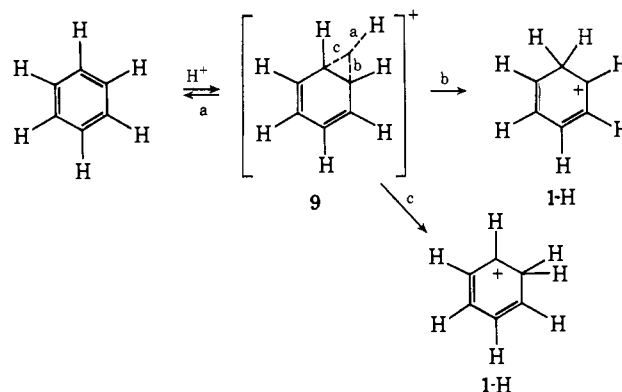
C. Cleavage and Isomerization Reactions. Carbocations have been categorized according to two limiting, distinct classes:^{1b} (1) carbenium ions, in which the carbenium center is a close to planar trivalent bound electron-deficient carbon atom; (2) carbonium ions, which are characterized by penta- or tetracoordinated carbocation centers, the essential characteristic being a bonding electron pair shared by three atoms.

Formation of carbenium ions from π - or σ -donor systems involves interaction of a pair of electrons from the donor with the electrophilic reagent, *i.e.*, first a carbonium ion is formed which subsequently, *via* opening of the three-center bond, rearranges into the

corresponding trivalent carbenium ions. (We are depicting the two-electron three center bonds with dotted branched lines joining the atoms involved.^{1b} Carbonium ions not observed are bracketed.)

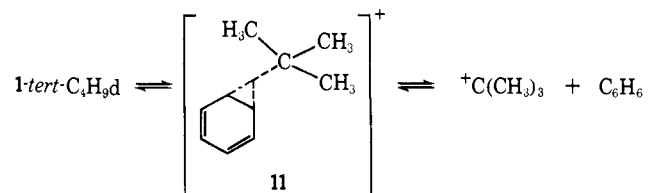
Protonation of an aromatic system (*i.e.*, benzene) thus is considered to occur initially by electrophilic attack of the proton on the aromatic π -electron system (Scheme II) to form the tetracoordinated benzenium

Scheme II



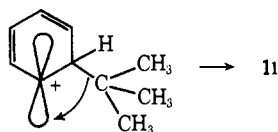
ion 9 transition state. Ion 9 is a three-center bound carbonium species and cleavage of the three-center bond may occur in any of three ways depicted as a, b, and c, the latter two of which lead to benzenium ions 1-H. Ions 1-H can also undergo the reverse reaction, *i.e.*, electrophilic attack of the C₂(C₆) carbenium center on the C₁-H₁ σ bond resulting in carbonium ion 9. Such processes occur in the 1-Ra-d equilibria. The rapidly equilibrating, degenerate set of benzenium ions 1-Ha-d lacks the substantial barrier presented to isomerization of the monoalkylbenzenium ions 1-Ra-d. In the 1-Ha-d system, the higher stability of a and c forms relative to b and d which was observed in the 4-alkylbenzenium ions is not present, as there is no alkyl group present to stabilize these forms.

Cleavage of the *tert*-butyl group (as *tert*-butyl cation) from the *tert*-butylbenzenium ion (or that of other cleavable groups in alkylbenzenes) takes place with ease in superacid solutions and can be considered to involve a facile carbonium ion isomerization process, such as the 1-*tert*-C₄H₉a-d isomerization. Protolysis of the *tert*-butyl side chain in *tert*-butylbenzene is not considered to be due to a direct electrophilic attack by an external proton at the C₁-C _{α} bond, such a process being sterically and electronically unfavorable. As alkylation and dealkylation can be considered identical processes based on the principle of microscopic reversibility, it is suggested that dealkylation and positional isomerization occur *via* transition state (or intermediate) of the type 11 which is identical with that formed in the

