# Stable Carbonium Ions. XXII.[1a] Phenylethyl Cations[2]

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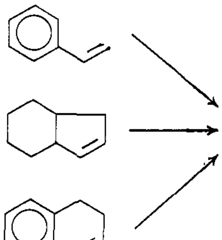
**Abstract:** Using the methods developed previously for generating stable carbonium ions from alcohols in $FSO_3H-SbF_5-SO_2$, halides in $SbF_5-SO_2$, and olefins in $FSO_3H-SbF_5-SO_2$ solution, a series of stable phenylethyl cations were observed. Both classical static phenylethyl cations (like the diphenylethyl, phenyl-*p*-tolylethyl, phenylmethylethyl, diphenylisopropyl, diphenylbenzylcarbonium ions) and equilibrating classical ions (like the pentaphenylethyl, tetraphenylethyl, and tetramethylphenylethyl cations) were directly observed by nmr spectroscopy. Investigation of 3-phenyl-2-butanol and 1-*p*-tolyl-1-phenyl-2-propanol in strong acid systems, on the other hand, indicates the formation of diprotonated arenonium type ions, but not bridged phenonium ions. Halide, ester, and olefinic precursors of the latter alcohols give in strong acid solution tertiary benzylic carbonium ions, by apparent 1,2-hydrogen shift of the intermediary formed less stable secondary carbonium ions. The difference between behavior in strong acid systems and solvolysis systems are discussed.

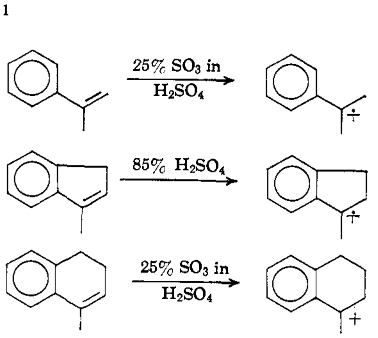
In the past years considerable interest has been centered on phenylethyl cations, particularly in connection with Cram's bridged phenonium ions[3] and Brown's reinterpretation of this conception.[4] These arguments have centered largely around the nature of the interpretation of the cationic transition states in the studies of solvolysis rates and the stereochemistry of the resulting products.[3-5] Extensive radiolabeling studies of phenylethyl solvolysis reactions have been carried out by Collins, and they have been recently reviewed.[6]

Stable monoarylcarbonium ions have been recently observed by pmr spectroscopy. The phenyldimethylcarbonium ion has been reported independently in $SO_2-SbF_5$,[7] $ClSO_3H$,[8] and 25% oleum solutions.[9] The electronic spectra of this and other monoarylcarbonium ions have been also observed.[1] In general, however, this area has not yet received extensive study. Attempts previously reported to generate secondary monoaryl cations were unsuccessful and only polymeric products were obtained[9,10] (see eq 1).



polymeric products in 80% $H_2SO_4$ to 65% $SO_3$ in $H_2SO_4$ or in $FSO_3H-SbF_5$ at -60° (1)

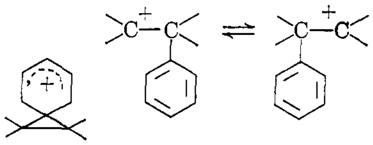
However, the tertiary analogs shown in eq 2 have been observed.[9,11]



(2)

Diarylcarbonium ions have been extensively studied by ultraviolet spectroscopy[12-16] but nmr studies are limited. The diphenylcarbonium ion, however, has been characterized by nmr spectroscopy.[7,8] Studies of carbonium ions generated from different phenylethyl systems using direct spectroscopic examination of these ions have never been reported in spite of the extensive interest in these systems. The direct examination of the ions in such systems was the goal of this work.

