methylnorbornyl cation was observed in the reverse direction as observed in bicyclononyl cations.[32] The driving force for this intramolecular transformation might be the result of strain involved in ion I.

Experimental Section

Proton Nuclear Magnetic Resonance Spectra. All pmr spectra were recorded at 60 MHz using a Varian Associates Model A56-60A spectrometer equipped with a variable temperature probe. TMS contained in a concentric capillary was used as a reference signal.

Preparation of Solutions of the Bicyclo[3.3.0]-1-octyl Cation. The bicyclo[3.3.0]-1-octyl cation can be generated from five bicyclo-[2.2.2]octyl derivatives **1–5**, five bicyclo[3.3.0]octyl derivatives **9–13**, bicyclo[3.2.1]-2-octanol, 2-norbornanecarbinyl derivatives **8** (X = OH and Cl), and tricyclo[3.3.0.$0^{2,6}$]octane **6** in FSO_3H–SbF_5–SO_2ClF (or SO_2) or in SbF_5SO_2ClF (or SO_2) at −78°. A solution of FSO_3H and SbF_5 (or SO_2) is prepared and cooled to −78° in a Dry Ice–acetone bath. To this solution is added with continuous vigorous stirring using a vortex-type stirrer a cold (−78°) solution of bicyclooctyl derivatives to give an approximately 10% solution. The solution is then transferred with a cold pipet to a precooled nmr tube.

The Rearrangement of the Bicyclo[3.3.0]-1-octyl Cation to the 2-Methylnorbornyl Cation. The bicyclo[3.3.0]-1-octyl cation solution prepared as described above is slowly heated to −10° in nmr probe. The 2-methylnorbornyl cation is slowly formed, and the solution is cooled back to −70° and the spectrum recorded. The nmr spectrum of the 2-methylnorbornyl cation has been reported previously.[29,30]

Quenching experiments with methanol of KOH–ice were carried out as described previously.[37]

Materials. Compounds **1**, **3**, **10**, **12**, and **8** (X = OH) are commercially available and were used without further purification.

Tricyclo[3.3.0.$0^{2,6}$]octane (6). Compound **6** was prepared in low yields by the method of Baldwin and Greeley.[40]

Bicyclo[3.2.1]-2-octanol.[4] 2-Bicyclo[3.2.1]octanone (Aldrich) was reduced by lithium aluminum hydride in the usual manner. Work-up of the reaction mixture gave a mixture of alcohols which was used without separation, mp 179–181°.

2-Chlorobicyclo[3.2.1]octanes (7, X = Cl). The method of Stille and Sonnenberg[39] was used to prepare the chlorides from bicyclo-[3.2.1]octanols.

2-Norbornanemethyl Chloride (8, X = Cl). Compound **8** was prepared by treating the commercially available 2-norbornane-methanol with $SOCl_2$–pyridine;[39] bp 69–70°.

Acknowledgment. Support of this work by a grant of the National Science Foundation is gratefully acknowledged.

(40) J. E. Baldwin and R. H. Greeley, *J. Amer. Chem. Soc.*, 87, 4514 (1965).

Stable Carbocations. CXXI.[1a] Carbon-13 Magnetic Resonance Spectroscopy Study of Ethylenarenium Ions (Spiro[2.5]octadienyl Cations)[1b,c]

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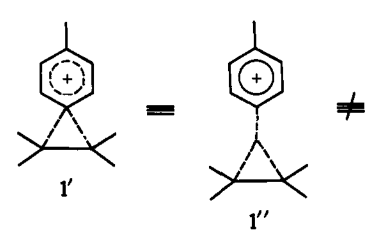
Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received March 1, 1971*

Abstract: The parent ethylenebenzenium ion **8-H** has been obtained *via* phenyl participation from β-phenylethyl chloride in SbF_5–SO_2ClF solution and examined by carbon-13 (cmr) as well as proton (pmr) magnetic resonance spectroscopy. Other ethylenarenium ions were studied where aryl = *p*-anisyl, mesityl, and *p*-tolyl, and were also completely characterized by cmr spectroscopy. The unsymmetrical ethylene-2,4-dimethylbenzenium ion was also examined. The results of these studies show the stable, long-lived ions obtained to be symmetrically bridged ethylenarenium ions, *i.e.*, spiro[2.5]octadienyl cations. Delocalization of charge in secondary cyclopropylcarbinyl ions into the cyclopropane ring resembles closely the spirocyclopropane ring portion of the studied ions. The cyclohexadienyl ring portion of the ions shows charge distribution similar to that of the analogous arenium ions (protonated arenes). The bisected conformation of the ions as well as their geometry is essentially the same as originally suggested by Cram. The carbocations derived from 2,3-dimethyl-3-(*p*-X-phenyl)-2-butyl systems **11-X** were also examined by cmr and, in the cases where X = H, Br, and CF_3, are shown to be bridged in nature by comparison to suitable models for which pertinent ^{13}C parameters were measured. The model compound, tetramethylethylenebromonium ion, was reexamined because of the available new data and is now shown to be a symmetrically bridged species.

Since the pioneering studies of Cram,[2] solvolytic β-arylethyl systems have been some of the most carefully scrutinized in organic chemistry. Cram demonstrated the existence of a discrete molecular species in

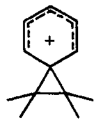
(1) (a) Part CXX: G. A. Olah and Y. Halpern, *J. Org. Chem.*, submitted for publication. (b) Preliminary communication: G. A. Olah and R. D. Porter, *J. Amer. Chem. Soc.*, **92**, 7627 (1970). Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 15, 1970, Abstract ORGN 57. (c) Concerning the definition and naming of carbocations (the generic name for all cations of carbon compounds, as carbanions are the anions) we recently suggested a clear differentiation between trivalent carbenium and penta- or tetracoordinated carbonium ions (G. A. Olah, *J. Amer. Chem. Soc.*, in press). Consequently the name ethylenarenium ions is used for ethylenarylonium ions (ethylenephenonium ions) which are carbenium and not pentacoordinated carbonium ions and should not be considered "nonclassical." Similarly $C_6H_7^+$ is the benzenium ion and not the benzenonium ion.

(2) (a) D. J. Cram, *J. Amer. Chem. Soc.*, 71, 3863 (1949); (b) D. J. Cram and R. Davis, *ibid.*, 71, 3871 (1949); D. J. Cram, *ibid.*, 71, 3875 (1949); (c) the use of dotted lines as in **1′** to represent ions of the type **1** has become common, but the structure **1′** as it implies "nonclassicality" is not consistent with our experimental findings. σ-Bond delocalization

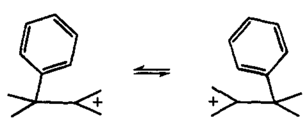


1′ 1″ ≠ 1

the Wagner–Meerwein rearrangement of 3-phenyl-2-butyl systems, *i.e.*, a carbocyclic three-membered carbenium ion. These were among the first systems in which bridged carbocations were proposed. The evidence for symmetrically bridged alkylenarenium ion 1[2c] intermediates in the acetolysis of 3-phenyl-2-butyl,[2a] 2-phenyl-3-amyl,[2b] and 3-phenyl-2-amyl[2b] tosylates was stereochemical in nature. It was quickly reinforced by kinetic studies, the first such study being carried out by Winstein and coworkers[3] demonstrating β-phenyl anchimeric rate enhancement to solvolysis. In 1962, Brown[4] proposed an alternative explanation to the bridged structure of ethylenarenium ions (as well as to nonclassical cations derived from 2-norbornyl **2** and cyclopropylcarbinyl **3** precursors). Brown's alternative to **1** at that time was pictured as a pair of open-chain, rapidly equilibrating carbenium ions **4**.[5] Brown recognized at that time the possibility of (a) additional stabilization of proposed intermediates by delocalization of positive charge across space away from the carbenium ion carbon into the aromatic π-electron cloud as in species **5** and (b) the possible existence of **1**[6] as originally



1



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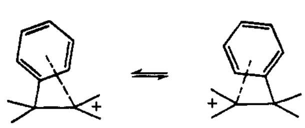

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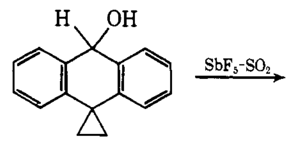
proposed by Cram. Based on subsequent experimental work on β-arylethyl[7] and 2,3-dimethyl-3-aryl-2-butyl[8] systems with different aromatic ring substituents, Brown suggested partially π-bridged ions **5** as intermediates, increasing in importance with decreasing σ^+ substituent constant values. Recently, however, a joint study with Schleyer using a combination of kinetic rate and product composition studies[9] has caused his acceptance of the fully bridged, symmetrical cation intermediates of type **1** in the case of trifluoroacetolysis of 3-aryl-2-butyl (secondary–secondary) and 2-arylethyl (primary–primary) systems.

There was recently evidence presented by Gregoriou based on kinetic hydrogen isotope effect studies in trifluoroacetolysis of secondary–secondary systems indicating that cationic intermediates involve nucleofuge in some way still associated with the carbenium carbon.[10a] Gregoriou's results indicate that trifluoroacetic acid is not a limiting SN1 solvent. Brown[10b] came to the same conclusion in a kinetic study of acetolysis of the 3-phenyl-2-butyl system.

