

placed upon any set which happens to fit the limited data available; we present two sets, for $h_0 = 1.3$ and $h_0 = 1.6$, which fit reasonably well; other combinations fit as well. Use of aip's $h_{C'}$ or h_{C^*} would change the other parameters necessary for fit; even higher k_{C^*O} values would be necessary. We do not feel our data justify introducing more parameters.

Clearly, a negative h_X is required to raise $|\rho_X|$ to the over 0.06 observed for Ie. The upward shift in $|\rho_X|$ seen upon methylation at X could be accounted for by using a lower h_X value to adjust for the C-H and C-alkyl electronegativity difference, but a hyperconjugation calculation might be more reasonable (and introduce two more "adjustable" parameters). The decrease of $|\rho_X|$ as the electronegativity of X is raised is expected; use of Streitwieser's suggested h_N value¹⁹ of 1.5 gives a calculated ρ_N for phthalimide anion not far from that arrived at by arguing from Q values (compare Tables II and III). We are surprised at the near constancy in ρ_a and ρ_b values in this group of compounds; certainly the chemistry of enolate and amide carbonyls is so different that we had expected different h and k values to be necessary. Perhaps there are compensating changes in the many parameters necessary to describe the spin density, and the result is an artifact of this system.

To fit the two experimental splittings of the phthalic anhydride spectrum (Ia, X = O), using $Q = 24$ again,

(19) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 135.

$h_0 = 1.49$, $k_{C^*O} = 1.49$, $k_{C'C^*} = 1.20$ gives a reasonable fit. It may be simply accidental that the three spectra which deviate the most are those which formally have two unshared pairs of electrons at X. There is a significant shift of spin density into the benzene ring with X = S (Ib) in comparison with all the other spectra, however. Sulfur was the only third-row element studied, and some special bonding effect of the sulfur may well be involved. Lücken²⁰ has suggested that 3d orbital interactions of the sulfur atoms of dithiins fit the esr spectra better than just 2p interactions. The effect here is not large, and we cannot assign a mechanism for the effect of the sulfur.

McLachlan theory does not seem adequate to explain the differences observed in the I spectra in detail, but in general gives reasonable spin densities.²¹

Acknowledgment. We wish to thank the Wisconsin Alumni Research Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(20) E. A. Lücken, *Theoret. Chim. Acta* (Berlin), 1, 397 (1963).

(21) Since submission of this paper, R. E. Sioda and W. S. Koski, *J. Am. Chem. Soc.*, **89**, 475 (1967), have published esr spectra of phthalimide and phthalic anhydride anions in DMF, reporting splittings similar to although not identical with ours in DMSO. Our work indicates the spectrum they report for 2-phenyl indandione must be for the deprotonated species. G. A. Russell, E. R. Talaty, and R. H. Horrocks, *J. Org. Chem.*, **32**, 333 (1967), report spectra for the semidiones of diacylenes in five- and six-membered rings.

Stable Carbonium Ions. XXXI.¹ *p*-Anisonium and Methylphenonium Ion Formation via Aryl Participation in Strong Acid Solution

George A. Olah, Melvin B. Comisarow, Eli Namanworth, and Brian Ramsey

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received January 21, 1967

Abstract: The first observation (nmr) of arylium ion formation via aryl participation in strong acid solution was achieved. The *p*-anisonium, 2,4,6-trimethylphenonium, and pentamethylphenonium ions were obtained in SbF_5-SO_2 solution at low temperature upon ionization of the corresponding β -phenylethyl chlorides. Conditions permitting bridged phenonium (arylium) ion formation over competing classical benzylic ion (styryl cation) formation were established. The spirocyclopropylbenzenonium ion structure of phenonium ions is discussed.

Considerable interest has been focused on phenonium (arylium) ions. In recent years it was spearheaded by Cram's^{2,3} studies of phenonium ion systems and Brown's⁴ suggested reexamination of this concept.

These arguments have centered largely around the nature of the cationic transition states in the rate studies of solvolysis systems and the stereochemistry of the resulting products.⁵ Extensive radiolabeling studies of

phenylethyl solvolysis reactions have been carried out by Collins and these have been recently reviewed.⁶

Results and Discussion

No direct observation of phenonium ion formation via phenyl participation from phenylethyl⁷⁻⁹ or related

(5) A. Streitwieser, "Solvolytic Displacement Reactions" McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(6) C. J. Collins, *Advan. Org. Chem.*, **2**, 1 (1964).

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

(8) M. Brookhart, F. A. L. Anet, and S. Winstein, *ibid.*, **88**, 5657 (1966).

(9) M. Brookhart, F. A. L. Anet, D. J. Cram, and S. Winstein, *ibid.*, **88**, 5659 (1966).

(1) For a preliminary report see part XXX, G. A. Olah, E. Namanworth, M. B. Comisarow, and B. Ramsey, *J. Am. Chem. Soc.*, **89**, 711 (1967).

(2) D. J. Cram, *ibid.*, **71**, 3863 (1949); **74**, 2129 (1952).

(3) For a critical summary see D. J. Cram, *ibid.*, **86**, 3767 (1964).

(4) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *ibid.*, **87**, 2137 (1965).

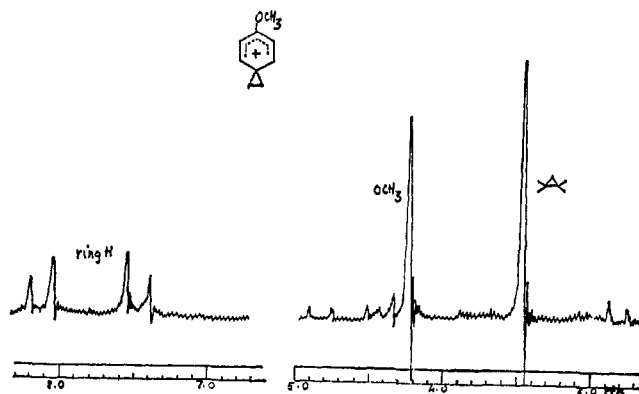


Figure 1.

