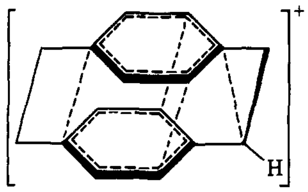

A

should provide little or no delocalization of charge because of its unfavorable geometry. The inductive and steric inhibition of solvation effects of the two phenyl groups should decrease the solvolysis rate in the absence of anchimeric assistance by the β-phenyl group. The fact that the acetolysis rate of III is about 10^2 times faster than that of aliphatic secondary tosylates[10] is not incompatible with a blend of deeclipsing and β-aryl participation in ionization effects which enhance the rate, and steric inhibition of delocalization and solvation and of inductive effects which decelerate the rate.

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[10] S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1120 (1952).

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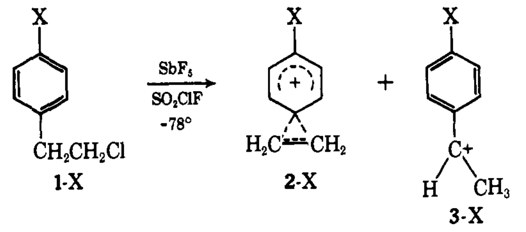
Stable Carbonium Ions. CXV.[1a] The Ethylenephenonium and Ethylene-*p*-toluonium Ions[1b]

Sir:

There has been considerable interest in recent years in β-phenylethyl systems especially as related to the fundamental studies of Cram[2] with regard to the suggested phenonium ion intermediates in their solvolysis reactions. Stable, long-lived phenonium ions have been particularly elusive in strong acid media with the exception of those strongly stabilized by ring substituents (methoxy, trimethyl, and pentamethyl).[3] We report now our success in preparing the parent ethylenephenonium ion **2**-H and the ethylene-*p*-toluonium ion **2**-CH_3. These ions were prepared from their chloride precursors **1**-H and **1**-CH_3, respectively, in SbF_5–SO_2ClF solution at −78°. In all cases they are accompanied by the formation of the substituted styryl cations **3**-X.[4] The ratio of **2**-X to **3**-X once observed, does not change over a period of 40 hr at −60°. Quenching solutions of the ions with a slurry of a buffered solution of water in SO_2ClF at −78° gave α- and β-phenylethyl alcohols in a 1:3 ratio[5] as the only identifiable products. Overall yield in the quenching experiments, however, was low due to obvious polymerization under the reaction conditions.



X = H, CH_3

Pmr spectra of **2**-H and **2**-CH_3 consist of a sharp singlet for the methylene protons at δ 4.80 and 4.42, respectively, at considerably higher field than found in previously studied substituted ethylenearylonium ions.[6] This indicates the expected larger amount of charge delocalization into the cyclopropyl ring because of the lesser charge delocalizing ability of the aryl system. Figure 1 shows the pmr spectrum of **2**-H with absorptions due to **3**-H deleted. The downfield "aromatic" region contains overlapping absorptions for both **2**-H

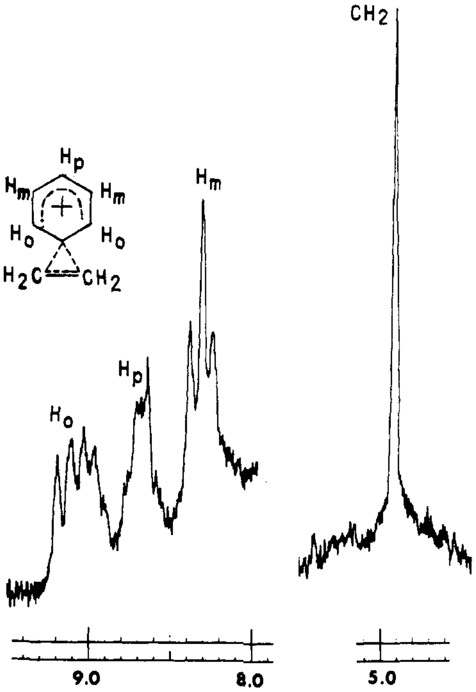


Figure 1. Pmr spectrum (100 MHz) of ethylenephenonium ion **2**-H in SbF_5–SO_2ClF solution at −78°.