Superacid systems by their nature come closest to being limiting nonnucleophiles, as they lead to stable carbocations as products. The value of spectroscopic observation of stable carbocations in solution has been well recognized[11] and is made possible by the strongly acidic media of extremely low nucleophilicity. This method has been used on β-arylethyl systems and observations (by pmr) of ethylenarenium ions in these solvents have been reported. The first such example, provided by Eberson and Winstein, was the observation of ethylene-9-anthracenium ion **7** formed by ionizing the spiro alcohol **6** in SbF_5–SO_2.[12] Ion **7** was obtained



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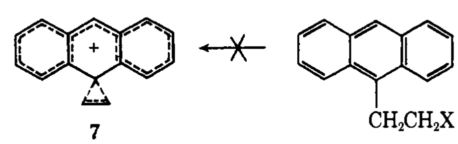

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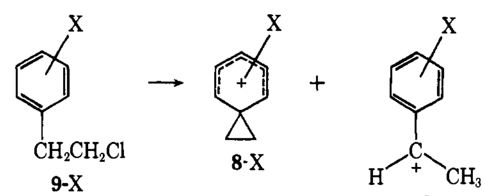
from an alcohol having a preformed cyclopropane ring remote from the point of ionization, but attempts to prepare the ion by ionization of β-(9-anthryl)ethyl precursors directly failed.[13] Formation of stable ethylenarenium ions from β-arylethyl precursors *via* aryl participation was first accomplished in our laboratories from precursors with strongly activated aromatic rings.[14a] Primary–primary ethylenarenium ions **8-X** were obtained from the corresponding precursor chlorides **9-X** in SbF_5–SO_2 at $-78°$ where X = *p*-methoxy,



9-X **8-X** **10-X**

mesityl, and pentamethylphenyl.[15] The formation of

is better depicted by the triangular dotted line representation of the two-electron, three-center bond (ref 1c) as in structure 1'' (*C*-ethylenephenonium ion). Our findings indicate the carbocation 1 to be the structure observed and a distinctly different species from 1''(1'). In fact, interconversion of ions 1 and 1'' is considered to be possible only through the open-chain β-phenylethyl cation (see subsequent discussion).

(3) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, 74, 1113 (1952).

(4) H. C. Brown, *Chem. Soc., Spec. Publ.*, No. 16, 140 (1962).

(5) (a) A summary of evidence in favor of the possibility of open ions at the time was given by H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Amer. Chem. Soc.*, 87, 2137 (1965). (b) Arguments summarizing earlier kinetic and stereochemical data on the intermediacy of 1 are given by D. J. Cram, *ibid.*, 86, 3767 (1964).

(6) See footnote 22 of ref 5a.

(7) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *J. Amer. Chem. Soc.*, 89, 370 (1967).

(8) (a) H. C. Brown and C. J. Kim, *ibid.*, 90, 2082 (1968). (b) Initial studies on tertiary–tertiary (referring to substitution at α and β carbons of the precursor) systems were by D. J. Cram and J. D. Knight, *ibid.*, 74, 5839 (1952).

(9) H. C. Brown, C. J. Kim, C. J. Lancelot, and P. v. R. Schleyer, *ibid.*, **92**, 5244 (1970).

(10) (a) S. L. Loukas, M. R. Volkov, and G. A. Gregoriou, *Chem. Commun.*, 251 (1970); (b) H. C. Brown, personal communication.

(11) For a recent survey, see G. A. Olah, *Science*, **168**, 1298 (1970).

(12) (a) L. Eberson and S. Winstein, *J. Amer. Chem. Soc.*, **87**, 3506 (1965). (b) Another more recent example of such a preparation is provided by D. Chamot and W. H. Pirkle, *ibid.*, **91**, 1569 (1969).

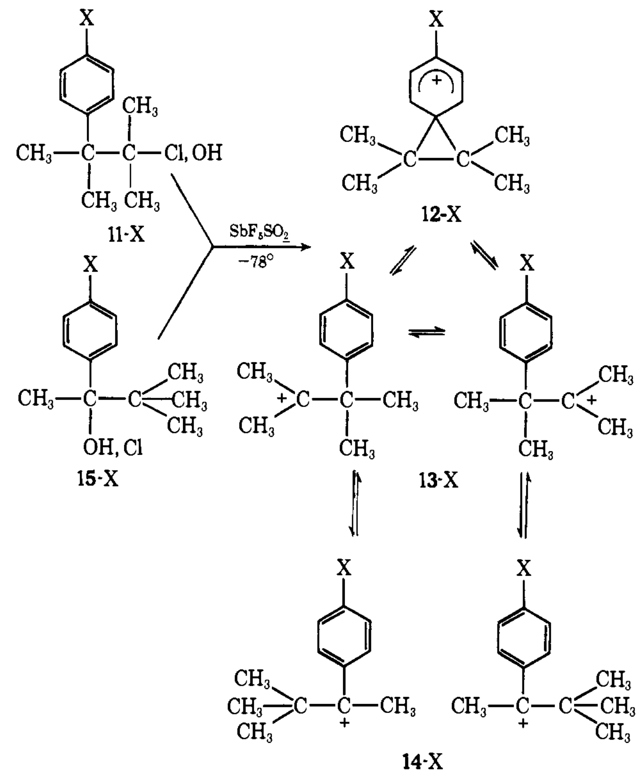
(13) We attempted in this study to effect the ionization of β-(9-anthryl)ethyl chloride and alcohol in SbF_5–SO_2ClF to give 7, but were not successful. The possible reason is peri alkylation of the anthracenium system in SbF_5–SO_2ClF.

(14) (a) G. A. Olah, M. B. Comisarow, E. Namanworth, and B. Ramsey, *J. Amer. Chem. Soc.*, **89**, 5259 (1967); (b) G. A. Olah, M. B. Comisarow, and C. J. Kim, *ibid.*, **91**, 1458 (1969).

(15) The following abbreviations will be used throughout this paper for six-membered ring substituted ethylenebenzenium ions: **8**-H, ethylenebenzenium ion; **8**-CH_3, ethylene-*p*-toluenium ion; **8**-OCH_3, ethylene-*p*-anisenium ion; **8**-m-Xyl, ethylene(2,4-dimethylbenzenium) ion; **8**-Mes, ethylene(2,4,6-trimethylbenzenium) ion; **8**-PMP, ethylenepentamethylbenzenium ion. Similar suffixes are used for their precursors **9**-X and for the related styryl cations **10**-X. The same system will also be used for arenium ions (*e.g.*, 19-mes, protonated mesitylene).

these ethylenarenium ions was accompanied by concurrent formation of methylarylcarbenium ions **10-X**. Pmr spectroscopy, although extremely informative in resolving structural problems of static carbocations, presents problems as far as unequivocal differentiation of bridged ions from rapidly equilibrating open-chain ions is concerned (*i.e.*, **1** from **4** or **5**) and involves estimation in the latter case of time-averaged chemical shifts which differ only slightly. The tertiary–tertiary 2,3-dimethyl-3-*p*-X-phenyl-2-butyl system **11-X** has also been studied by pmr.[14b] Ionization of **11-X** gives rise to the set of equilibrating ions shown in Scheme I.

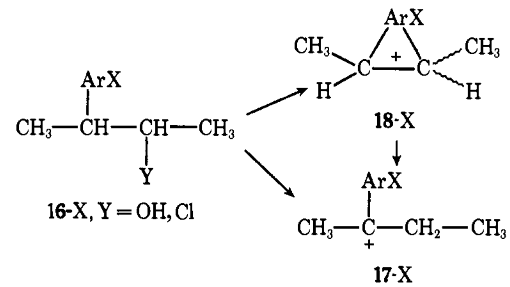
Scheme I



The same equilibrium is obtained by ionizing the benzylic precursors **15-X**. The aromatic para substituent controls which of the ions **12-X** through **14-X** is the most stable. When X = OCH_3, **14-OCH₃** is the most stable. We have since demonstrated (by pmr) **14-CH₃** also to be the most stable of the alternate possible ions.[16] In cases where X = H and CF_3, pmr data are less clear, and though the quenching data indicate **14-H** to be of minimal importance and **14-CF₃** practically absent, spectroscopic differentiation between the alternatives **12-X** and **13-X** for these systems requires a more sensitive probe than pmr.

Carbon-13 magnetic resonance (cmr) has been employed recently with great success in studies of stable organic cations.[17] The sensitivity of the method to both charge density and carbon geometry has been used in thorough studies of the norbornyl cation[18] and $C_{2,3}$-cyclopropylcarbonium ion.[19] Both of these ions have been shown to be σ-bridged carbonium ions. Carbon chemical shifts ($\delta_{^{13}C}$) and coupling constants ($J_{^{13}C-H}$) for the methylene carbons in **8-OCH₃** have been reported and used to demonstrate its σ-bridged character as well.[17]

Under our stable ion conditions, we have found that the secondary–secondary 3-aryl-2-butyl system **16-X** does not form aryl-bridged ions **18-X**, but leads to the formation of benzylic ions **17-X**. Rearrangement of the initially formed secondary ions to the more stable benzylic ions **17-X** takes place very rapidly. The absence of bridged ions **18-X** apparently results from the high relative stability of **17-X**. The stability of **17-X** is not surprising and a comprehensive study of benzyl cations[16] reveals that even **17-CF₃** is quite stable. Stabilities of ions **18-X** should range between those of



ions **8-X** and **12-X**. These ions have substantially different stabilities in relation to their related open-chain ions of type **4**: tertiary for **12-X** *vs.* primary for **8-X** cations. This will be explained in more detail (*vide infra*).

We now present our data of the study of these two extreme examples of ethylenarenium ions: ions **12-X** which are tertiary–tertiary systems where X = H, Br, and CF_3; and ions **8-X**, which are primary–primary systems. We have also succeeded in obtaining complete nuclear magnetic resonance spectroscopic data on the parent system, the ethylenebenzenium ion itself, the related, but previously also elusive ethylene-*p*-toluenium ion, and cmr data on ethylene-*p*-anisenium ions **8-OCH₃** and the ethylenemesitylenium ion **8-Mes** for which pmr data were reported previously. Experimental data supporting both the bisected geometry of and the cyclopropyl-like nature of the ethylenic system in ions **8-X** and **12-X** are presented. Suitable model systems were used for comparison and analogies drawn enabled us to reinterpret our previous data of the tetramethylethylenebromonium ion in terms of the symmetrically bridged structure.