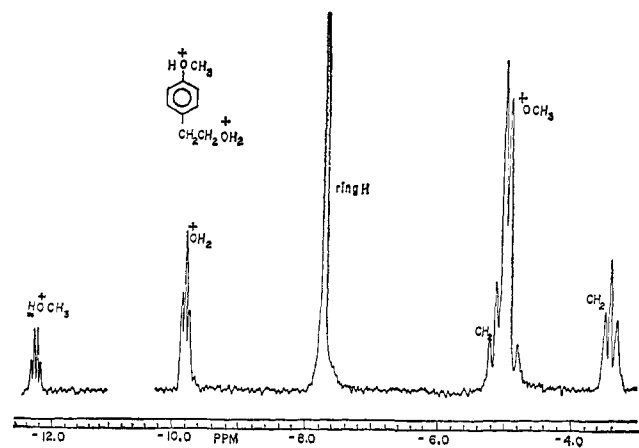
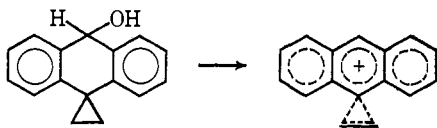


Figure 2.

systems (anthrylethyl¹⁰) in strong acid solutions has been achieved so far.

Phenylethyl cations, like the 3-phenyl-2-butyl cation, rearrange in strong acid systems ($\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$) to the more stable benzylic cations.^{7,9}

The observation of Ebersson and Winstein¹¹ of the bridged anthrylethyl cation was achieved not by the aryl participation route but indirectly, by ionization of the spirocyclopropyl alcohol.



We wish now to report the first direct (nmr spectroscopy) observation of arylonium ion formation *via* aryl participation.

Whereas our previous attempts to this effect¹² proved to be unsuccessful on closer reinvestigation,^{7,8} we feel that evidence presented in this paper will stand up to any scrutiny and will provide conclusive evidence for arylonium ion formation *via* aryl participation in strong acid solution.

Taking advantage of the known powerful participating effect of the *p*-anisyl group¹³ we were able to observe

(10) L. Ebersson and S. Winstein, *J. Am. Chem. Soc.*, **87**, 3506 (1965).

(11) L. Ebersson and S. Winstein, *ibid.*, **87**, 2506 (1965).

(12) G. A. Olah and C. U. Pittman, Jr., *ibid.*, **87**, 3509 (1965).

(13) (a) S. Winstein, *et al.*, *ibid.*, **74**, 1140 (1952); **75**, 147 (1953); **78**, 328, 2763 (1956); also (b) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppelle, *ibid.*, **89**, 370 (1967).

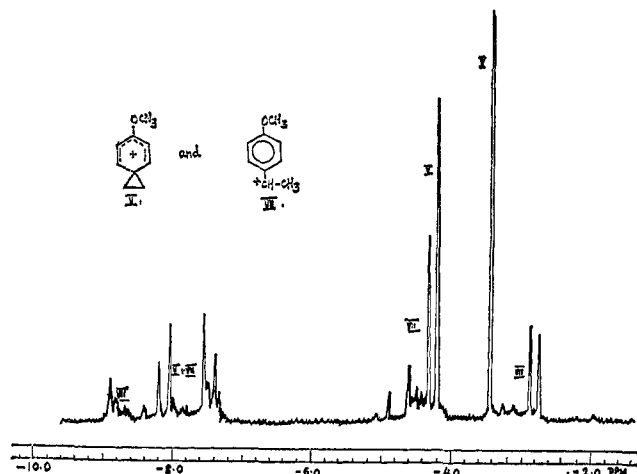
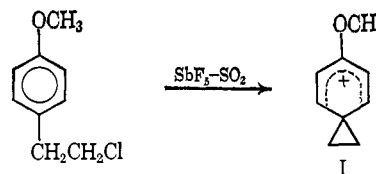


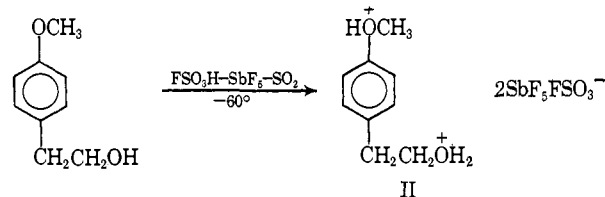
Figure 3.

the *p*-anisyl cation I upon ionizing 1-*p*-anisyl-2-chloroethane in SbF_5-SO_2 at -70° .



The nmr spectrum of I (Figure 1) is very simple. It contains only three types of protons. The cyclopropane protons are at -3.47 ppm (relative area 4), the methoxy protons at -4.25 ppm (relative area 3), and the AB-ring quartet (relative area 4) at -8.12 and -7.47 ppm.

Attempts to generate the *p*-anisyl cation from β -*p*-anisylethanol in $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$ were unsuccessful, because a stable diprotonated dication II is formed (Figure 2).



In some preparations of the *p*-anisyl cation from β -*p*-anisylethyl chloride and SbF_5-SO_2 at higher temperatures, besides the anisyl cation (I) there was present also smaller amounts of the benzylic *p*-anisylmethylcarbonium ion (III), formed *via* hydride shift from the open chain primary carbonium ion in competition with bridging (Figure 3). The *p*-anisylmethylcarbonium ion (*p*-methoxystyryl cation) (III) was observed in pure form from α -*p*-anisylethanol in $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$ or through its chlorosulfite in $\text{SOCl}_2-\text{SbF}_5-\text{SO}_2$ (Figure 4).