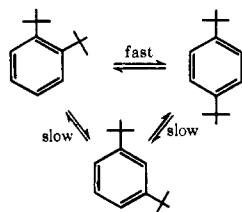


alkylation of benzene with the *tert*-butyl cation. Formation of 11 can be best depicted *via* electrophilic attack by the electron-deficient orbital at C₂(C₆) in 1-

tert-C₁H₉d on the C₁-C_α bonding electron pair. Isom-

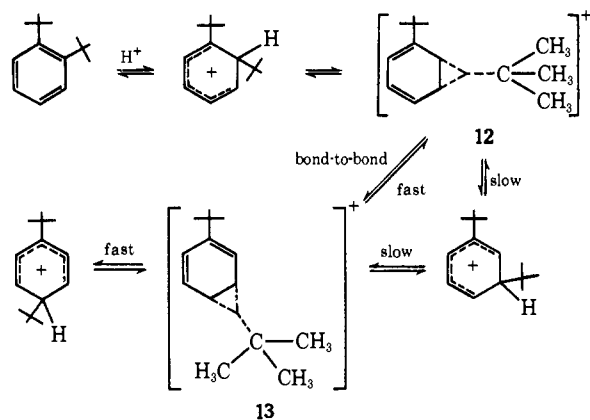


erization of di-*tert*-butylbenzenes,³⁵ *tert*-butyltoluenes,³⁶ as well as other dialkylbenzenes with water-promoted aluminum chloride is a facile process. It was shown³⁵ that the ortho to para rearrangement of di-*tert*-butylbenzenes occurs faster than the ortho to meta conversion. The same observation was made in the



case of *tert*-butyltoluenes,³⁶ but not for secondary or primary migrating species.³⁷ These observations cannot be explained in terms of a series of consecutive benzenium-benzonium-benzenium ion rearrangement steps, because this route would lead only to the thermodynamically controlled product distribution (*i.e.*, high meta isomer content) and could not account for the initial ortho-para isomer conversions. Recently we proposed that carbonium ions can undergo intramolecular "bond-to-bond" rearrangements. This was suggested for the "polytopal"-type rearrangement of the methonium ions CH₅^{+1b} and higher homolog alkonium ions, and as a mode of interconversion of cyclopropyl-carbonium ions.³⁸ The same carbonium ion "bond-to-bond" rearrangement can be involved in the isomerizations observed for the di-*tert*-butylbenzenes (Scheme III). The scheme indicates that the benzenium ion 12

Scheme III



⇌ 13 process must be quite rapid to enable the concentration of the para isomer to be large, relative to

(35) G. A. Olah, C. G. Carlson, and J. C. Lapierre, *J. Org. Chem.*, **29**, 2687 (1964).

(36) G. A. Olah, N. W. Meyer, and N. A. Overchuk, *ibid.*, **29**, 2310 (1964).

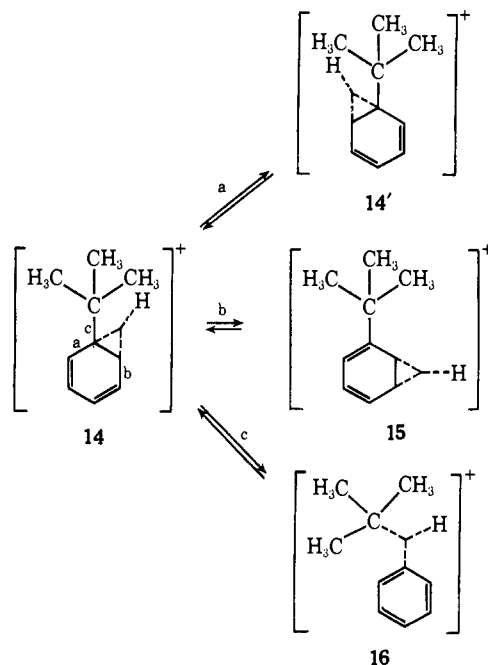
(37) (a) G. A. Olah, M. W. Meyer, and N. A. Overchuk, *ibid.*, **29**, 2315 (1964); (b) *ibid.*, **29**, 2313 (1964); (c) D. Allen and L. D. Yats, *J. Amer. Chem. Soc.*, **81**, 5289 (1959); **82**, 2853, 4856 (1960); (d) G. Baddeley, *J. Chem. Soc.*, 994 (1950).