Results

A. The Ethylenebenzenium Ion. Ionization of β-phenylethyl chloride in SbF_5–SO_2ClF at $-78°$ gives a mixture of ions, the 100-MHz pmr spectrum of which is shown in Figure 1. The strong singlet at δ 4.80 is due to the methylene protons of ion **8-H** while the doublet at δ 3.73 is due to the methyl group in ion **10-H** being coupled to the methine quartet at δ 10.30. A small unexplained peak at δ 4.65, slightly upfield of the methylene protons, always appears in these spectra, as do broad

(16) G. A. Olah, R. D. Porter, and C. J. Jeuell, *J. Amer. Chem. Soc.*, in press. The ion 14-CH₃ has been frozen out on the pmr time scale at $-120°$ using the solvent system SbF_5–SO_2ClF–SO_2F_2. Raising the temperature of the solution to $-60°$ shows the resulting singlet of the time-averaged methyl groups to be a properly weighted average of the *tert*-butyl and methyl substituents on the 14-CH₃ carbenium carbon.

(17) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969). This paper gives a general survey of the cmr study of carbocations, arguments used in assigning their structure, and their relationship with charge densities.

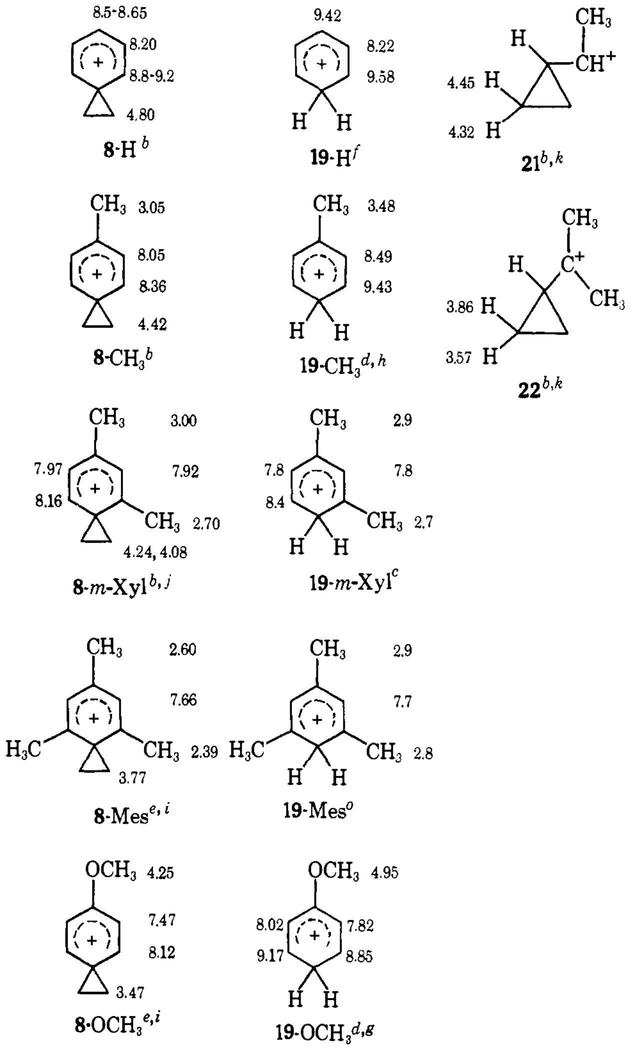
(18) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *ibid.*, **92**, 4627 (1970).

(19) G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *ibid.*, in press.

absorptions in the δ 3.4–3.9 and 7.7–9.0-ppm regions which are due to some formation of polystyrenes. The **8-H** and **10-H** ion absorptions coincide in the aromatic region. A series of secondary **10-X** ions including the styryl cation formed from α-arylethyl precursors has been reported previously,[20] but in the case of the styryl cation itself, the ion formed by this route was of such low concentration and accompanied by side reaction products to such an extent that δ_H values could not be accurately assigned.

The ratio of **8-H** to **10-H** varied appreciably depending on the experimental conditions under which solutions of ions were prepared. Attempts to maximize conditions in favor of either ion were not successful. Once the ions were formed, their ratio, which ranged from 1:2 to 10:1, did not change over a period of 40 hr at −78°. That is, there was no tendency for the two ions to equilibrate. In spite of the varied ratios of the two ions, the aromatic pmr regions did not change appreciably. The triplet at δ 8.20 is due to the meta proton absorption, the absorptions at δ 8.57 to the para proton, and the absorption at δ 8.8–9.2 we assign to the ortho protons. Pmr assignments of ions **8-X** are given in Chart I. Included in Chart I are model arenium ions **19-X**[15] formed from **20-X** arene precursors by protonation in $HF-SbF_5$.[21] These **19-X** ions are the analogous structures to the cyclohexadienyl ring portion of the **8-X** ions for which they are used as models. The secondary monomethylcyclopropylcarbenium ion **21**[19] and the tertiary dimethylcyclopropylcarbenium ion **22**[19] are included as models for the cyclopropyl portion of **8-X**.

Chart I. Pmr Parameters of Ethylenarenium Ions **8-X** and Model Cyclohexadienyl **19-X** and Cyclopropylcarbinyl Secondary (**21**) and Tertiary (**22**) Ions[a]



[a] δ_H in parts per million relative to external capillary TMS. [b] Solvent SbF_5-SO_2ClF. [c] Solvent $HF-SbF_5-SO_2$, ref 21a. [d] Solvent $HF-SbF_5-SO_2ClF$. [e] Solvent SbF_5-SO_2. [f] Solvent $HF-SbF_5-SO_2ClF-SO_2F_2$ at −134°, ref 21c. [g] Reference 21d. [h] Reference 21b. [i] Reference 14a. In these cases **9-X** in SbF_5-SO_2ClF gives the corresponding styryl ions **10-X** exclusively with no apparent formation of **8-X** ions desired. [j] Based on interpretation explained in text. [k] Reference 19.

20-CH₃ → **19-CH₃**

Cmr spectra were generally obtained by the indor method[22] with carbon-13 in natural abundance. The signal-to-noise ratio, as seen in Figure 1, indicates some of the difficulties encountered in sensitivity relating to the natural 1.1% carbon-13 abundance. For this reason, time averaging was employed enabling ^{13}C spectra of the ions to be completely characterized. The carbon-13 spectrum for the ion **8-H** was obtained by the method of mainline ($^{12}C-H$) enhancement; that is, complete decoupling of $^{13}C-H$ satellites. Monitoring the δ 4.80 methylene peak at 100 MHz and sweeping the 25.1-MHz region with a low-power decoupling irradiation, in order not to effect short-range $^{13}C-H$ decoupling, showed a doublet centered at $\delta_{^{13}C}$ +23[23] and a singlet at $\delta_{^{13}C}$+ 123. Assignments of these absorptions are to the ortho ring carbons and to the spiro carbon atom, respectively. Methyl substitution on the ortho carbons of the aromatic ring in the cases **8-Mes**[15] and **8-PMP**[15] results in the low-field peak enhancement appearing as a singlet ($\delta_{^{13}C}$ +9 and +15, respectively), thereby substantiating the assignment that these carbon atoms are of ortho position. Raising the power level of the decoupler showed a broad absorption at $\delta_{^{13}C}$ +134 due to the cyclopropyl-type methylene carbons as the short-range $^{13}C-H$ decoupling is effected. This is complicated by broadening of the spiro carbon enhancement by this broader, more powerful irradiating band. Enhancement of the meta proton absorptions was used to obtain $\delta_{^{13}C}$ of the meta and para carbons. They are $\delta_{^{13}C}$ +56 and $\delta_{^{13}C}$ +34, respectively. Two meta absorptions were observed centered at $\delta_{^{13}C}$ +56 and +62. Because the $\delta_{H_{meta}}$ absorptions for **8-H** are coincident with those of **10-H**, the assignments of these two chemical shifts are to the meta carbons of **8-H** and **10-H**, respectively. The relative intensities of these enhance-

(20) G. A. Olah, R. D. Porter, and D. P. Kelly, *J. Amer. Chem. Soc.*, **93**, 464 (1971).

(21) (a) G. A. Olah, *ibid.*, **87**, 1103 (1965); (b) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and Gh. D. Mateescu, *ibid.*, in press; (c) G. A. Olah, R. H. Schlosberg, D. P. Kelly, and Gh. D. Mateescu, *ibid.*, in press, **92**, 2456 (1970); (d) G. A. Olah and Y. K. Mo, *ibid.*, in press.

(22) (a) E. B. Baker, *J. Chem. Phys.*, **37**, 911 (1962); (b) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **89**, 7072 (1967); (c) A. M. White and G. A. Olah, *ibid.*, **91**, 2943 (1969); (d) W. H. Horsley and H. Sternlicht, *ibid.*, **90**, 3738 (1968).

(23) All carbon-13 chemical shifts are given relative to $^{13}CS_2$.

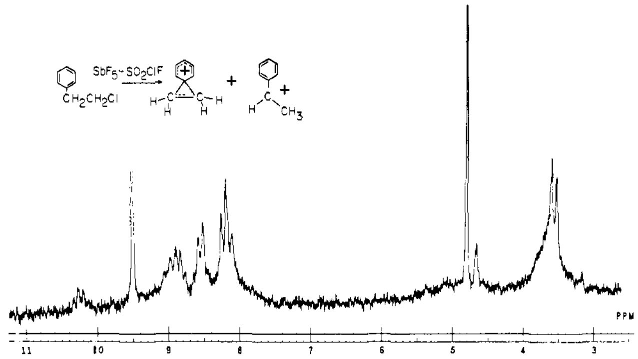
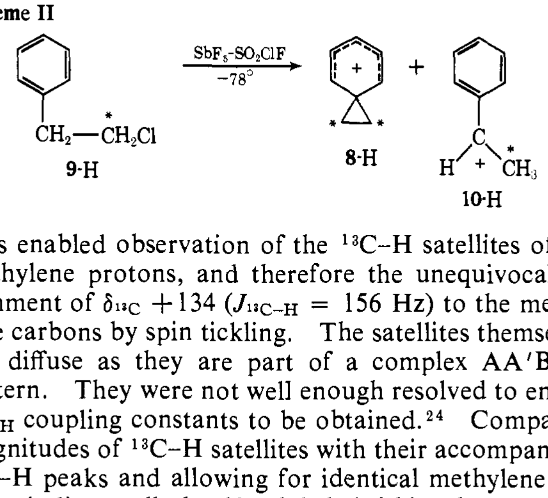


Figure 1. 100-MHz pmr spectrum of ethylenebenzenium ion **8**-H and styryl cation **10**-H in SbF_5–SO_2ClF at −78°.

ments and comparison to the relative **10**-H concentrations in the pmr spectrum indicate the correctness of the assignments. The assignment of the para carbon was made from an enhancement giving a weak doublet. Only one such doublet was observed, indicating the para carbon of **10**-H to be not in sufficient abundance.