To our knowledge, ion III is the first styryl cation observed directly in strong acid solution. The relative complexity of the nmr spectrum of III in the ring proton region and that of the methine absorption is due to the relatively high barrier of rotation in benzyl cations.¹⁴

Quenching of solutions of I with methanol at -80° gives in better than 80% yield the β -methyl ether

(14) C. A. Cupas, J. M. Bollinger, and G. A. Olah, Abstracts, 152nd National Meeting of the American Chemical Society, Sept New York, N. Y., 1966, p S22.

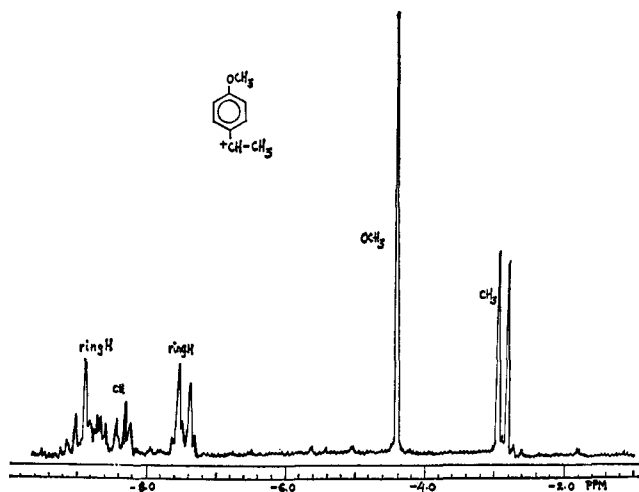
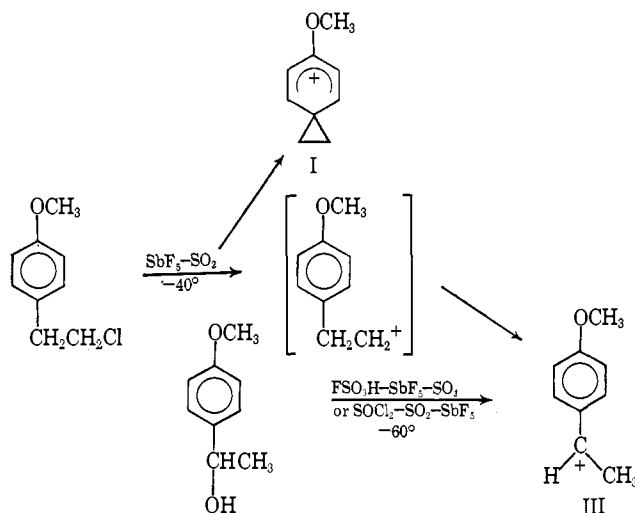


Figure 4.

(*p*-CH₃OC₆H₄CH₂CH₂OCH₃) with some α -methyl ether and *p*-methoxystyrene also formed. Methanolysis of ion III gave the α -methyl ether (with some *p*-methoxystyrene and its polymer) as the products.



C- and O-protonation of anisole with strong acids is well known.^{15,16} The *p*-methoxybenzenonium ion (IV) provides a good model for the *p*-anisyl cation. Figure 5 shows the pmr spectrum of C-protonated anisole in FSO₃H-SbF₅-SO₂ solution at -30°.

The close correlation of spectra of I and IV further substantiates the assignment of I as the *p*-anisyl cation. The methoxy group is more deshielded in ion IV than in ion I, because in the latter charge is delocalized also into the cyclopropane ring. This may also explain that even at -60° in I rotation of the methoxy group is relatively free (less C-O double bond character than in ion IV) and the *ortho* ring protons are equivalent. The AB quartets are well separated in both I and IV, indicating the benzenonium ion character of the ions and substantial differences in the shieldings of A and B. Further, the cyclopropyl protons in spiro[2.5]octa-1,3-dien-2-one were found by Baird and Winstein¹⁷ as a sharp singlet. Ebersson and Winstein observed the

(15) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **42**, 502 (1964); T. Birchall, R. J. Gillespie, and P. J. Smith, *ibid.*, **42**, 1433 (1964).

(16) D. M. Brouwer, E. L. Mackor, and C. MacLean, *Rec. Trav. Chim.*, **85**, 114 (1966).

(17) R. Baird and S. Winstein, *J. Am. Chem. Soc.*, **85**, 567 (1963).

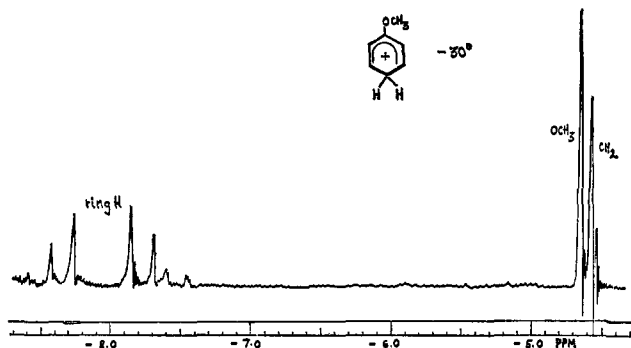
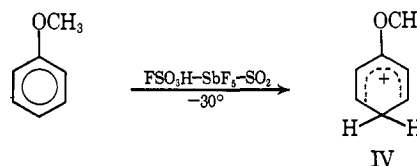


Figure 5.

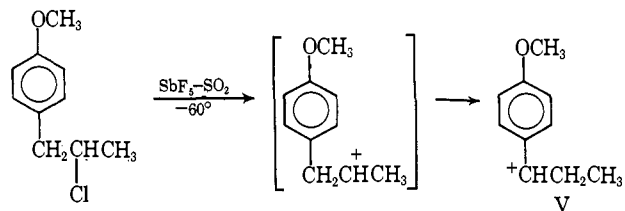
cyclopropyl protons in the bridged anisyl cation at -3.44 ppm. Comparing these data with those of the



p-anisyl cation I provides a strong case of direct analogy and further strengthens the assignment of I as a bridged phenonium ion.