(38) G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *J. Amer. Chem. Soc.*, **94**, 146 (1972).

that of the meta isomer, in the initial stages of the reaction. In the case of the migration of alkyl groups in alkylbenzenes (*via* suggested carbonium ion processes), it is clear that the involved benzene-*tert*-butonium ions are more stable than the benzeneisoproponium ions, etc. For this reason, the "bond-to-bond" rearrangement process of Scheme III is favorable for the *tert*-butyl migrating group relative to secondary and primary systems, in accordance with experimental evidence.³⁹

"Bond-to-bond" carbonium ion rearrangements can also be considered to explain not only dealkylative cleavage, but also alkyl group isomerizations. Consider alternative routes for the "bond-to-bond" rearrangements of ion 14 (Scheme IV) and that dealkyla-

Scheme IV

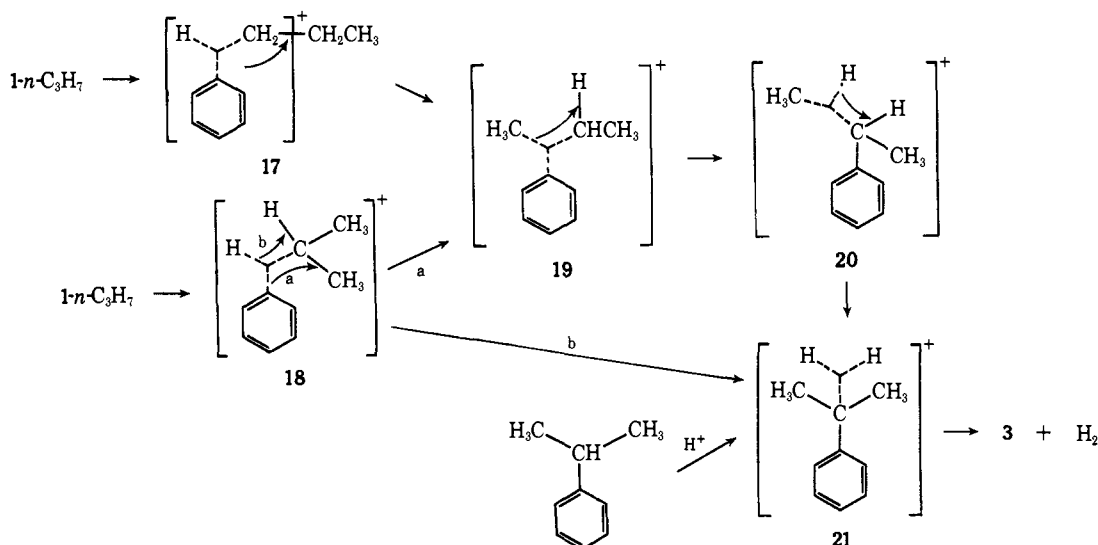


tion of *tert*-butylbenzenium ion may occur *via* route 16 (C_{1α}-*tert*-butylbenzeneprotonium ion). Although this is obviously not as favorable as benzenealkonium ion formation, it provides a convenient route to isomerizations observed in other ion systems.

Protolysis of isopropylbenzene indicated C_α-H_α σ-bond protonation of the side chain competitive with the formation of 1-*i*-C₃H₇ ions by the π route. This appears to have been a competitive reaction prior to formation of ions 1-*i*-C₃H₇ as all solutions contain a small amount of ion 3. For both ions 1-*n*-C₃H₇ and 1-*i*-C₃H₇ warming of the solutions results in the formation of phenyldimethylcarbenium ion 3. Again, bond-to-bond carbonium ion rearrangement appears to be the preferred process. Scheme V shows a condensed version depicting some of the bond-to-bond rearrangements which can occur to give the ion 3 from 1-*n*-C₃H₇ as well as from 1-*i*-C₃H₇. Competitive initial protolytic attack on isopropylbenzene to give ion 21 is also shown. The analogous bond-to-bond process to that seen for ion 1-*tert*-C₄H₉ to give 16 (Scheme IV) gives rise in these systems to ions 17 from 1-*n*-C₃H₇ and 18, from 1-*i*-C₃H₇. The bond-to-bond rearrangements 17 → 19 → 20 → 22 show a route to ion 3 from

(39) H. C. Brown and H. Jungk, *J. Amer. Chem. Soc.*, **77**, 5579 (1955).

Scheme V



ion $1-n-C_3H_7$. Ion $1-i-C_3H_7$ is shown as well. Two (a and b) of the possible routes of bond-to-bond migrations are shown for **18**. Five bond-to-bond rearrangements resulting in the migration of the three-center bound proton alone can be depicted. There are possible migrations of phenyl and isopropyl groups, cleavages (*i.e.*, **21** \rightarrow **3** + H₂ or **21** \rightarrow isopropylbenzene + H⁺), and reversions to carbenium ions (*i.e.*, **18** \rightarrow $1-i-C_3H_7$), to consider as well. It is expected that only cleavage to relatively stable products is observed (*i.e.*, **19** probably does not cleave at all as it must give C₆H₅⁺, CH₃⁺, or C₂H₅⁺, all of which are poorly stabilized ions; ion **21**, on the other hand, may cleave readily in any fashion to give either H⁺ or ion **3**).