Because of the complications mentioned above, it was worthwhile to substantiate our assignments of the methylene carbon chemical shift by the use of carbon-13 enrichment. The precursor α-^{13}C-β-phenylethyl chloride was used with 25% ^{13}C enrichment (Scheme II).

Scheme II



This enabled observation of the ^{13}C–H satellites of the methylene protons, and therefore the unequivocal assignment of $\delta_{^{13}C}$ +134 ($J_{^{13}C-H}$ = 156 Hz) to the methylene carbons by spin tickling. The satellites themselves are diffuse as they are part of a complex AA′BB′X pattern. They were not well enough resolved to enable J_{H-H} coupling constants to be obtained.[24] Comparing magnitudes of ^{13}C–H satellites with their accompanying ^{12}C–H peaks and allowing for identical methylene carbons indicate all the ^{13}C label (within the 10% accuracy of the determination) in the styryl ion **10**-H remains in the methyl group. This did not change over a period of 6 hr.

To substantiate the indor results, a carbon-13 fast Fourier transform (FFT) spectrum[25] of **8**-H at 22.63 MHz was obtained. Although the solution was of low concentration and contained inevitable impurities, the only resonances observed were at δ +133, +60, +31, and +22. This is in agreement with chemical shifts obtained by indor for methylene as well as meta, para, and ortho carbons, respectively, of the cyclohexadienyl ring in **8**-H. The spiro carbon absorption at δ +123 observed by indor is presumably not observed in (FFT) spectrometry due to the (anticipated) long relaxation time of that carbon.[26]

(24) F. S. Mortimer, *J. Mol. Spectrosc.*, 5, 199 (1960).
(25) R. R. Ernst and W. A. Anderson, *Rev. Sci. Instrum.*, 37, 93 (1966).
(26) Similar difficulties were encountered by H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961). The relaxation times of C-9 and C-10 in azulene were prohibitively long, precluding their observation by direct resonance.

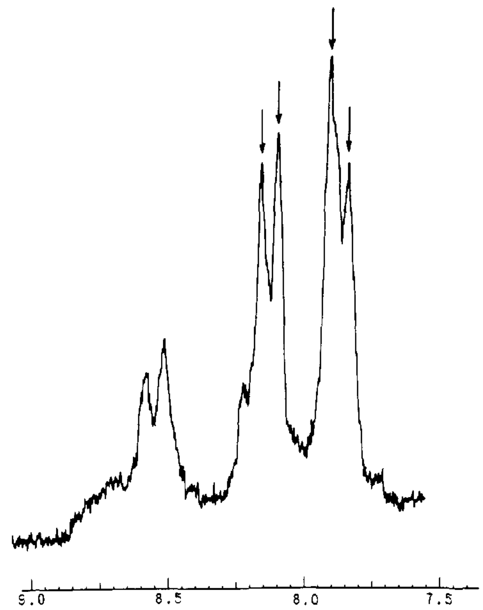


Figure 2. Aromatic region of 100-MHz pmr spectrum of ethylene-*p*-toluenium ion **8**-CH_3 (arrows) and *p*-methylstyryl cation **10**-CH_3 in SbF_5–SO_2ClF at −78°.

Solutions of ions were quenched in a rapidly stirred slurry of K_2CO_3-buffered ice in SO_2ClF at −78°. Only α- and β-phenylethyl alcohols were obtained as products of the quench experiments (as observed by gas–liquid chromatography) except for some polymeric material. The ratio of β to α alcohols was 3:1, although a lower ratio (2:3) would have been anticipated based on ion composition according to the pmr spectrum of the ion mixture quenched. As the styryl ion is sensitive to even a slight rise in temperature, local heating during the quenching process probably causes a competitive rapid polymerization of this ion, and therefore a shift in α to β product ratio.

B. The Ethylene-*p*-toluenium Ion. As was the case for **8**-H, **8**-CH_3 is formed from **9**-CH_3 in SbF_5–SO_2ClF, always concomitantly with **10**-CH_3. Pmr parameters are given in Chart I. The arenium region of the ion mixture is displayed in Figure 2. Arrows indicate ortho and meta absorptions due to **8**-CH_3. Assignment was made by comparison of the pmr spectrum with that obtained from **10**-CH_3 which had been formed by ionization of α-*p*-tolylethyl alcohol.[20] Carbon-13 chemical shifts were obtained in essentially the same fashion as for **8**-H with the exception that the para carbon shift was obtained by enhancement of the methyl substituent. Carbon-13 chemical shifts for **8**-CH_3 are given in Chart II. Protonated arenes,[21b,d] **19**-X, prepared by protonation of their aromatic precursors **20**-X in HF–SbF_5–SO_2ClF solution at −80°, were selected as models for the arenium portion of the ethylenarenium ions. Although the details on magnetic resonance spectra of ions **19**-X will be reported separately, cmr shifts of these analogs to **8**-X are given for comparison in Chart II. Pertinent cmr shifts of the model secondary **21** and **22** cyclopropylcarbenium ions[19] are given as well, for comparison to ethylenic carbons in **8**-X ions.

C. Other Ethylenarenium Ions. Ions **8**-Mes and **8**-OCH_3 were prepared from their precursors **9**-Mes and **9**-OCH_3 in SbF_5–SO_2 as described previously.[14a] Pmr

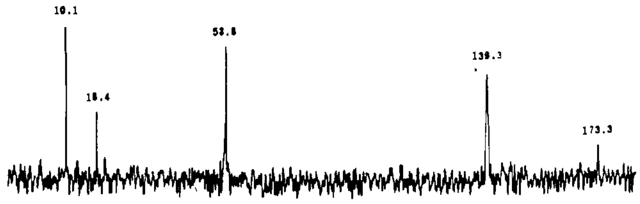
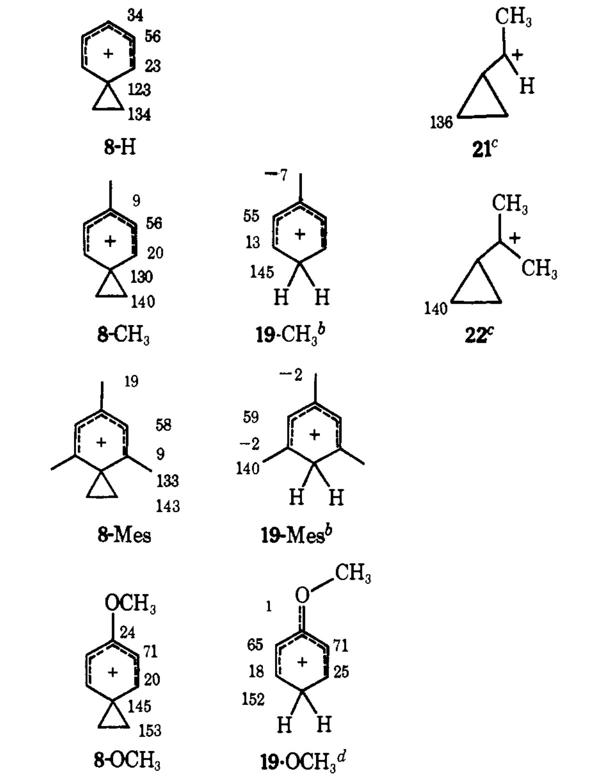


Figure 3. 22.63-MHz fast Fourier transform spectrum of ethylenemesitylenium ion **8**-Mes at −60° in SbF_5–SO_2.

spectra of these ions are included in Chart I for completeness. Complete carbon-13 characterizations of **8**-Mes and **8**-OCH_3 were made and are included in Chart II along with **19**-Mes[27] and **19**-OCH_3.[21d]

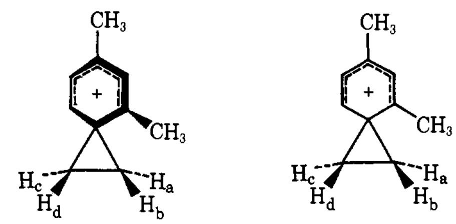
Chart II. Carbon-13 Chemical Shifts[a] of Ethylenarenium Ions (**8**-X) and Related Arenium Ions (**19**-X) and Cyclopropylcarbinyl Cations **21** and **22**



[a] Relative to $^{13}CS_2$. Only ring carbon shifts are given. [b] Reference 21b. [c] Reference 19. [d] Reference 21d.

The ethylenemesitylenium ion **8**-Mes can be obtained in high concentration with no nmr-detectable **10**-Mes present. This has not been our experience with the other **8**-X ions in this study. For this reason, we chose this ion too for the study by fast Fourier transform nmr. The spectrum obtained is shown in Figure 3. A fluorine lock was used on 1,1-difluoroethylene contained in a capillary, the cmr absorptions due to the reference [two triplets centered at δ +39 ($F_2{}^{13}C{=}CH_2$) and δ +104 ($F_2C{=}{}^{13}CH_2$)] having been eliminated from the carbon spectrum for clarity. All carbon–proton coupling has been removed by broad-band decoupling irradiation. Cmr absorptions are observed at δ +10.1 (ortho), +19.4 (para), +58.8 (meta), +139.3 (methylene), and +173.3 ppm (methyl). The spiro carbon is not observed in this spectrum (nor was it in the FFT spectrum of **8**-H) due, presumably, to slow relaxation time. Such a restriction does not apply to the other ring carbons including those bearing methyl substituents, and assignments in Chart II are verified (δ +173.3 being due to the cyclohexadienyl ring methyl substituents).