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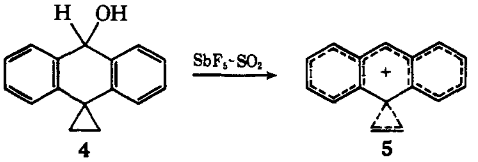
[1] (a) Part CXIV: G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *J. Amer. Chem. Soc.*, in press. (b) Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

[2] (a) D. J. Cram, *J. Amer. Chem. Soc.*, **71**, 3683 (1949); (b) D. J. Cram, *ibid.*, **74**, 2129 (1952); (c) for a summary, see D. J. Cram, *ibid.*, **86**, 3767 (1964).

[3] G. A. Olah, M. B. Comisarow, E. Namanworth, and B. Ramsey, *ibid.*, **89**, 5259 (1967). The first observation of a stable phenonium ion (reported by L. Eberson and S. Winstein, *J. Amer. Chem. Soc.*, **87**, 3506 (1965)) was the case of the ethylene-9-anthracenonium ion **5** obtained from the alcohol **4**, but the ion was not obtained *via* aryl participation.



[4] (a) G. A. Olah, R. D. Porter, and D. P. Kelly, *J. Amer. Chem. Soc.*, in press. (b) The pmr spectrum of 3-H is given in ref 4a. No detailed analysis was possible and assignment of protons in the aromatic region was precluded by low ion concentration and polymeric impurities.

[5] Based on the nmr spectrum of the ion quenched, the anticipated ratio of α- to β-phenylethyl alcohol would have been about 1:2 The higher proportion of β-phenylethyl alcohol is probably due to competition from reaction of 3-H to form polystyrenes during the quenching process. Analysis by glpc was accomplished with a Carbowax K 20-M on Anakron ABS 12 ft × 1/8 in. column at 140°.

[6] For comparison, methylene proton chemical shifts for other ethylenarylonium systems are: aryl = 2,4-dimethylphenyl, δ 4.16; mesityl, δ 3.77; pentamethylphenyl, δ 3.61; *p*-anisyl, δ 3.45.

Table I. Carbon-13 Chemical Shifts[a] of Ethylenarylonium Ions **2-X** and Arenonium Ions **6-X**

		Ring carbons					Ring carbons			
Ion	Methylene	α	Ortho	Meta	Para	Ion	α	Ortho	Meta	Para
2-H	+134	+123	+23	+56	+34					
2-CH$_3$	+140	+130	+20	+56	+9	**6**-CH$_3$	+145	+13	+55	−7
2-Mes	+143	+133	+9	+58	+19	**6**-Mes	+140	−2	+59	−2
2-OCH$_3$	+153[b]	+145	+20	+71	+24	**6**-OCH$_3$	+152	+25 +18	+71 +65	+1

[a] Parts per million relative to $^{13}CS_2$. [b] See ref 8.

and **3**-H; consequently only estimates can be made for assignment of the chemical shifts for **2**-H: ortho, δ 8.8–9.2; para, δ 8.5–8.65; meta, δ 8.20.[4b] Only dilute solutions could be obtained which also showed some broadened absorptions underlying the aromatic as well as the methylene region, probably due to formation of polystyrenes.

The aryl ring protons of ion **2**-CH$_3$ show an AA′BB′ quartet (ortho, δ 8.36; meta, δ 8.05). The pmr data of **3**-CH$_3$ have been reported previously[4a] (ortho, δ 8.91; meta, δ 8.25). It is interesting to note that **2**-CH$_3$ is shielded relative to **3**-CH$_3$. Although **2**-CH$_3$ undoubtedly has more positive charge delocalized into the aryl ring than **3**-CH$_3$, anisotropic effects are different in the two cases[7] and therefore can effect chemical shifts which cannot be directly related to charge distributions. The *p*-CH$_3$ group in **2**-CH$_3$ shows a singlet absorption at δ 3.05.