A phenonium ion may be defined as a structure of type I as opposed to equilibrating classical ions given in structures IIa and b. In a rapidly equilibrating classical ion such as II, the phenonium ion I would be the transition state between the two hybrids IIa and IIb and would not represent a discrete intermediate on the energy curve. On the other hand, if the phenonium ion is a discrete intermediate it would represent a minimum on the potential energy curve. The following types of energy diagrams can be envisioned (Figures 1a,



I IIa IIb

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[1] (a) Part XXI: G. A. Olah, C. U. Pittman, Jr., R. Waack, and M. Doran, *J. Am. Chem. Soc.*, **88**, 1488 (1966); (b) National Science Foundation Postdoctoral Research Investigator, 1965; (c) National Science Foundation Postdoctoral Research Investigator, 1965–1966; (d) Predoctoral Research Investigator, 1965–1966. (e) An earlier version of the manuscript was received on Jan 15, 1966.

[2] For preliminary reports see G. A. Olah and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, 87, 3507, 3509 (1965).

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

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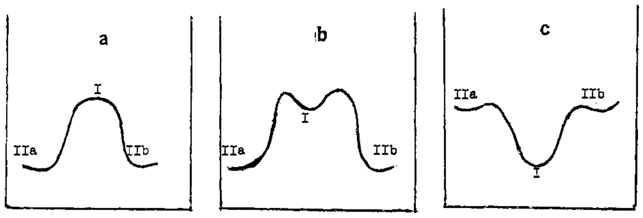
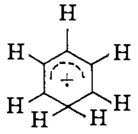


Figure 1.

b, c). As pointed out by Brown, Figures 1a and 1c represent the two limiting extremes between which any degree of variation should be possible.[4]

The phenonium ion may be considered as a cyclohexadienyl cation (benzenonium ion) with a spirocyclopropyl substituent. The cyclopropyl ring defines a plane which intersects the plane of the six-membered ring at an angle of 90°. Cyclopropyl rings $\alpha$ to a charged carbon are known to delocalize charge into the ring extensively, and cyclopropylcarbonium ions have now been well studied.[17-19] However, the properties of a spirocyclopropane ring joined to a positively charged system are less known. Eberson and Winstein recently were able to prepare the anthrylethyl-bridged cation[20] and to demonstrate by direct pmr observations extensive charge delocalization into the cyclopropane ring.

Models for the benzenonium part of phenonium ions are protonated aromatic compounds. In the phenonium ion, the phenyl ring's aromaticity is destroyed and it is a cyclohexadienyl cation closely resembling protonated benzene (III).



III

A large variety of protonated benzoid compounds have now been examined by pmr spectroscopy.[21-25] Protonated hexamethylbenzene, pentamethylbenzene, durene, isodurene, prehnitene, mesitylene, pseudocumene, hemimellitene, *o*-, *m*-, and *p*-xylenes, and toluene were prepared by direct protonation of the aromatic ring with HF + $BF_3$, HF + $SbF_5$, or $AgSbF_6$ + HCl, $FSO_3H$-$SbF_5$. The HF + $SbF_5$ acid system was even found to protonate benzene at low temperature.[21]

The infrared spectrum of protonated benzene in the solid state at 77°K has been shown to be practically independent of the Lewis acid.[26] These spectra differ markedly from the spectrum of benzene.[27]

## Results and Discussion

**A. Classical Static Arylcarbonium Ions.** Using the method developed previously for generating carbonium ions from alcohols in $FSO_3H$-$SbF_5$-$SO_2$,[28] a number of stable phenylethyl cations were observed. The diphenylethylcarbonium ion (IV), the phenyl-*p*-anisylethylcarbonium ion (V), the phenylmethylethylcarbonium ion (VI), and the *p*-tolylmethylethylcarbonium ion (VII) were generated from the corresponding tertiary alcohols (eq 3-6). The pmr spectra of IV, V, VI,