The formation of the bridged *p*-anisyl cation I via phenyl participation in strong acid solution from the ionization of β -anisylethyl chloride in SbF₅-SO₂ solution at low temperature in our view is connected with two main factors: (a) the methoxy substituent substantially enhances the participating power of the phenyl ring; and (b) a relatively inactive primary halide precursor is used, the ionization of which at low temperature does not take place without the full participating effect of the phenyl ring. This, of course, means that the open-chain primary carbonium ion *per se* is not involved in the process and therefore 1,2-hydride shift (giving the benzylic classical ion) does not compete in a significant way with bridging. If the temperature is raised, aryl participation becomes less important and subsequently benzylic ion formation can become a competing process.

The use of secondary precursor halides (as shown in the 3-phenyl-2-butyl system⁷) is expected to favor benzylic classical ion formation as the final product. Ionization of the secondary halide is facilitated with less necessity of strong phenyl participation. The formed open-chain secondary ion itself should have much higher stability and subsequent 1,2-hydride shift should lead to the more stable benzylic ion. These suggestions were indeed experimentally verified. When 1-*p*-anisyl-2-chloropropane was ionized in SbF₅-SO₂ solution at -60°, no bridged ion formation was observed. Instead the secondary benzylic ion V was formed.



The spectrum of ion V (Figure 6) is that of a benzylic phenylethyl carbonium ion. It also shows a small ab-

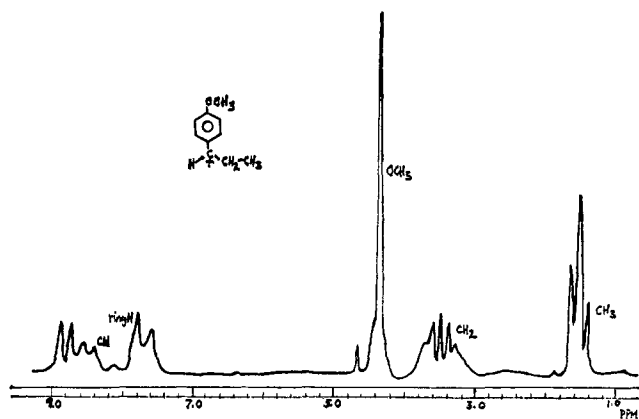


Figure 6.

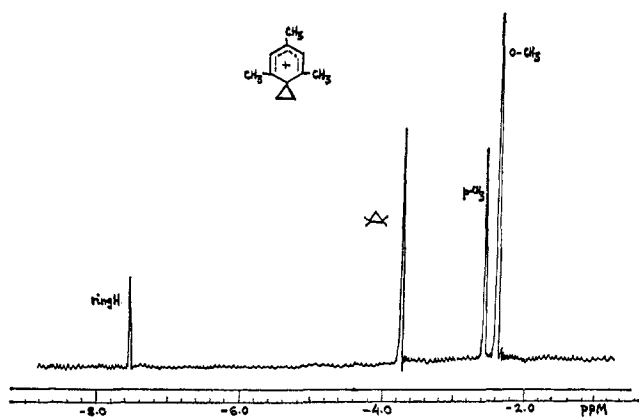
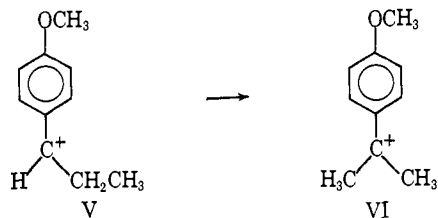


Figure 7.

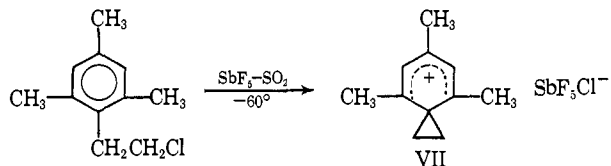
sorption peak at -4.82 ppm indicative of the formation of the tertiary *p*-anisylidimethylcarbonium ion (VI) formed by rearrangement of the secondary ion V. At



low temperature ion VI is present only in minor quantity. But if the temperature is raised, its amount increases.

Once the factors determining phenonium ion formation *via* phenyl participation in strong acid systems were clarified, it became quite easy to obtain further examples of stable phenonium ions.

The 2,4,6-trimethylphenonium ion VII was obtained from β -mesitylethyl chloride in $\text{SbF}_5\text{-SO}_2$ solution at



-60° . The pmr spectrum of ion VII (Figure 7) shows the 2- and 6-methyl protons at -2.39 ppm and the 4-methyl protons at -2.60 ppm. The cyclopropyl protons show a sharp singlet at -3.77 ppm, as do the 3 and

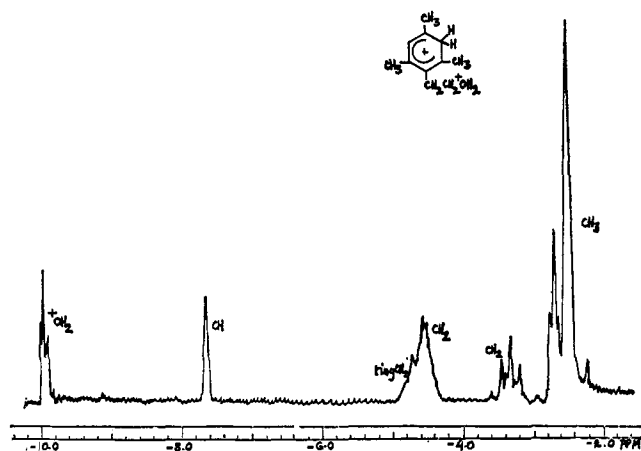


Figure 8.