Carbon-13 magnetic resonance (cmr) is known to be a more sensitive probe for characterization of carbonium ions than is pmr.[4,8] We felt it therefore of importance to obtain cmr spectra of ions **2**-H and **2**-CH$_3$ in spite of the difficulties encountered by being able to obtain only relatively dilute solutions (2%) of these species. Indor spectra were initially obtained by observing mainline (^{12}C–H) peak enhancement[4a] of the methylene protons at low ^{13}C decoupling power. The time-averaged indor spectra[4] of both **2**-H and **2**-CH$_3$ showed a singlet ($\delta_{^{13}CS_2}$ +123 and δ +130) and doublets centered at δ 23 and 20, respectively. These absorptions are assigned to the spiro and ortho carbon atoms, respectively. That the assignment of the ortho carbon atoms is correct is substantiated by similar observation of the enhancement of the methylene protons of the ethylenemesitylenonium ion (**2**-Mes) in which case, at low field, a singlet is observed (δ 9) as would be expected to result from ortho substitution. Because of the broadness of the methylene absorption as well as the increased width of the spiro carbon absorption at the high power levels necessary to observe the short range decoupling,[9] it was felt necessary to observe the methylene carbon absorption also from ^{13}C–H satellites. To accomplish this, 25% enriched α-^{13}*C*-β-phenylethyl chloride was used.[10] Analysis of the labeled ion showed $J_{^{13}C-H}$ to be 156 Hz and methylene $\delta_{^{13}CS_2}$ +134. Comparison of the magnitudes of the ^{13}C satellites in **2**-H with those found in the accompanying **3**-H indicates that in **3**-H all the ^{13}C label is in the methyl and none in the carbenium ion carbon.[11] This indicates that formation of **3**-H must occur through direct intramolecular hydrogen shift upon ionization of **1**-H and not through bridged ion **2**-H. This observation, along with our chemical-shift data, rules out any appreciable open chain classical carbenium ion equilibration in this system.

In Table I are summarized the cmr data for **2**-H and **2**-CH$_3$, as well as those obtained for **2**-OCH$_3$ and the ethylenemesitylenonium ion (**2**-Mes).[12] For comparison, Table I also shows the relevant data of the corresponding substituted benzenonium ions (**6**-CH$_3$, *p*-toluonium; **6**-Mes, mesitylenonium; **6**-OCH$_3$, *p*-anisonium).[13] The following conclusions can be reached concerning ions **2**-X. (1) The ^{13}C chemical shifts of the aryl ring systems resemble closely those of the analogous arylonium ions. This indicates at least in a first approximation that the charge residing in the aryl ring is distributed in much the same fashion in both cases. (2) The "spiro" carbon atoms in **2**-X are much the same type as the methylene carbons (denoted α in Table I for easier comparison) observed in arylonium ions **6**-X. This observation by itself means there must be σ bridging to the α carbon atom in **2**-X and that general delocalization through space of the π cloud to a separate carbenium carbon atom (as suggested by Brown)[14] is not characteristic of ions **2**-X. (3) The methylene carbons of phenonium ions **2**-X are of cyclopropyl nature, as indicated by similarity with carbon nmr shifts of cyclopropylcarbinyl cations.[15] Although the

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[7] An interesting comparison may also be made of 2-CH$_3$ with the *p*-methylbenzenonium ion (ortho, δ 9.17; meta, δ 8.26). Clearly, less positive charge is delocalized into the aromatic ring in the fashion of a toluonium ion in 2-CH$_3$ as would be expected. This is obviously the best basis model for the system where there is full delocalization into the ring.

[8] See G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969), and references contained therein. Also see more recent papers in this series.

[9] One characteristic of indor mainline enhancement (complete ^{13}C–H decoupling) is that short-range coupling requires significantly more power than does long-range coupling. By employing low irradiating power levels, one may observe only ^{13}C–C–H, ^{13}C–C–C–H, and frequently (though not in these cases) longer range indor enhancements, while not supplying sufficient power for ^{13}C–H. As power levels are increased, the ^{13}C–H is observed, but meanwhile, the longer range observed ^{13}C absorptions are broadened, because of the greater width of this more powerful irradiating band.