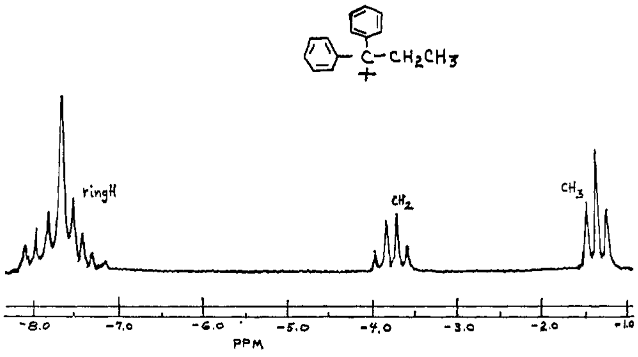
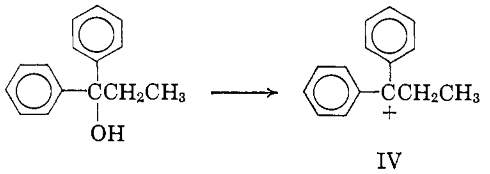
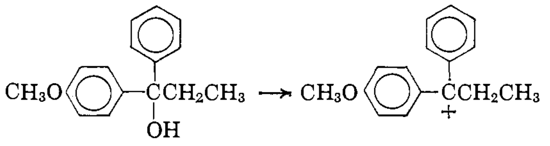


Figure 2.



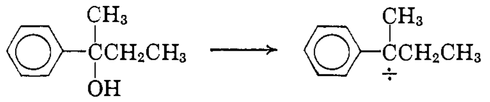
(3)

IV



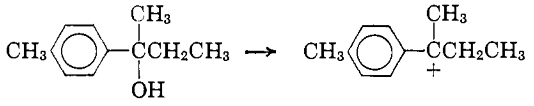
(4)

V



(5)

VI



(6)

VII

and VII are given in Figures 2, 3, 4, and 5. All spectra, if not otherwise indicated, were obtained in $FSO_3H$-$SbF_5$-$SO_2$ solution at −60°. Assignments are shown on the figures, with omittance of solvent–acid peaks.

The diphenylisopropylcarbonium ion (VIII), Figure 6, the phenylisopropylcarbonium ion (IX), Figure 7, and diphenylbenzylcarbonium ion (X), Figure 8, were formed both from their *corresponding $\alpha$ alcohols* and from their *corresponding $\beta$ alcohols* (eq 7-9). In each case the initial ionization of the $\beta$ alcohol must be followed by a 1,2 hydrogen shift.

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(26) H. H. Perkampus and E. Baumgarten, *Ber. Bunsenges. Physik. Chem.*, 67, 576 (1963).

(27) H. H. Perkampus and E. Baumgarten, *ibid.*, 67, 16 (1963).

(28) G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, 87, 2997 (1965).

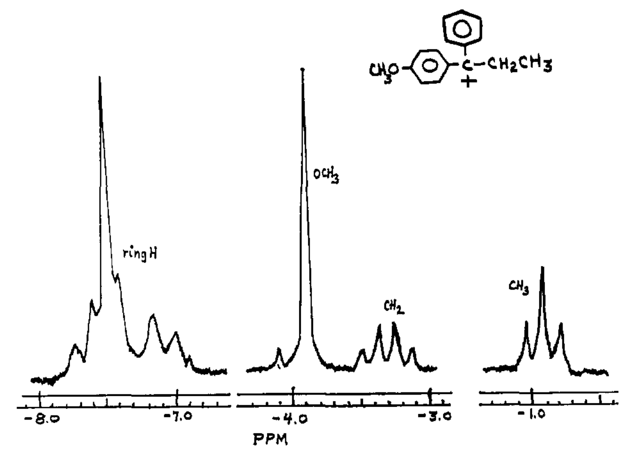
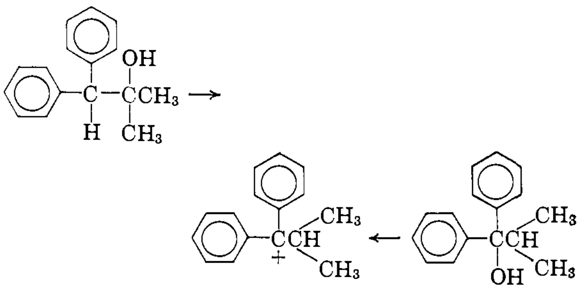
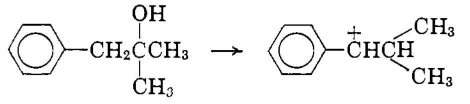


Figure 3.