In the course of these studies we felt it would be of interest to observe an unsymmetrical ethylenarenium ion which could be expected to display nonequivalence of the methylene proton absorptions. Ion **8**-m-Xyl was prepared from **9**-m-Xyl in SbF_5–SO_2ClF at −78° and the pmr parameters are given in Chart I. The methylene protons appear as an AB quartet which we interpret as a deceptively simple AA′BB′ pattern. The multiplicity arises from a small H_a–H_b (H_c–H_d) cou-



8-*m*-Xyl, bisected $\delta_a = \delta_c$; $\delta_b = \delta_d$ **8**-*m*-Xyl, planar $\delta_a = \delta_b$; $\delta_c = \delta_d$

$$J_{ad} = J_{cb} = 8.1 \text{ Hz}$$
$$J_{ab} = J_{cd} \sim 0$$
$$J_{ac} = J_{bd} = 4\text{–}11 \text{ Hz}$$

pling. For cyclopropane-like systems J_{gem} has been shown to vary. Cyclopropanes themselves have J_{gem} values between −8 and −4 Hz.[28] Propylene oxide has a methylene J_{gem} value of 5 Hz,[29] while propylene sulfide shows an analogous J_{gem} = +0.4 Hz.[30] In addition to this, it has been concluded that J_{gem} values for both the ethylenebromonium and ethyleniodonium ions are zero.[31] In all cases, J_{cis} and J_{trans} values have covered the range 4.5–11.0 and 2.3–14.5 Hz, respectively. The bisected form of **8**-m-Xyl shows the chemical equivalences H_b–H_d and H_a–H_c, so no J_{cis} coupling constant is observed. We assign J_{gem} = 0, for which we have stated precedent, and J_{trans} = 8.1 Hz. With these values, we arrive at our simple apparent AB system. Were **8**-m-Xyl to assume a planar conformation, the spectrum would be complex unless either J_{cis} or J_{trans} were close to zero. Such an assumption would be made with no precedent in available model systems.

D. Tetramethylethylenarenium Ions. Ions **12**-X where X = H, Br, and CF_3 were prepared from their precursor chlorides **11**-X by ionization in SbF_5–SO_2 at −60°. Pmr data for both precursors and ions have been described[14b] for cases where X = H and CF_3. The pmr parameters of the additional ion, to which we assign the structure **12**-Br, are given in the experimental section. For ions **12**-H, **12**-Br, and **12**-CF_3, the cmr chemical shift of the dimethyl-substituted methylene carbons (C_1, C_2) was obtained by indor enhancement of the singlet due to the four methyl groups. In none of

(27) It should be pointed out that the ^{13}C spectrum of protonated mesitylene **19**-Mes (as Al_2Cl_7 and Al_2Br_7 complexes) has been reported by V. Koptyug, A. Rezvukhin, E. Lippmaa, and T. Pehk, *Tetrahedron Lett.*, 4009 (1968). They found an effect of the counterion on ^{13}C chemical shifts and we felt it therefore necessary to redetermine these parameters in our superacid solvent system. The differences are small (2 ppm).

(28) H. M. Hutton and T. Schaefer, *Can. J. Chem.*, **41**, 684 (1963); **41**, 2429 (1963).

(29) C. A. Reilly and J. D. Swalen, *J. Chem. Phys.*, **35**, 1522 (1961).

(30) J. I. Musher and R. G. Gordon, *ibid.*, **36**, 3094 (1962).

(31) G. A. Olah, J. M. Bollinger, and J. Brinich, *J. Amer. Chem. Soc.*, **90**, 2587 (1968).

these ions were we able to obtain the spiro carbon chemical shift. Protonated arenes (arenium ions) often show, by the diffuse nature of H_{ortho} indor enhancements (and often their absence) in the methylene region of the ^{13}C spectrum, that C_α–H_{ortho} have $J_{^{13}CCH}$ close to or equal to zero. This explains the reason for the lack of observation of indor enhancement due to C_α in **12-X** while monitoring H_{ortho} absorptions. We also failed in obtaining the spiro carbon indor enhancement by monitoring the analogous H_{ortho} absorptions in **8-CH$_3$**, an ion unequivocally identified, and obtainable in concentrations which, with any more than minimal $J_{^{13}CCH}$ coupling, should have resulted in strong enhancement. Carbon-13 chemical shifts of C_1 (C_2) should be sensitive to differences anticipated between **12-X**, **13-X**, and **14-X**.

In order to be able to make reasonable estimates of the C_1 and C_2 chemical shifts observed in ions **12-X**, **13-X**, and **14-X**, it was necessary to examine an extensive series of model compounds. The estimates of C_1 (C_2) carbon shifts are presented in Table I, along with the experimentally observed values. Estimates for C_1 and C_2 shifts were made on the following basis.

Table I. Comparison of Estimated Time-Averaged Chemical Shifts[a] for C_1 and C_2 in Ions **13-X** and **14-X** and Those Experimentally Observed for Ions Obtained from **11-X** Systems

X	Calcd 13-X	Calcd 14-X	Obsd
H	−14	35	60
Br	−16	37	60
CF_3	−14	26	53

[a] Parts per million relative to $^{13}CS_2$.

(a) **For Ions 13-X.** Rapidly 1,2-aryl equilibrating open ions are estimated by applying a small correction for a known, equilibrating alkyl system, the pentamethylethyl cation **23**.[17] The assumption is made that the β-aryl group in one of the open ions will have little effect on the carbenium carbon, but possibly cause a large change in the β-carbon itself. The C_1 and C_2 shifts obtained from the precursors **11-X** to the ions of interest were measured and compared to those C_1 and C_2 shifts obtained for pentamethylethyl alcohol **24-OH** and chloride **24-Cl**. The values are given in Table II. Ion **23** is known to exhibit an average C_1, C_2 cmr shift of −11. Because our correction of this value from the precursors is applied to only one (*i.e.*, C_1) carbon, the calculated average cmr shift is only adjusted by half the overall $\Delta\delta_{^{13}C_1}$ (**11-X–23**).

(b) **For Ions 14-X.** Carbon-13 chemical shifts for the benzylic carbon C_1 and the central *tert*-butyl carbon C_2 in **14-OCH$_3$** have been obtained and are included in Table II. The C_2 cmr shift $\delta_{^{13}C}$ +145.6 is not expected to change significantly with X in **14-X** and this value is used in calculations for C_2 in all three cases, X = H, Br, and CF_3. Estimates for C_1, the carbenium ion carbon, are taken from the carbenium carbons of para-X-substituted cumyl cations **25-X**, which are: $\delta_{^{13}C}$ −61 (**25-H**),[32] −75 (**25-CF$_3$**),[32] and −58 (**25-Br**). These are corrected by the chemical-shift difference between carbenium carbons of **25-OCH$_3$**, $\delta_{^{13}C}$ −25,[32] and **14-OCH$_3$**, $\delta_{^{13}C}$ −44, $\Delta\delta_{^{13}C}$ = +19 ppm, giving $\delta_{^{13}C}$ estimates of −80 (**14-H**), −77 (**14-Br**), and −94 (**14-CF$_3$**). Other studies[16] indicate aromatic substituents do not effect the change in cmr shifts of the carbenium ion carbon due to replacement of α-methyl protons by methyl substituents in para-X-cumyl cations **25-X**.

(32) G. A. Olah, C. L. Jeuell, and A. M. White, *J. Amer. Chem. Soc.*, 91, 3961 (1969).

Table II. Carbon-13 Chemical Shifts[a] of Model Compounds Used in Obtaining Estimates of Ions **13-X** and **14-X**

No.	Compound	C_1	C_2
24-Cl	CH_3 CH_3 CH_3—C_1——C_2—Cl CH_3 CH_3	+153	+118
24-OH	CH_3 CH_3 CH_3—C_1——C_2—OH CH_3 CH_3	+156	+118
11-H	C_6H_5 CH_3 CH_3—C_1——C_2—Cl CH_3 CH_3	+147	+118
11-Br	*p*-BrC_6H_4 CH_3 CH_3—C_1——C_2—OH CH_3 CH_3	+148	+121
11-CF$_3$	*p*-$CF_3C_6H_4$ CH_3 CH_3—C_1——C_2—Cl CH_3 CH_3	+147	+119
14-OCH$_3$	*p*-CH_3O—C_6H_4 CH_3 CH_3—C_1^+——C_2—CH_3 CH_3	−44	+146

[a] Parts per million relative to $^{13}CS_2$.

Discussion

A. The Ethylenarenium Ions. Correlations of carbon-13 chemical shifts in Chart II as well as pmr shifts in Chart I show ions **19-X** to be excellent models for the arenium ring portions of the analogous ions **8-X**. Assuming relationships of the cmr shifts to positive charge of the ortho, meta, and para carbons in the arenium ring, it can be seen that positive charge density within the six-carbon ring is highest at the expected ortho and para carbons, with only a minimal amount at the meta position. This is as expected based on molecular orbital calculations.[33] The relationship of π-electron density and ^{13}C chemical shifts as proposed by Spiesecke

(33) (a) M. Simonetta and S. Winstein (*ibid.*, 76, 18 (1954)) carried out Hückel calculations on the bridged ethylenebenzenium ion; (b) E. I. Snyder (*ibid.*, 92, 7529 (1970)) reported CNDO/2 and EHT/MO calculations on **8-H** and competing open ions. The energy minimum by CNDO/2 for the open ions was seen to be at $C_{\alpha\text{-aromatic}}$–$C_{\beta\text{-alkyl}}$–$C_{carbenium}$ = 109° which is more consistent with **4** than **5** although 34% of positive charge density is in the ring in the case of the open ion. Charge density distribution on the aromatic ring in **4** *via* CNDO/2 shows C_α > C_{para} > C_{meta} > C_{ortho} in positive charge density, indicative of retained aromatic character. Snyder's overall conclusion was that the symmetrically bridged species was energetically favored, although he demonstrates an abnormally large bias toward the cyclopropane ring in the CNDO method. EHT–MO calculations showed the open ion to be more stable, but the deviation of these results from available experimental evidence in related systems was seen to be very large.

and Schneider[26] has been used in aromatic carbocation systems as an indicator of positive charge density distribution in the aromatic ring.[16,26,27,34,35] The cyclopropane-like portion of the ions competes effectively for positive charge, as a cyclopropylcarbenium ion system. Spectroscopic considerations leading to our assignment of the ions as **8-X** are the following.