[10] α-^{13}*C*-β-Phenylethyl chloride was synthesized by $^{13}CO_2$ carbonation of benzylmagnesium chloride in a fashion described by Dauben, Reid, and Yankwich; M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert, and P. F. Yankwich, "Isotopic Carbon," Wiley, New York, N. Y., 1949, p 180. The phenylacetic acid was reduced with lithium aluminum hydride, and the resulting β-phenylethyl alcohol chlorinated with thionyl chloride-*N*,*N*-dimethylaniline.

[11] There are two distinct categories of carbocations, trivalent and pentacoordinated, which are best denoted carbenium and carbonium ions, respectively. See G. A. Olah, *J. Amer. Chem. Soc.*, in press.

[12] Methylene carbon chemical shifts were obtained by mainline enhancement for all but (see text) 2-H, and 2-OCH$_3$ (see ref 8).

[13] Full details of these 6-X arenonium ions will be reported separately. It should also be pointed out that the ^{13}C spectra of protonated mesitylene in AlCl$_3$ and AlBr$_3$ systems have 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 shifts and we felt it therefore necessary to redetermine 6-Mes in our superacid solvent system. The differences are small (2 ppm).

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

[15] See G. A. Olah, D. P. Kelly, C. L. Jevell, and R. D. Porter, *ibid.*, **92**, 2544 (1970). The methylene chemical shifts are: for dimethylcyclopropylcarbinyl cation, δ +140; for the monomethyl analog, δ +136.

type of delocalization in the two systems is quite different, the cyclopropylcarbinyl cations are the best model and cmr shifts would be expected in the same region of the carbon-13 scale. The chemical shift of the methylene carbons is not consistent with open chain equilibrating primary carbenium ions or with a system of high degree of ethylenic character.[8] (4) Charge distribution and chemical shifts have the expected relationship with regard to substituent effects. The methylene carbon shifts are quite consistent with substituent effects based on what has been observed for other arylonium ion systems studied. The most deshielded cyclopropyl carbon absorption is that of **2**-H; the most shielded is that of **2**-OCH_3, as would be expected from the ability of the aryl ring to bear positive charge. Interestingly, at the temperature studied (−78°), there is no observed rotational barrier to the C_{arom}–O bond of the *p*-methoxy substituent. This is also the case in the *p*-methoxycumyl cation,[16] and in the *p*-methoxystyryl cation.[3] However, nonequivalence of the ortho protons and carbons, indicating a sizable rotational barrier, is observed for the *p*-methoxybenzyl[17] cation as well as for C-protonated anisole (*p*-methoxybenzenonium ion).

In summary, the direct observation of the ethylene-phenonium and ethylene-*p*-toluonium ions and their ^1H and ^{13}C nmr spectroscopic study fully substantiate their bridged spirocyclopropylbenzenonium ion type structure and eliminate the possibility of open chain rapidly equilibrating β-phenylethyl cations. We feel that the data obtained give direct structural evidence for these long controversial ions, and also indicate the charge distribution into the aryl ring and spirocyclopropyl system.

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

(16) G. A. Olah, M. B. Comisarow, and C. J. Kim, *J. Amer. Chem. Soc.*, **91**, 1458 (1969).

(17) G. A. Olah, R. D. Porter, and C. L. Jevell, to be published.

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A New Pathway to Unsymmetrical Disulfides. The Thiol-Induced Fragmentation of Sulfenyl Thiocarbonates[1]

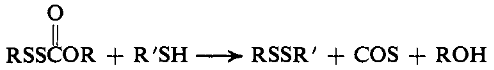
Sir:

The literature abounds with reports on synthetic options to unsymmetrical disulfides. Prominent among the more attractive routes to *homogeneous* unsymmetrical disulfides are the nucleophilic displacement reactions of sulfenyl[2] derivatives with thiols as depicted in eq 1.

$$RS^{\delta+}\text{—}X^{\delta-} + R'S^- \longrightarrow RSSR' + X^- \qquad (1)$$

The most notable sulfenyl reagents presently available for constructing mixed disulfides according to eq 1 are the sulfenyl halides,[4] sulfenyl thiocyanates,[5] sulfenyl hydrazides,[6] thiosulfates,[7] sulfenyl thioureas,[8] thiolsulfonates,[9] and sulfenimides.[10] Unfortunately, the synthetic entanglements created by the instability and unreactivity of the sulfenyl reagents and functional group interactions in the sulfenyl moiety have substantially reduced the scope and utility of the known procedures. More seriously, disulfide interchange (disproportionation) engendered by reaction conditions and side products, among other causative factors, constitutes a major obstacle to the design of homogeneous unsymmetrical disulfides *via* these electrophilic substrates.