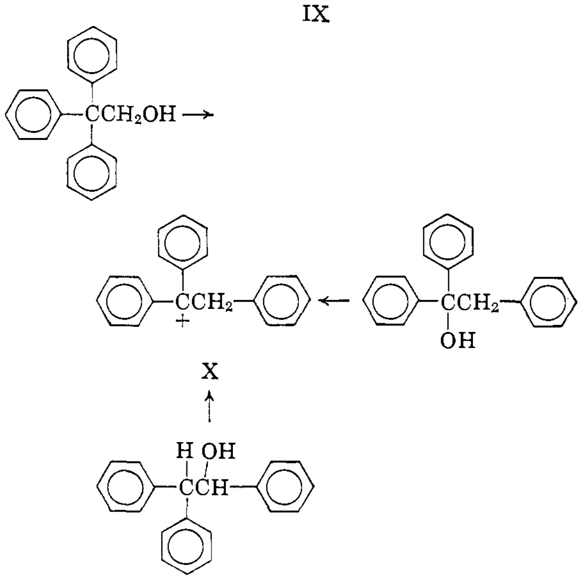
In ions VIII and IX, the methyl hydrogens of the isopropyl group appear as a well-resolved doublet between $-1.0$ and $-1.5$ ppm. These hydrogens are only slightly deshielded since they are in a $\beta$ position to the positive charge. The isopropyl hydrogen $\alpha$ to the charged carbon appears as a multiplet between $-4$ and $-4.5$ ppm in both ions VIII and IX. This hydrogen is split by the six methyl hydrogens and is not well resolved. The hydrogens $\alpha$ to the charged carbon are strongly deshielded, and their positions are in good agreement with the methylene quartets in ions IV, V, VI, and VII which are found between $-3.5$ and $-4.0$ ppm.


(7)

VIII


(8)

IX


(9)

X

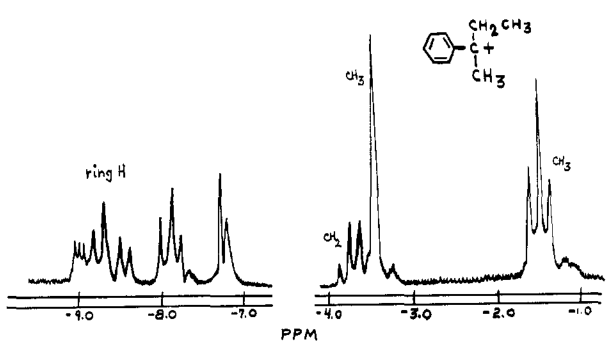


Figure 4.

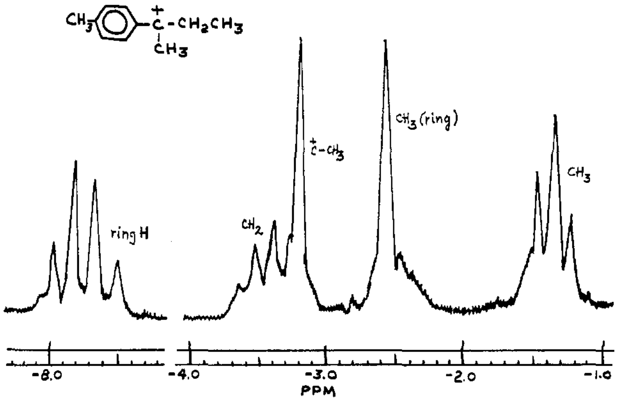


Figure 5.