(1) Carbon-13 as well as proton chemical shifts in the arenium ring approximate those in **19-X** in that they indicate the expected charge distribution. They should, however, approximate **19-X** in absolute values if the three-membered cyclopropane-like ring did not delocalize substantial positive charge.

(2) Methylene cmr chemical shifts in **8-X** range from $\delta_{^{13}C}$ +134 (**8-H**) to $\delta_{^{13}C}$ +153 (**8-OCH$_3$**) in the least and most arenium substituent stabilized ions. This compares favorably with cyclopropylcarbenium ions in which the cyclopropane rings are known to bear significant positive charge. Such examples include the methylcyclopropylcarbenium ion **21** $\delta_{^{13}CH_2}$ +136 and the dimethylcyclopropylcarbenium ion **22**, where $\delta_{^{13}CH_2}$ +140.[19] These two ions provide ample precedent for the positive charge bearing, three-membered carbocyclic ring portions of the ethylenarenium ions **8-H** (for cyclopropane itself the cmr chemical shift is +196.9[36]).

Pmr chemical shifts of methylene protons of **21** and **22** also support these ions as models for methylene groups of **8-X** ions as is evident from the data in Chart I.

The distinction should be emphasized between trivalent cyclopropylcarbenium ions with intact cyclopropane rings which aid strongly in positive charge delocalization as in **21** and **22**, and carbonium ions for which the essential feature is penta- and/or tetracoordinated carbon atoms involved in tricenter bonding as in the $C_{2,3}$-cyclopropylcarbonium ion (cyclopropylcarbinyl cation) and the $C_{1,2}$-norborn-6-onium ion (norbornyl cation), which are totally different in kind from these models.[1c]

(3) Incompatibility of the Observed Methylene Cmr Shifts with Those Anticipated for Open Ions of the Type **4**. Such an estimate was made for the assumed pair of 2-*p*-anisylethyl open-chain cations as having time-averaged alkyl cmr shifts of +15 ppm.[17] Only minor differences from such an estimate would be anticipated for other members of the series **4**.

(4) The ^{13}C–H coupling constant obtained for **8-H** (from ^{13}C-labeled precursor) is $J_{^{13}C-H}$ = 156 Hz. Previously **8-OCH$_3$** was measured and shown to have $J_{^{13}C-H}$ = 176 Hz.[17] Both of these couplings are cyclopropane-like in nature and inconsistent with a less strained carbocyclic ring (for cyclobutane, $J_{^{13}C-H}$ = 130, larger rings have lower $J_{^{13}C-H}$ values, and for cyclopropane itself, $J_{^{13}C-H}$ = 162).[37]

(5) Proton–Proton Coupling. Analysis of the three-membered ring system where proton nonequivalence was induced by use of an unsymmetrical aromatic ring has been shown to be consistent with a bisected rather than a planar structure. Pmr parameters in Chart I indicate **8**-m-Xyl not to be anomalous in nature. We therefore extend this result by implication to other **8-X** species.

(6) The α-carbon (spiro carbon) chemical shifts are inconsistent with aromatic carbons of any kind and therefore cannot be rationalized on the basis of either a nonclassical ethylenephenonium structure[2c] or structure types **4** or **5**. These should show aromatic type α-carbon absorptions which would be at much lower field ($\sim\delta_{^{13}C}$ +60)[38] in **4** and at even lower field in an assumed ion **5** depending on the anticipated degree of the π-aromatic–carbenium carbon interaction. Agreement in range of observed shifts between these spiro carbon chemical shifts and those for the analogous methylene carbons in **19-X** is striking and we conclude the nature and geometry of these two carbons to be the same.

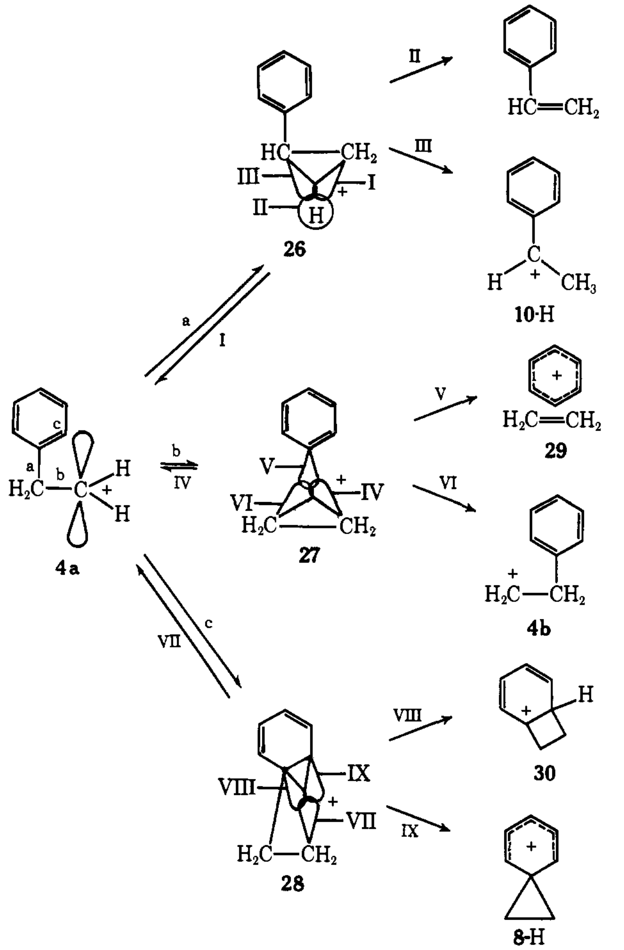
The labeling experiment for **8-H** had a side benefit already mentioned: that is, observation of the ^{13}C label in the methyl group of the styryl ion **10-H**, apparently in its entirety. Such an observation rules out equilibration of **8-X** with **10-X** which is as expected from the results obtained from ionization of α-alcohol precursors to give exclusively **10-X** ions. If the formation of **8-X** could have taken place by a route such as equilibration of **4** and/or **5**, then the **10-X** found from one of the open species **4** would show scrambled carbon label. That this is not observed suggests that hydride migration occurs immediately upon ionization and that aryl migration always results in **8-X** which cannot reopen to primary β-arylethyl species **4** or **5** which then proceed to **10-X** *via* hydride shift. It should be mentioned that similar results have been indicated in the ^{14}C-labeling studies of Coke[39] for deamination reactions.

All of the β-arylethyl ions formed under our stable ion conditions are of the **8-X** bisected nature. In these ions, positive charge resides partially in the arenium ring and is distributed in the same way as experimentally observed in arenium ions (protonated arenes) and predicted by molecular orbital calculations. As the ions are also of cyclopropylcarbinyl cation nature the remainder of the positive charge is in the cyclopropane ring, the extent of which is significant and controlled to a large extent by the electron-donating nature of the arenium ring substituents.

The nature of carbonium ion type transition states in electrophilic substitution reactions of hydrocarbons (saturated and/or unsaturated) has been discussed recently.[1c] Accordingly, in the ionization of **9-X**, the initially formed open benzylcarbenium ion (β-phenylethyl cation) **4a** has three ways for delocalization involving bonds within reasonable bonding distance of the carbenium ion carbon and of proper orbital orientation (Scheme III). These are: (a) the C–H σ bond at the benzylic carbon **26**; (b) the $C_{benzylic}$–$C_{aromatic}$ σ bond **27**; (c) the aromatic π system **28**.

(34) G. A. Olah and Gh. D. Mateescu, *J. Amer. Chem. Soc.*, **92**, 1430 (1970).
(35) (a) G. J. Ray, R. J. Kurland, and A. K. Colter, *Chem. Phys. Lett.*, 2 (5), 324 (1968); (b) *Tetrahedron*, in press. We express our thanks to Dr. A. K. Colter for communicating his results on complete ^{13}C characterization of a series of para-substituted triphenylcarbenium ions ahead of publication.
(36) (a) J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **86**, 1870 (1964); (b) G. E. Maciel and G. B. Savitsky, *J. Chem. Phys.*, **69**, 3925 (1965).
(37) E. L. Eliel, N. L. Allinger, S. J. Angyal, and C. A. Morrison, "Conformational Analysis," McGraw-Hill, New York, N. Y., 1965, p 199.
(38) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, Elmsford, N. Y., 1966, p 1001.
(39) J. L. Coke, *J. Amer. Chem. Soc.*, **89**, 135 (1967).

Scheme III



In all cases, **26**, **27**, and **28**, there exist three routes for the three-center bound carbonium ion to cleave to carbenium ions, at least one of which is back to **4a** (microscopic reversibility). Our spectroscopic data indicate only **10-X**, *via*

$$\mathbf{4a} \xrightarrow{a} \mathbf{26} \xrightarrow{III} \mathbf{10\text{-}X}$$

and **8-X**, *via*

$$\mathbf{4a} \xrightarrow{c} \mathbf{28} \xrightarrow{IX} \mathbf{8\text{-}X}$$

to be the observed products.

The bridged ("nonclassical") ion **27** is not observed nor does it lead to observed products.[2c] This is obvious as **29** is not formed and the alternative product route VI should have resulted in scrambled methylene carbons in **10**-H. That the basicity of the π-electron system is greater than the C–C σ bond is well known from aromatic substitution and that **8**-H is formed in preference to **30** is not surprising. Benzocyclobutane itself is well known and is stable even at higher temperatures.[40] From a steric argument, ion **30** is therefore possible. It is not, however, observed in these systems.