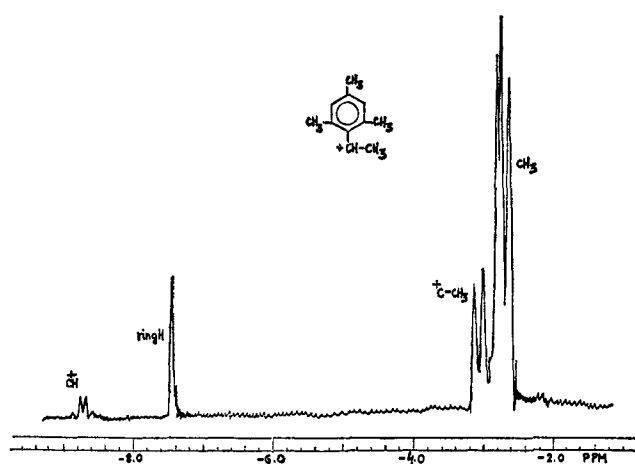
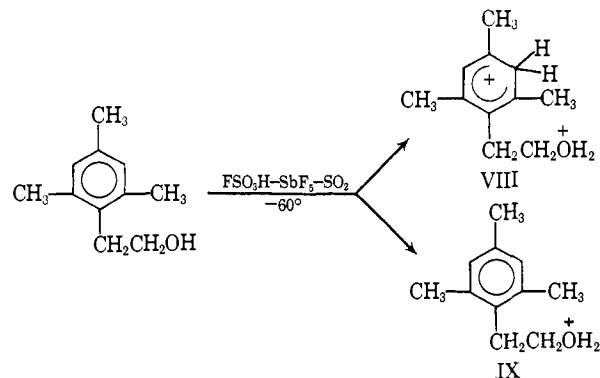


Figure 9.

5 ring protons at -7.66 ppm. Attempts to generate ion VII from β -2,4,6-trimethylphenylethyl alcohol in excess $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2$ resulted only in the diprotonated ion VIII (Figure 8)¹⁸ or with 1 equiv of acid only the monoprotated alcohol IX is formed.



In preparations of ion VII at higher temperatures there was formed besides the bridged 2,4,6-trimethylphenonium ion VII also smaller amounts of the benzylic 2,4,6-trimethylphenylmethylcarbonium ion (X). Ion X was obtained in pure form (Figure 9) from α -2,4,6-trimethylphenylethyl alcohol in $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2$ or

(18) We have not observed ring sulfonation, although according to recent observations of Winstein⁹ this is a possible reaction of $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2$ solutions of benzenonium ions.

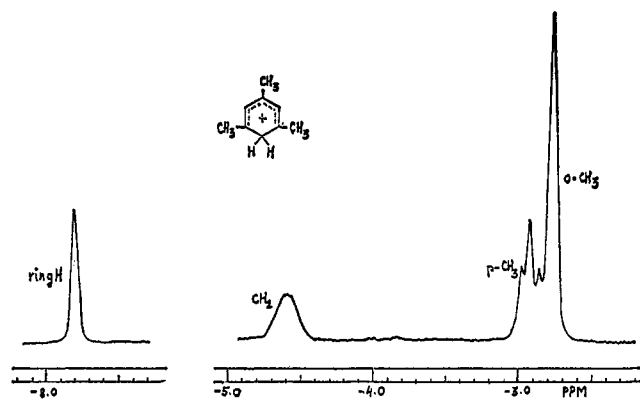
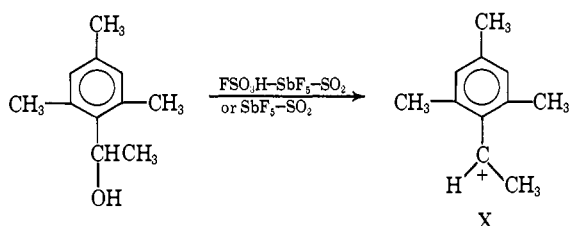


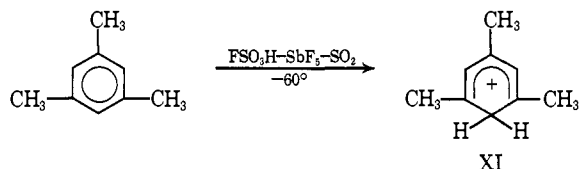
Figure 10.

$\text{SbF}_5\text{-SO}_2$ solution at -60° . The pmr spectrum of X is interesting because it indicates that rotation around the sp^2 -hybridized carbonium carbon atom at -60° is hindered, making the 2- and 6-methyl groups nonequivalent.



Quenching ion VII in methanol at -80° gave more than 80% of the β -methyl ether 2,4,6- $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CH}_2\text{CH}_2\text{OCH}_3$ with small amounts of the α ether and trimethylstyrene also formed. Methanolysis of ion X gave the α -methyl ether 2,4,6- $(\text{CH}_3)_3\text{C}_6\text{H}_2\text{CH}(\text{OCH}_3)\text{CH}_3$ and 2,4,6-trimethylstyrene.

Protonation of mesitylene to give the 2,4,6-trimethylbenzenonium ion (XI) is known.¹⁹⁻²² Figure 10 shows the pmr spectrum of XI in $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2$ solution at -60° . It is interesting to note that in this solvent system a long-range coupling of the methylene protons to the p -methyl protons ($J_{\text{H-H}} = 3.4$ Hz) is observable.



The close correlation of spectra of ions VII and XI, as well as good agreement with the previous observation of the cyclopropyl protons in the bridged anthryl-ethyl¹⁰ and p -anisonium I ion, give further support of assignment of ion VII as the bridged 2,4,6-trimethylphenonium ion.