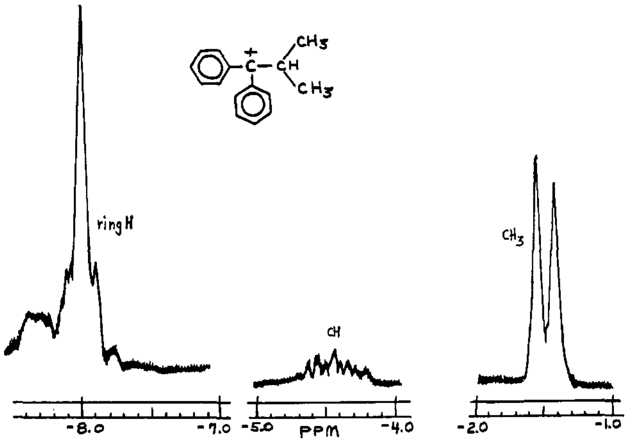


Figure 6.

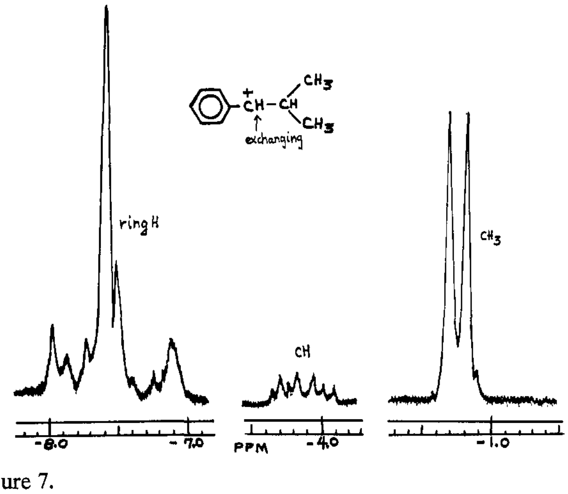


Figure 7.

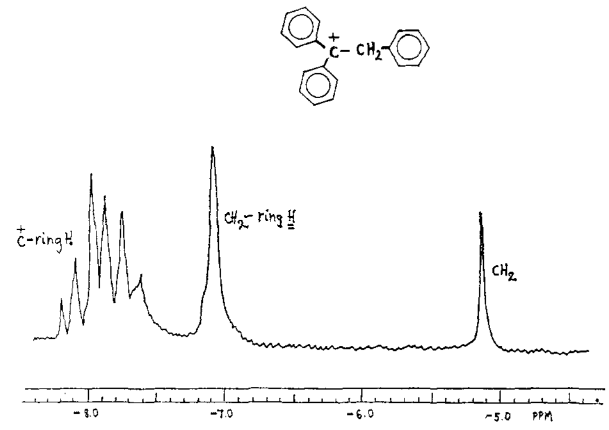


Figure 8.

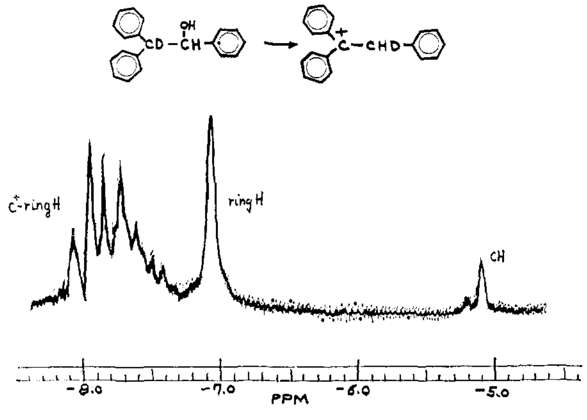
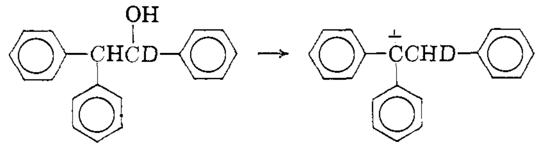


Figure 9.