Isomerization of *sec*-butyl- to isobutylbenzene is well known. Again, a bond-to-bond rearrangement sequence such as that depicted in Scheme V explains best the pathway for isomerization. In 1952 R. M. Roberts⁴⁰ and subsequently Nenitzescu⁴¹ reported some unusual isomerizations of butyl- and propylbenzenes with aluminum chloride. Among those observed were such isomerizations as that of [β -¹⁴C]-*n*-propylbenzene to [α -¹⁴C]-*n*-propylbenzene, as well as isomerization of *sec*-butylbenzene and isobutylbenzene to give in each case 2:1 equilibrium mixtures of isobutyl- and *sec*-butylbenzenes. Streitwieser⁴² suggested a mechanism involving α -phenylalkyl cations for the migration (and rearrangement) of primary alkylbenzenes. A critical reinvestigation by DeValois⁴³ makes this mechanism improbable. We suggest that a bond-to-bond carbonium ion rearrangement mechanism provides a satisfactory explanation for the reported observations.

(40) (a) R. M. Roberts and S. G. Brandenberger, *J. Amer. Chem. Soc.*, **79**, 5484 (1957); (b) R. M. Roberts, Y. W. Han, C. H. Schmid, and D. A. Davis, *ibid.*, **81**, 640 (1959).

(41) (a) C. D. Nenitzescu, I. Necsoiu, A. Glatz, and M. Zalman, *Chem. Ber.*, **92**, 10 (1959); (b) C. D. Nenitzescu, *Experientia*, **16**, 332 (1960).

(42) A. Streitwieser, Jr., and L. Reif, *J. Amer. Chem. Soc.*, **86**, 1988 (1964).

(43) P. J. DeValois, Ph.D. Thesis, University of Amsterdam, 1968.

Reaction of neopentylbenzenium ion $1-neo-C_5H_{11}$ to give isopropylphenylcarbenium ion is obviously subject to the same type of rearrangements and cleavage reactions as those of propyl- and butylbenzenium ions.

Experimental Section

All alkylbenzenes used in this study were commercially available in high purity. Antimony pentafluoride (Allied Chemical) was triply distilled; fluorosulfuric acid was doubly distilled.

Preparation and Nmr Study of Ions. Nmr spectra were recorded on Varian A60A, A56/60A, or HA-100 spectrometers. Carbon-13 magnetic resonance data were obtained by the indor method described in detail in previous publications.^{13c,24} Solutions of benzenium ions were prepared as reported previously in this series for protonations in superacid media and studied directly by nmr spectrometry. Quenching solutions of benzenium ions and analysis of recovered hydrocarbons (by glc and pmr) were also carried out as described.

Deuteration of Toluene. Toluene was treated with 2 mol equiv of DF-SbF₅ in SO₂ClF (in an nmr tube) at -30° for 3 hr. The solution was then cooled to -80° and its pmr spectrum recorded. The spectrum of formed ion **1-CH₃a-d** showed equal peak areas for H_{2,6}, H_{3,5}, and the methylene protons. The methyl protons do not exchange with DF-SbF₅-SO₂ClF, as there is no change in intensity of the CH₃ absorption and also control experiments with toluene- α,α,α -d₃ with HF-SbF₅-SO₂ClF showed no H-D exchange. Comparison of peak areas (H_{2,6}, H_{3,5}, and CH₂ vs. CH₃) in pmr spectra allowed us to calculate the amount of deuterium incorporated into ion **1-CH₃a**. The calculations show only 1.1 atoms of D per ion **1-CH₃a**. Mass spectrometric analysis of hydrocarbon recovered after quenching also is in agreement with this result. Data thus prove that intermolecular exchange (with the superacid solvent) is slow. Additional evidence for the intramolecular nature of the exchange process comes from the study of the temperature-dependent pmr spectra of toluene in superacid solution (Figure 1b). The collapsed singlet (above -30°) of H_{2,6}, H_{3,5}, and CH₂ is found at the average position of these three absorptions (as observed at low temperatures). Intermolecular proton exchange (with superacid solvent) would deshield the collapsed singlet from the average of the three original absorptions, since the acid peak is the most deshielded absorption line.

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