The ionization of the secondary 1-mesityl-2-chloropropane in $\text{SbF}_5\text{-SO}_2$ resulted in the formation of the benzylic mesitylethylcarbonium ion (XII) (Figure 11). β -Pentamethylphenylethyl chloride in $\text{SbF}_5\text{-SO}_2$ solution at -60° gave the bridged pentamethylphenonium

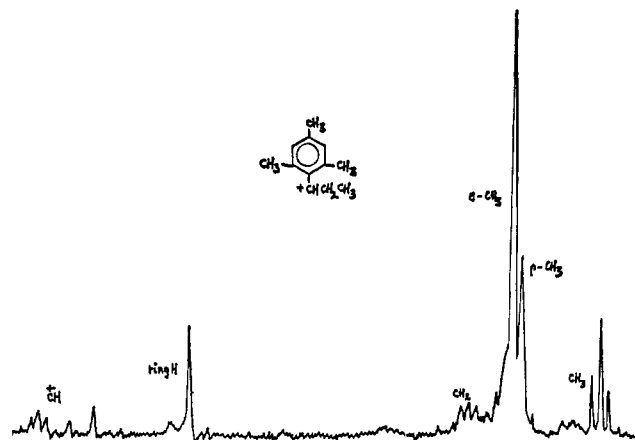


Figure 11.

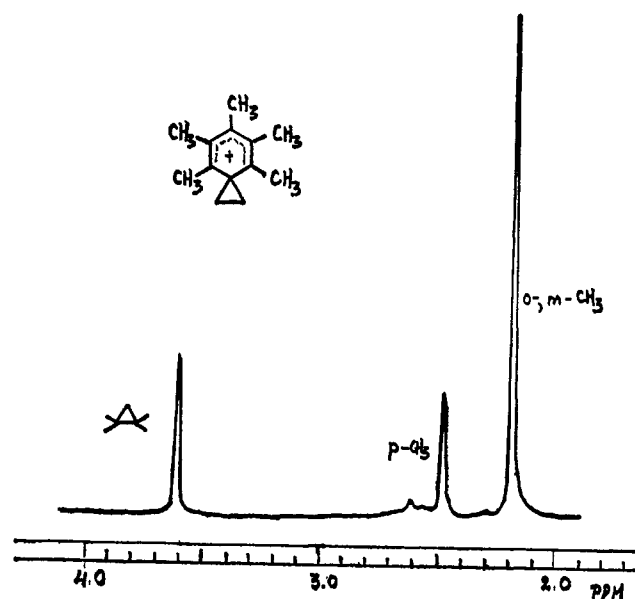
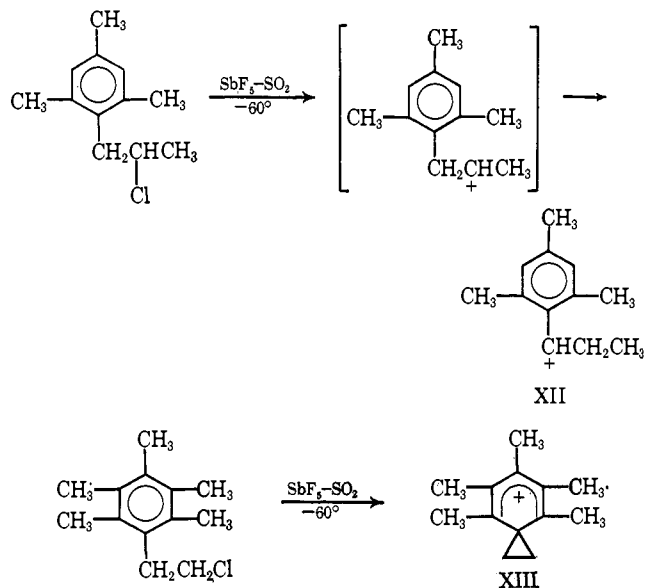


Figure 12.

ion (XIII) (Figure 12). The pmr spectrum of ion XIII shows the cyclopropyl protons at -3.62 ppm, the p - CH_3 protons at -2.48 ppm, and the o - and m -methyl protons at -2.19 ppm. The lack of a chemical shift



(19) G. A. Olah, *J. Am. Chem. Soc.*, **87**, 1103 (1965).

(20) G. Dallinga, E. L. Mackor, and A. A. Verrijn Stuart, *Mol. Phys.*, **1**, 123 (1958); E. L. Mackor, A. Hofstra, and J. H. van der Waals, *Trans. Faraday Soc.*, **54**, 66 (1958).

(21) G. MacLean and E. L. Mackor, *Mol. Phys.*, **4**, 241 (1961); *Discussions Faraday Soc.*, **34**, 165 (1962).

(22) T. Birchall and R. J. Gillispie, *Can. J. Chem.*, **42**, 502 (1964).

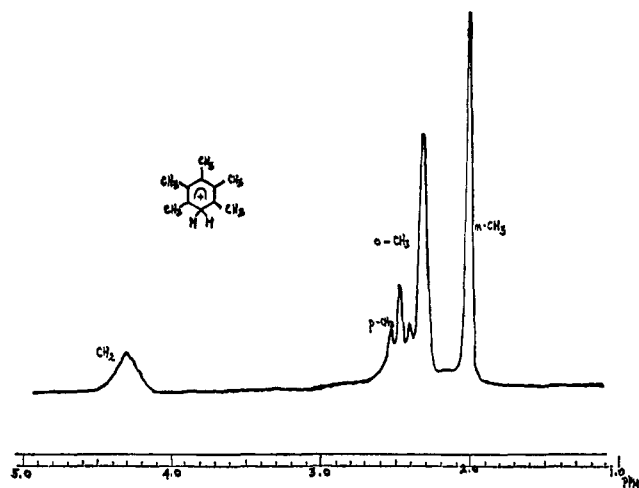
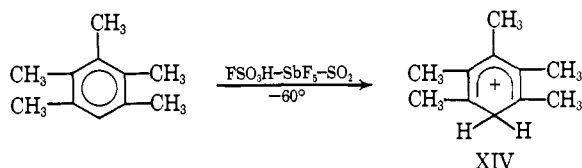


Figure 13.