Ion X is also generated from 2,2,2-triphenylethanol by a 1,2 phenyl shift following ionization (eq 9). In all these cases in the strongly acidic solvent ($FSO_3H$–$SbF_5$) the most stable isomeric carbonium ion is produced.

The formation of XI from 1,1,2-triphenyl-2-deuterio-2-ethanol is especially noteworthy (eq 10). The methylene proton peak at −5.12 ppm has a relative area of two in ion X (Figure 8) but only that of one in ion XI (Figure 9), showing that the deuterium has not exchanged with solvent protons in the process of ionization or subsequent hydrogen shifts.



XI (10)

Equations 9 and 10 indicate generation of the diphenylbenzyl cation from the β alcohol by ionization followed by a 1,2 hydrogen shift. However, it is quite possible that prior to hydrogen shift a rapid equilibration of the phenyl groups could occur as indicated below. The 1,2 hydrogen shift could then take place in any three of the species. To test this possibility of prior phenyl migration, three isomeric alcohols, 1,2-diphenyl-1-*p*-tolyl-1-ethanol, 1,1-diphenyl-2-*p*-tolyl-1-ethanol, and 1,1-diphenyl-2-*p*-tolyl-2-ethanol, were examined in $FSO_3H$–$SbF_5$ from −60 to 0°. Equations 11 through 13 summarize the results in accordance with the data of the corresponding pmr spectra shown in Figures 10–12.

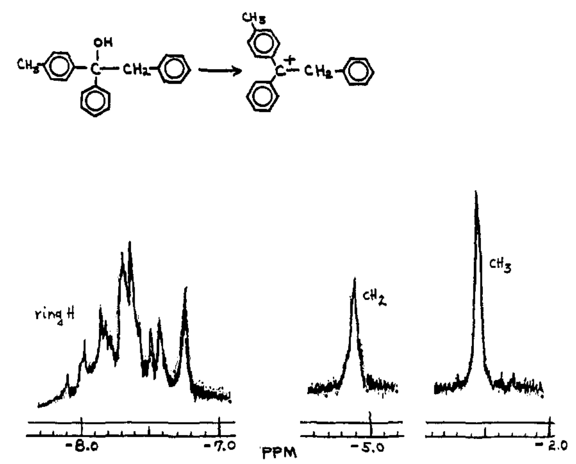


Figure 10.

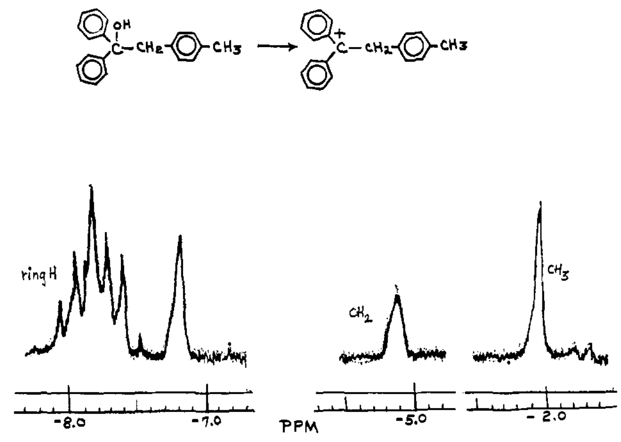


Figure 11.