In the present communication, we wish to report a unique and extremely facile heterolytic fragmentation route to unsymmetrical disulfides. We have discovered that the thiol-mediated fragmentation of sulfenyl thiocarbonates (I) at room temperature gives unsymmetrical disulfides cleanly and quantitatively in accord with eq 2.



$$\underset{\text{I}}{RSS\overset{O}{\overset{\|}{C}}OR} + R'SH \longrightarrow RSSR' + COS + ROH \qquad (2)$$

We believe that the heterolytic fragmentation route offers decided advantages over the presently known SN2 pathways to mixed disulfides. The key synthetic merits, which will be touched upon briefly here, comprise the facile preparation of the sulfenyl reagents, the lack of functional group interactions, the remarkable stability and high reactivity of the sulfenyl electrophiles, and the absence of side products in the mixed disulfide.

The sulfenyl thiocarbonate reactants (Table I) are easily prepared in excellent yields *via* the reaction of

Table I. Sulfenyl Thiocarbonates[a]

Entry	Structure	Bp [mp], °C (*P*, mm)	% yield
Ia	EtSSC(=O)OMe	53–54 (1)	95
Ib	EtSSC(=O)OEt[b]	74–75 (0.5)	94
Ic	$HOCH_2CH_2SSC(=O)OMe$	112 (0.35)	98
Id	$HCl\text{-}NH_2CH_2CH_2SSC(=O)OMe$	[107–108]	99
Ie	$HCl\text{-}NH_2CH_2CH_2SSCO(CH_2)_{11}CH_3$	[92–93]	92

[a] The analytical and spectral data for all compounds were fully consonant with the structures shown. [b] Reference 11 reports bp 69° (0.12 mm).

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(1) Part I in the series: New Synthetic Concepts in Organosulfur Chemistry.

(2) From a mechanistic standpoint, Foss[3] proposed that a wide spectrum of sulfur analogs could be fitted into the family of compounds which exhibited "sulfenyl behavior" in the sense of eq 1. The classification suggested by Foss has proved valuable since it accommodates new examples as they are encountered, and emphasizes the broad scope of this area of study.

(3) (a) O. Foss, *Acta Chem. Scand.*, **1**, 307 (1947); (b) M. Kharasch, Z. S. Ariyan, and A. J. Havlik, *Quart. Rep. Sulfur Chem.*, **1**, 97 (1966).

(4) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 3, Chemical Publishing Co., New York, N. Y., 1960, p 368.

(5) R. G. Hiskey and B. F. Ward, Jr., *J. Org. Chem.*, **35**, 1118 (1970), and earlier references.

(6) T. Mukaiyama and K. Takahashi, *Tetrahedron Lett.*, 5907 (1968); V. Bockelheide and J. L. Mondt, *ibid.*, 1203 (1970); S. J. Brois, unpublished results.

(7) D. L. Klayman and R. J. Shine, *Quart. Rep. Sulfur Chem.*, **3**, 231 (1968).

(8) K. Sirakawa, O. Aki, T. Tsujikawa, and T. Tsuda, *Chem. Pharm. Bull. (Tokyo)*, **18**, 235 (1970); S. J. Brois and H. W. Barnum, unpublished results.

(9) L. Field and J. D. Buckman, *J. Org. Chem.*, **33**, 3865 (1968), and earlier references.

(10) K. S. Boustany and A. B. Sullivan, *Tetrahedron Lett.*, 3547 (1970); D. N. Harpp, D. K. Ash, T. G. Back, J. G. Gleason, B. A. Orwig, W. F. Van Horn, and J. P. Snyder, *ibid.*, 3551 (1970).