It should also be mentioned that an equilibrium mixture of the type **4a** ⇌ **8-X** ⇌ **4b**[5a] requires electrophilic attack by the cyclohexadienyl ring in **8-X** on the C_{spiro}–C_{alkyl} bent σ bond (structure **28**). In view of this, the lack of crossover[9,41] on solvolysis between open equilibrating ions (k_s) and bridged structures (k_Δ) is not surprising. Scheme III shows scrambled open ions to occur most readily *via*

$$\mathbf{4a} \xrightarrow{b} \mathbf{27} \xrightarrow{VI} \mathbf{4b}$$

Structure **27** can be shown (IV, V, VI) not to cleave to **8-X**; therefore, **27** and **28** are intermediates on discrete separate reaction pathways.

B. Tetramethylethylenarenium Ions. Table I presents the cmr data for the methylene carbons of the bridged ions **12-X**. In the comprehensive pmr studies on these ions,[14b] quenching results indicated benzylic ions **14-X** were of minimal importance in the cases now under consideration. Pmr parameters indicated **12**-H and **13**-CF_3 to be preferable assignments for the two ions from **11**-H and **11**-CF_3. We can now, however, eliminate **13**-CF_3 on the basis of comparison of calculated cmr values (from model compounds) and comparison with experimental data.

For the three ions **12-X**, where X = H, Br, and CF_3, two possible explanations other than the ions **12-X** as the principle contributing ions must be considered. The first is the possibility of partially bridged ions **5** being the observed species giving an anomalously high cmr chemical shift. The second possibility is a mixture of fully bridged **12-X** ions and open **13-X** ions such that the two give the time-averaged cmr chemical shift experimentally observed. We now consider these possibilities.

(1) The degree of partial π bridging in ions **5** should be largely controlled by aromatic ring substituents.[42] A partially delocalized ion from **11**-H would therefore be more extensively charge delocalized than would be a similar species arising from **11**-CF_3. The effect of **5** on our experimental results would be to raise the cmr chemical shift of C_1 to higher field as a result of additional shielding from the aromatic system. Therefore, let us assume for the moment that such an interaction has taken place and estimate the $\Delta\delta_{^{13}C}$ values for the carbenium ion C_1 carbon as a result of ring interaction.

(a) Our estimate (Table I) for **13**-H was $\delta_{^{13}C}$ −14 for time-averaged C_1 and C_2. We observed carbon chemical shift $\delta_{^{13}C}$ +60 and therefore assume the π bridging to have shielded the carbenium ion C_1 by 74 × 2 = 148 ppm (assuming C_2 to be relatively unaffected).

(b) For **13**-CF_3 we change the estimated carbon shift of $\delta_{^{13}C}$ −14 to the $\delta_{^{13}C}$ +53 observed, implying shielding of the carbenium carbon C_1 by [+53 − (−14)] × 2 = 134 ppm. Both these $\Delta\delta_{^{13}C^+}$ (open–partially bridged) shielding values are large, but the more striking fact is that they are close in magnitude. This is unexpected because differences in substituent effects of para CH_3 and para H are great even where the interaction is large rather than variable (*i.e.*, one anticipates more π bridging for the *p*-H case where there is stabilization relative to para CF_3 which is electron withdrawing, and

(40) M. P. Cava and A. A. Deana, *J. Amer. Chem. Soc.*, **81**, 4266 (1959).

(41) (a) A. F. Diaz and S. Winstein, *ibid.*, **91**, 4300 (1969); (b) P. v. R. Schleyer and C. J. Lancelot, *ibid.*, **91**, 4297 (1969); (c) J. M. Harris, F. L. Schadt, P. v. R. Schleyer, and C. J. Lancelot, *ibid.*, **91**, 7508 (1969); (d) J. L. Coke, F. E. MacFarlane, M. C. Mourning, and M. G. Jones, *ibid.*, **91**, 1154 (1969); (e) M. G. Jones and J. L. Coke, *ibid.*, **91**, 4284 (1969); (f) R. J. Jablonski and E. I. Snyder, *ibid.*, **91**, 4445 (1969).

(42) See ref 8a. In this case the authors examined the cases where X = OCH_3, CH_3, H, as well as the meta CH_3 case. Their arguments (correlations of degree of π bridging with deviations from σ^+–rate plots) can be extended to para CF_3 substituents.

hence destabilizing. The shielding effect should be more profound in the former than in the latter). For partial π bridging across, the implication is that interaction is small and only a slight perturbing effect on the carbenium ion center is expected. To have the cmr shift of such a carbon shielded by 134–148 ppm is unacceptable. A case where such an interaction is a maximum is exemplified by replacing a methyl group of the *tert*-butyl cation (carbenium cmr chemical shift $\delta_{^{13}C^+} = -135$) with an aromatic substituent as in the case of the cumyl cations **25-X**. The change in the carbon chemical shift $\delta_{^{13}C^+}$ effected by such a replacement is from -135 to -61 ppm or $\Delta\delta_{^{13}C^+} = +74$ in the case of **25-H**; -135 to -75 or $\Delta\delta_{^{13}C^+} = 60$ ppm for **25-CF$_3$**. These two examples with maximum aryl interaction indicate the $\Delta\delta_{^{13}C}$ experimentally observed to be unacceptable for partially bridged ions, as it should be less for partial bridging than for a full, benzylic interaction.

(2) From the information in Table I, it can be seen that if **12-X** $\rightleftharpoons$ **13-X** occurs with significant contribution from both species, the proportion of **12-X** must be substantial in order to shield C_1 to the extent it does relative to the predicted values for **13-X**. It is logical to reason that para CF_3 and para H substituents on the aromatic ring in **13-X** would have little effect on the stability of such an ion. Conversely, the expectation is that the two would vary greatly in their ability to stabilize ions **12-X** as they do under solvolytic conditions of arylcarbinyl systems as well as in aromatic substitution reactions.[43] That is, in an equilibrium **12-X** $\rightleftharpoons$ **13-X** it is expected that the ratio [**12-X**]:[**13-X**] should be much higher in the case where X = H than for X = CF_3, and a fortuitous mixture of the two having apparently the same ratio with **13-X** being a major species is unlikely. Such an assumption would be required to justify experimental data in terms of **12-X** $\rightleftharpoons$ **13-X** with significant contribution from **13-X**.

It should be pointed out that in neither of these systems do we reject Scheme I proposed previously. Ions **14-X** clearly play a part in the system as seen by the quenching studies. By implication **13-X** must therefore play a part as well. We also have no data to rule out partially bridged ions **5** as intermediates as well, which may either replace **13-X** or fall as energy minima in equilibrium **12-X** $\rightleftharpoons$ **5** $\rightleftharpoons$ **13-X**. We must, however, reject **13-X**, **5**, and **14-X** as being of appreciable concentration in the observed **12-X** system.

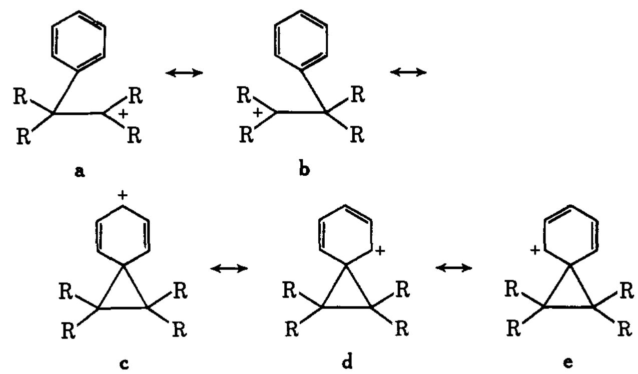
(3) The reaction scheme (Scheme III) shown for 2-arylethyl **9-X** derived ions can be used to explain the tertiary–tertiary **11-X** system as well as the secondary–secondary system **16-X**.

(a) 2,3-Dimethyl-3-aryl-2-butyl system **11-X** initially forms a **4a** (**13-X**) type ion which may then react by pathways a, b, or c. Path a reaction gives the tetramethyl analog to **26**, a $C_\beta CH_3$ σ bond interaction with the carbenium carbon. The **26** analog may form the 2-alkene which is not observed, **14-X**, or **13-X**. Ions **14-X** are benzylic and tertiary, but we know from **11-OCH$_3$** and **11-CH$_3$** systems that reversion to scrambled **14-X** occurs rapidly. This *must* occur through a **14-X** → **26** → **14-X** route. For **14-X**, **14-Br**, and **14-CF$_3$**, this pathway is favored because of the lesser aromatic substituent stabilizing ability of these para substituents. Path b results in **13-X** $\rightleftharpoons$ **13-X** or the aryl cation which is likely not a stable species. Path c results in an analog to **30** which is not observed, **13-X**, or **12-X**. We have shown **12-X** to be the most stable species in these systems, but the stability of the tertiary **13-X** ions makes the reverse pathways a and b facile, thereby explaining **14-X**-derived quenching products.

(b) 3-Aryl-2-butyl systems **16-X** follow the same scheme. Pathway a leads to olefin, open ion (secondary), arylisopropylcarbenium ion (secondary) *via* methyl shift of arylmethylethylcarbenium ion **17-X** (tertiary) *via* hydride shift. Return *via* path a of **17-X** to the open secondary ion is not favored. Path b is unproductive. Path c leads to bridged ions, which, although return to open ions *via* **28** is probably not as favorable as in the **12-X** case, apparently occurs, resulting in the eventual buildup of **17-X** ions.

C. The Tetramethylethylenebromonium Ion (a Reevaluation). The average C_1–C_2 carbon-13 chemical shift observed for the tetramethylethylenebenzenium ion **12-H** is deshielded 74 ppm from that of the ethylenebenzenium ion **8-H**. Similar cmr shifts determined for ethylene oxide **31** and tetramethylethylene oxide **32** give $\Delta\delta_{^{13}C}$(**31** − **32**) +21.2. The ethylenebromonium ion is well established from pmr and cmr studies as the symmetrically bridged ion.[17,31] In using it as a basis for predicting the expected cmr chemical shift of three-membered ring carbons in the tetramethylethylenebromonium ion, we need a better model than that of the ethylene oxides used previously.[17] The downfield cmr shift correction of 21.2 ppm is suitable for the effect of the four methyl groups in a three-membered system in the absence of positive charge. However, in the case of cyclic ions a more profound effect on charge density and hence on cmr shifts might be anticipated.