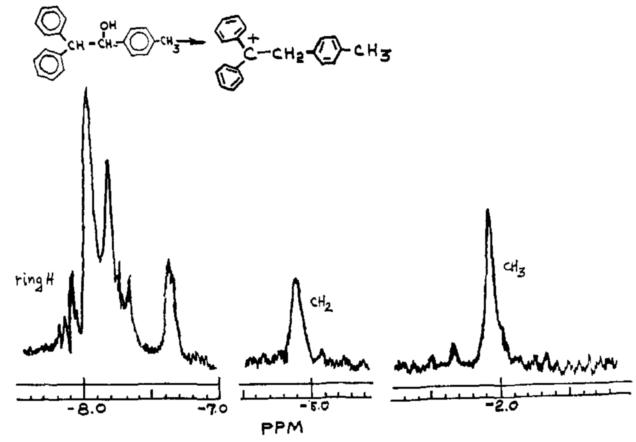
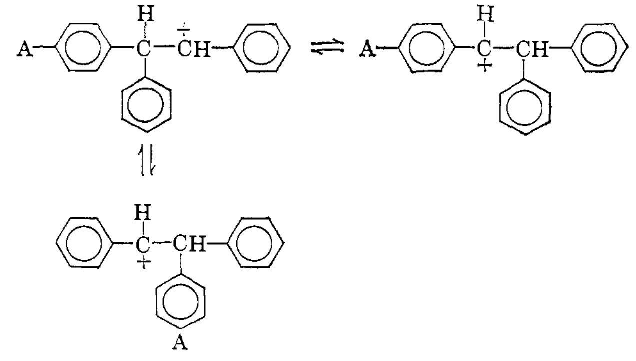
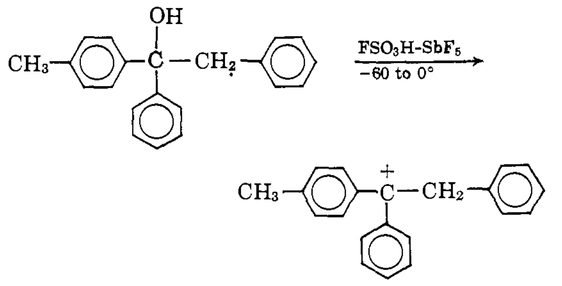


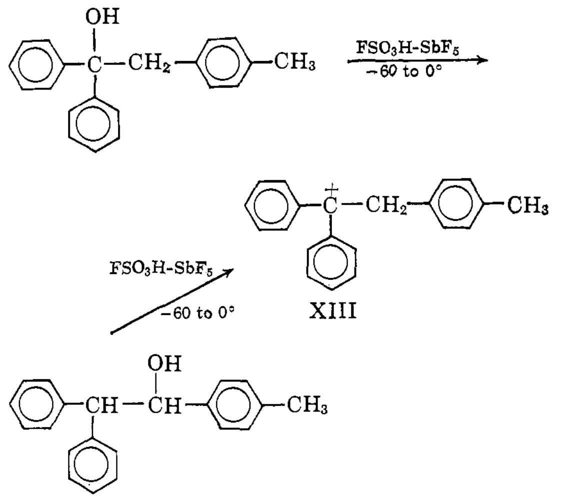
Figure 12.





XII

(11)



XIII

(12)

(13)

Generation of diphenylbenzylcarbonium ions from the corresponding diphenylbenzylcarbinols is straightforward, and no rearrangement occurs in $FSO_3H-SbF_5$. Thus ions XII and XIII were unequivocally characterized. The position of the *p*-methyl group in XII is −2.52 ppm which is downfield from the *p*-methyl group in XIII (−2.04 ppm). This is expected since in XII the methyl group is on a phenyl ring directly attached to the positive charge, and it is expected to be more deshielded than the methyl group in ion XIII. In ion XIII the methyl group is on the "benzylic" phenyl ring and is insulated from the deshielding effect of positive charge. Ionization of 1,1-diphenyl-2-tolyl-2-ethanol gave an ion whose pmr spectrum contained only one methyl band (at −2.07 ppm). This spectrum (Figure 12) is identical with the spectrum of ion XIII. Thus, on ionization of this $\beta$ alcohol a 1,2 hydrogen shift occurs with no prior rapid phenyl migration. In this system hydrogen shift must be more rapid than the phenyl shift. Had prior phenyl migration occurred, both ions XIII and XII would have been observed (the ratio of XII to XIII would be 2 to 1 if prior phenyl migration were rapid enough to allow equilibration of the phenyl groups).