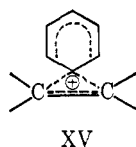
difference between the *o*- and *m*-methyl groups is interesting and is undoubtedly due to a buttressing effect between these groups causing the *o*-methyl groups to be very proximal to the face of the cyclopropane ring. Upfield shifts of this type are well known.²³

Methanolysis of the pentamethylphenonium ion XIII give a more than 90% yield of 1-pentamethylphenyl-2-methoxyethane. Again, the pentamethylbenzenonium ion (XIV) (Figure 13) serves as a useful model for XIII and shows close resemblance.



Conclusions

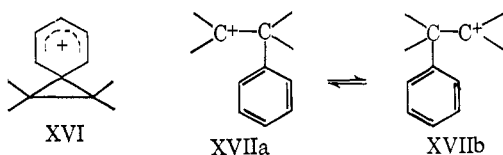
The structure of phenonium ions has been suggested by Cram²⁴ as XV



and also has been described in terms of resonance hybrid structures.

Phenonium ions using Bartlett's definition²⁵ should not be necessarily classified as nonclassical ions, because they do not have completely delocalized carbon-carbon bonding σ electrons in the ground state.

A phenonium ion may be written as a structure of type XVI as opposed to equilibrating classical ions given in structures XVIIa and b.



(23) C. U. Pittman, Jr., and G. A. Olah, *J. Am. Chem. Soc.*, **87**, 2998, 5123 (1965).

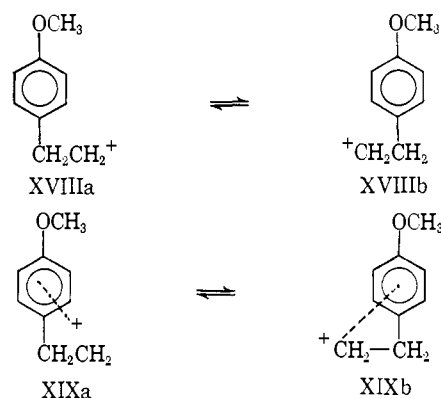
(24) D. J. Cram, *ibid.*, **71**, 3863 (1949).

(25) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965.

Deno and Brown⁴ have preferred structure XVI for phenonium ions which corresponds to a spirocyclopropylbenzenonium ion (σ complex) of which the benzenonium ion (cyclohexadienyl cation) is an alicyclic analog.

The phenonium ions I, VII, and XIII exhibit cyclopropyl proton shifts at -3.5 to 3.8 ppm which are substantially downfield from where they appear in covalent cyclopropyl compounds. Thus the cyclopropyl ring does delocalize significant positive charge. However, this same deshielding is generally found for cyclopropylalkyl,²³ cyclopropylphenyl,²³ dicyclopropyl,²³ tricyclopropyl,^{26,27} and cyclopropylalkenylcarbonium²⁸ ions. Thus, the spirocyclopropyl ring of the phenonium ion does not appear to be a special case. The plane of the six-membered ring intersects the plane of the cyclopropyl ring with an angle of 90° . Recently, direct experimental evidence was obtained for the so-called "bisected form" of cyclopropylcarbonium ions.²³

It has been argued that solvolytic reactions leading to the formation of resonance-stabilized bridged cations should exhibit significant rate enhancements over comparable reactions leading to static or equilibrating ions.³ On the other hand, Brown argued⁴ that the reaction of the open-chain carbonium ions might be the faster; thus the actual reaction might proceed through rapidly equilibrating classical or equilibration π -bridged ions. In the case of the *p*-anisylethyl systems these are



In our view, our present results clearly answer the question that the bridged phenonium ions in strong acid solution are quite distinct from rapidly equilibrating classical or π -bridged ions. The nmr data of the phenonium ions prove the spirocyclopropylbenzenonium structure. The highly deshielded ring pattern is *not* a phenyl ring pattern, but a benzenonium ion pattern. Should rapid equilibration take place, the nmr time scale would be too slow to differentiate between a symmetrical ion or rapid equilibration. However, the crucial point is that equilibration would involve phenyl ring structures and not benzenonium structures. The observation of benzenonium structures in ions I, VII, and XIII eliminates equilibrating classical or π -bridged ions. Thus we feel that for the first time, stable phenonium ions were observed in acidic solutions formed *via* phenyl participation and their structures were proven.

Having previously demonstrated⁷ stable classical static and classical equilibrating phenylethyl cations in

(26) N. C. Deno, *Chem. Eng. News*, **42**, 88 (Oct. 5, 1964).

(27) N. C. Deno, H. G. Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Houser, and M. J. Wisotsky, *J. Am. Chem. Soc.*, **84**, 2016 (1962).

(28) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. W. Lincoln, and J. O. Turner, *ibid.*, **87**, 4533 (1965).

acidic solutions, the observation of stable bridged phenylethyl cation (phenonium ions) in the present work completes the study of all three possible ion types in these systems.

Experimental Section

β -*p*-Anisylethyl alcohol was prepared by LiAlH_4 reduction of *p*-methoxyphenylacetic acid (Aldrich), bp 122–125° (5 mm) [lit.²⁹ 102–105° (0.3 mm)].

β -*p*-Anisylethyl chloride was formed from the alcohol using thionyl chloride and pyridine in ether solution at 0°. After work-up, the chloride was collected by fractional distillation, bp 90–92° (2 mm).

α -*p*-Anisylethyl Alcohol. *p*-Methoxyacetophenone (Eastman) was reduced with LiAlH_4 in ether solution, bp 84° (3 mm) [lit.³⁰ 104° (3 mm)].

β -Mesitylethyl Chloride. 2-Mesitylethyl alcohol³¹ was converted to the chloride with thionyl chloride and pyridine in ether solution at 0°, bp 128–132° (12 mm).

α -Mesitylethyl Alcohol. Mesityllithium (from butyllithium and 2-bromomesitylene) (Eastman) was treated with acetaldehyde in ether solution at –10°. After work-up, the product was isolated by distilling off volatile impurities under vacuum and recrystallizing from pentane and then acetone, mp 72–74°.