The magnitude of the difference $\Delta\delta_{^{13}C}$[(**8-H**) − (**12-H**)] will depend not only on the anisotropic effects of methyl groups relative to protons exemplified in the ethylene oxides, but also on charge densities within the ethylenarenium ions themselves. Considering the resonance structures **33a–c**, in the case where R = CH_3



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(*i.e.*, **12-H**), resonance forms **33a** and **33b** will contribute more to the overall charge density in the bridged ion than the case where R = H (**8-H**). For this reason, the magnitude $\Delta\delta_{^{13}C}$[(**8-H**) − (**12-H**)] is not surprising.

Using the model system (**8-H**) − (**12-H**) gives $\Delta\delta_{^{13}C}$ +74 which enables us to project a more accurate expected cmr chemical shift for tetramethylethylenebromonium ion. The correction of −74 ppm applied to

(43) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, 1, 35 (1963).

the cmr shift of the ethylenebromonium ion (carbon chemical shift $\delta_{^{13}C}$ +121) gives a projected cmr shift for the tetramethylethylenebromonium ion of +47 ppm. The observed cmr shift is +55 ppm, in excellent agreement with the assignment of the symmetrical bridged structure to the ion. There is thus no indication of either unsymmetrical (partial) bridging or a mixture of open-chain and bridged ions.

Conclusions

The parent 2-arylethyl systems **9-X** form, *via* aryl participation, *classical, bridged spiro*[*2.5*]*octadienyl cations* **8-X**. The cmr spectroscopic evidence indicates the aliphatic sp^3 spiro carbon atoms and the cyclopropylcarbinyl-type cyclopropane rings in all systems **8-X** and **12-X**. Although the bent σ system bears significant positive charge it is a cyclopropylcarbenium **8-X** ion, and not a σ-delocalized carbonium ion as would be implied by structure **27**.[2c] The tertiary–tertiary **12-X** ions undergo reversion through **28**-like carbonium ion intermediates which can reopen to relatively stable **13-X** ions which accounts for the realization of the entire scheme **12-X** $\rightleftharpoons$ **13-X** $\rightleftharpoons$ **14-X** of ions in these systems, although only **12-X** is of appreciable concentration at any given time. Reopening of **8-X** *via* **28** to a primary ion (analogous to **12-X** $\rightarrow$ **13-X** conversion in **11-X** systems) is unfavorable. The **8-X** and **12-X** arylethyl cations are better models than previous ones in evaluating the nature of bridged ethylenebromonium ions from 2-bromoethyl cations. The 2,3-dimethyl-3-bromo-2-butyl cation considered in previous studies either as partially bridged or equilibrating is now indicated as the symmetrically bridged tetramethylethylenebromonium ion.

Experimental Section

α-Phenylethyl alcohol, β-phenylethyl alcohol, and β-phenylethyl chloride (**9-H**) were commercially available and were used without further purification. The preparation and spectral parameters of **11-H**, **11-CF$_3$**, **15-H**, and **15-CF$_3$** are described elsewhere[5b] as are **9-OCH$_3$**[5a] and **9-Mes**.[5a] **9-CH$_3$** was prepared from β-(*p*-tolyl)-ethyl alcohol by the procedure of Drake and McVey[44] in 76% yield (bp 65–67° (0.8 mm)).

Preparation of 9-*m*-Xyl. Thionyl chloride (4.5 ml) was added to 3.8 g of β-(2,4-dimethylphenyl)ethyl alcohol and 7.5 g of *N,N*-dimethylaniline at 0°. The mixture was stirred at room temperature for 3 hr, and then heated for 3 hr on a steam bath. Ice water was added (100 ml), the aqueous solution was extracted with ether, and the ethereal layer washed first with a 5% solution of Na_2CO_3 and then with water until neutral. After drying with anhydrous $MgSO_4$, the solution was filtered and ether removed. The remaining residue (3.9 g) was used without further purification: pmr (CCl_4)[45] 2.24 (s, 6 H), 3.57 (m, 2 H), 3.00 (m, 2 H), 6.89 (s, 3 H).

β-(2,4-Dimethylphenyl)ethyl Alcohol. The Grignard reagent prepared from 18.5 g of 4-bromo-*m*-xylene and 2.5 g of Mg in Et_2O was treated at 0° with ethylene oxide and worked up to give 4.7 g of alcohol: bp 82–84° (0.56 mm); pmr (CCl_4) 2.22 (s, 6 H), 2.73 (t, J = 6.7 Hz, 2 H), 3.64 (t, 2 H), 6.87 (m, 3 H).

[α-^{13}C]β-Phenylethyl Chloride. α-^{13}C-β-Phenylethyl alcohol with 26% ^{13}C label at C$_1$ was chlorinated with thionyl chloride–dimethylaniline:[44] bp 59–63° (1.7 mm); pmr (CCl_4) 7.20 (s, 5 H), 2.93 (m, 2 H), 3.61 (m, 2 H, $J_{H_1-H_2}$ = 7.0 Hz, $J_{^{13}C-H}$ = 151.2 ± 1.0 Hz).

[α-^{13}C]β-Phenylethyl Alcohol. Reduction of 2.6 g of [1-^{13}C]-phenylacetic acid with 0.85 g of lithium aluminum hydride in 25 ml of diethyl ether gave, after work-up and separation, 1.7 g of alcohol: bp 96° (4.0 mm); pmr (CCl_4) 7.13 (s, 5 H), 2.74 (t, 2 H, $J_{H_1H_2}$ = 7.6 ± 0.2 Hz), 3.68 (dt, J_{HH} = 7.6, $J_{^{13}C-H}$ = 131 ± 1 Hz, 2 H).

[1-^{13}C]Phenylacetic Acid. Ba^{13}CO$_3$ was used (Merck Sharp and Dohme) to effect $^{13}CO_2$ carbonation of benzylmagnesium chloride. The method and apparatus used were similar to those reported by Reid, Yankwich, *et al.*,[46] although our yield was slightly lower (60%).

Preparation of 11-Br. The alcohol was prepared by the addition of α,α-dimethyl-*p*-bromophenylacetic acid ethyl ester to 2 mol of methylmagnesium bromide.

α,α-Dimethyl-*p*-bromophenylacetic Acid Ethyl Ester. Ethyl *p*-bromophenylacetate[47] (223 g, 0.92 mol) in 2000 ml of DMF was added to a suspension of 90 g (2.25 mol) of NaH in 500 ml of DMF over a period of 45 min maintainning a temperature of 30–40°. A solution of 355 g (2.5 mol) of methyl iodide in 500 ml of DMF was then added over 45 min, maintaining the temperature at 30–35°. The reaction mixture was stirred for 15 min; then water was added dropwise to quench. After work-up, a 175-g (73%) yield of desired ester, bp 113° (1.5 mm), was obtained.

2-(*p*-Bromophenyl)-2-propyl Alcohol. *p*-Bromoacetophenone was treated with methylmagnesium bromide at 0° to give the alcohol: bp 114° (4 mm); pmr (CCl_4) 1.50 (s, 6 H), 7.57 (s. 4 H); pmr of ion (**23-Br**) in SbF_5–SO_2 at −60°, 3.25 (s, 6 H), aromatic (4 H), AB pattern, meta 7.88, ortho 8.44 ($J_{H_o-H_m}$ = 10.0 Hz).

Quenching of 8-H. The ion mixture formed from **9-H** in SbF_5–SO_2ClF (showed by pmr peak area integration to contain **8-H** and **10-H** in a 2:3 ratio) was added dropwise to a rapidly stirred slurry of K_2CO_3–ice–Dry Ice in SO_2ClF at −78°. The resultant mixture was extracted with ether and neutralized by water washing and the dried ethereal solution was subsequently concentrated. Glpc analysis showed a 3:1 ratio of α- to β-phenylethyl alcohols. Separation was accomplished with a Carbowax K-20M on Anakrom ABS 12 ft × $^1/_8$ in. column at 140°.

Preparation of Ions. Ions **8-X**, where X = H, CH_3, and *m*-Xyl, were prepared from the β-chloride precursors in the same way as described for the styryl ions in ref 20. For **8-Mes** and **8-OCH$_3$**, as well as the **12-X** ions, the method of ref 14b was employed, using SbF_5–SO_2.

Nmr Measurements. All spectra were obtained on a Varian Associates Model HA-100 nmr spectrometer, except for some of the precursors, which were examined with a Varian A56/60. The method of obtaining indor spectra has been detailed partially in the text. The experimental arrangement is described in ref 20 and 22c. Indor time averaging was used in this work in all cases, with the exception of **12-H** and **12-CF$_3$**. Fourier transform spectra were obtained on a Bruker HFX-90 spectrometer with a variable-temperature probe and subsequently on our Varian HA-100 FFT adapted spectrometer. Carbon–proton coupling was eliminated with a broad-band decoupler. Spectra were observed at −60° in 15-mm tubes with internal lock standard contained in a 5-mm nmr tube coaxially centered. Lock was to the fluorine singlet (due to the decoupling) in 1,1-difluoroethylene. The spectra therefore contained two triplets due to the 1,1-difluoroethylene. A Digital PDP-8 computer was used to perform the Fourier transformations.

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(44) N. L. Drake and W. C. McVey, *J. Org. Chem.*, 4, 464 (1939).

(45) s = singlet, m = multiplet, t = triplet, dt = doublet of triplets.

(46) M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert, and P. F. Yankwich, "Isotopic Carbon," Wiley, New York, N. Y., 1949, p 180.

(47) H. Gilman, Ed., "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1932, p 265.