1-*p*-Anisyl-2-propanol. The Grignard reagent from *p*-bromoanisole (Eastman) was prepared in the usual manner from 200 g (1.07 moles) of the halide in 400 ml of ether. After addition of 800 ml of benzene and cooling to –20°, a cold (–40°) solution of 80 g (1.4 moles) of propylene oxide in 100 ml of benzene was added over a period of 10 min. After standing overnight at room temperature and refluxing for 2 hr, the reaction mixture was cooled to –20 and hydrolyzed with 200 ml of H_2O . Work-up yielded 100 g (58%) of the title compound, bp 75° (0.007 mm).

1-*p*-Anisyl-2-chloropropane. 1-*p*-Anisyl-2-propanol (40 g, 0.24 mole) was cooled to –60° and slowly dissolved in 200 ml of cold (–40°) SOCl_2 . The reaction mixture was stirred and allowed to warm to room temperature. After stirring for 2 hr at room temperature, the excess SOCl_2 was removed on a rotary evaporator. Distillation yielded 38 g (87%) of the title compound, bp 125° (10 mm).

β -(Pentamethylphenyl)ethyl Alcohol. Using the above procedure for 1-*p*-anisyl-2-propanol 50 g (52%) of the title compound was

prepared from 114 g of bromopentamethylbenzene and 40 g of ethylene oxide, mp 108–109.5° (from hexane).

β -(Pentamethylphenyl)ethyl Chloride. β -(Pentamethylphenyl)ethyl alcohol (5 g) was dissolved in 50 ml of cold (–40°) SOCl_2 . After warming to 35° and stirring for 2 hr, excess SOCl_2 was removed on a rotary evaporator, mp 64–65° (from ether), yield 4.9 g (86%).

1-Mesityl-2-propanol. Using the above procedure for 1-*p*-anisyl-2-propanol the title compound was analogously prepared, bp 138–142° (0.5 mm).

1-Mesityl-2-chloropropane was prepared from the corresponding alcohol with thionyl chloride and pyridine in ether at 0°, bp 124–126° (15 mm).

1-*p*-Anisyl-1-methoxyethane. A solution of 16 g (0.097 mole) of α -*p*-anisylethyl alcohol in 60 ml of dry DMSO was added dropwise with stirring to a suspension of 6 g (0.167 mole) of NaH (in mineral oil) in 100 ml of dry DMSO. After stirring for 0.5 hr 50 g of CH_3I was added over a period of 60 min. After hydrolysis and work-up, the product was isolated by distillation, bp 72° (10 mm). Similarly prepared were 1-*p*-anisyl-2-methoxyethane, bp 80° (1.0 mm); 1-mesityl-1-methoxyethane, bp 60° (10 mm); 2-mesityl-2-methoxyethane (solid melting point not determined); and 2-pentamethylphenyl-2-methoxyethane, mp 59–60.5° (from ether).

Preparation of Carbonium Ions. A saturated solution of antimony pentafluoride (or $\text{SbF}_5\text{-FSO}_3\text{H}$, 1:1) in sulfur dioxide was prepared (at –10°). Portions (2 ml) of this solution were cooled to –78°, causing some acid to crystallize from solution. To this suspension was slowly added with rapid stirring approximately 0.3–0.4 g of halide (alcohol, hydrocarbon) in SO_2 . Slight warming was generally required to complete the ionization, whereupon a homogeneous solution resulted with only slight traces of color. Ion concentrations were approximately 10%. Nmr spectra were recorded on a Varian Associates Model A56-60A spectrometer with external capillary TMS as reference.

Methanolysis of the carbonium ions was accomplished by adding slowly the solution of the carbonium ion in sulfur dioxide to cold (–98°) rapidly stirred methanol slush. The reaction mixture was then poured on ether. After washing and drying, the ethereal layer was concentrated and analyzed by gas chromatography (capillary technique using a Perkin-Elmer Model 226 gas chromatograph). Identification of products was made by comparison of retention times and peak enhancement with authentic samples and also by nmr and infrared spectroscopy of isolated products.

Acknowledgment. Generous support of this work by grants of the National Science Foundation and the National Institutes of Health is gratefully acknowledged.

(29) S. Winstein and E. Jenny, *Helv. Chim. Acta*, **41**, 807 (1958).

(30) J. Grundy, *J. Chem. Soc.*, 5087 (1957).

(31) C. R. Houser and D. M. Van Eeman, *J. Am. Chem. Soc.*, **79**, 5512 (1957).

Alkaloid Biosynthesis and Interconversions. The Conversion of Caranine to Lycorine¹

W. C. Wildman and N. E. Heimer²

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50010. Received April 29, 1967

Abstract: A synthesis of [2β - ^3H]caranine from lycorine has been accomplished. When introduced into *Zephyranthes candida*, this radioactive precursor was transformed into lycorine in good yield. This interconversion indicates that the oxidation at C_2 may occur relatively late in the biosynthetic process by an inversion mechanism. The relative configurations at C_1 and C_2 in several lycorine derivatives were determined by hydrogen-bonding studies in the infrared.

Radioactive tracer studies have shown that both phenylalanine and tyrosine are utilized in the biosynthesis of lycorine (1).^{3,4} The former amino acid

is utilized specifically for the construction of the aromatic ring and C_7 ($\text{C}_6\text{-C}_1$ unit). Tyrosine provides the hydroaromatic ring and the aliphatic carbon atoms at

(1) This research was supported in part by Grant HE 7503 from the National Institutes of Health.

(2) NASA Fellow, 1966.

(3) A. R. Battersby, R. Binks, S. W. Breuer, H. M. Fales, W. C. Wildman, and R. J. Highet, *J. Chem. Soc.*, 1595 (1964).

(4) D. H. R. Barton and G. W. Kirby, *Proc. Chem. Soc.*, 392 (1960).