**B. Equilibrating Phenylethyl Cations.** Whereas the so far discussed phenylethyl cations all were open chain, classical static carbonium ion, in some cases we have observed strong evidence of rapid equilibration of phenylethyl cations, but no evidence of phenyl bridging (phenonium ion formation).

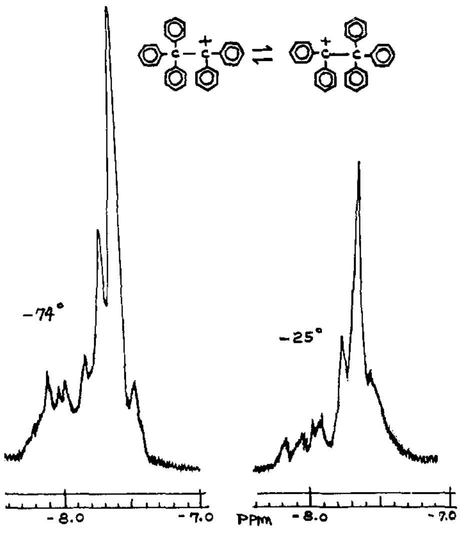
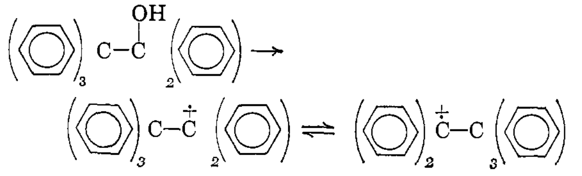


Figure 13.

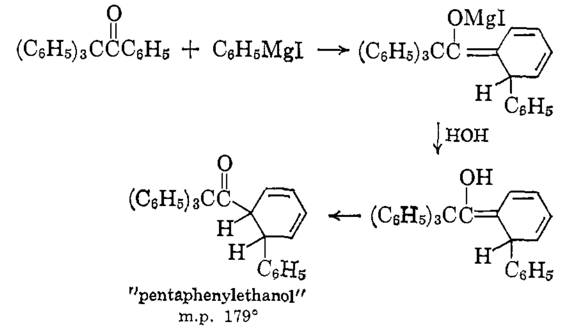
Generation of the pentaphenylethyl cation XIV from pentaphenylethanol (eq 14) showed that all five phenyl groups are equivalent and equilibrate rapidly even at −74° (Figure 13). That the phenyl peak contains all 25 hydrogens was demonstrated by calibration with a known amount of tetramethylammonium salt as internal reference. No evidence of bridged ion formation was found.



XIV

(14)

It is interesting to note that pentaphenylethanol has apparently not yet been reported in the literature. Schmidlin and Wohl[29] described "pentaphenylethanol" as being prepared from phenylmagnesium iodide and $\beta$-benzopinacolone, melting at 179°. Mosher, however, later reported[30] that the compound in all probability was actually a dihydro ketone, 1-triphenylacetyl-2-phenyl-1,2-dihydrobenzene.



Various attempts to prepare the alcohol were found unsuccessful (reaction of benzopinacolone with phenyllithium[31] or reaction of benzophenone with triphenylmethylmagnesium bromide). We found, however, that pentaphenylethanol could be prepared (crystalline compound, mp 142–144°, with proper analytical data, infrared and nmr spectra) by the reaction of triphenylacetic acid, or even better its methyl ester with phenyllithium, followed by hydrolysis.

$$(C_6H_5)_3CCOOCH_3 + 2C_6H_5Li \longrightarrow (C_6H_5)_3C\overset{OH}{\overset{|}{C}}(C_6H_5)_2$$

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[29] J. Schmidlin and J. Wohl, *Ber.*, 43, 1147 (1910).

[30] W. A. Mosher and M. L. Huber, *J. Am. Chem. Soc.*, 75, 4604 (1953).

[31] J. J. Eisch, personal communication.

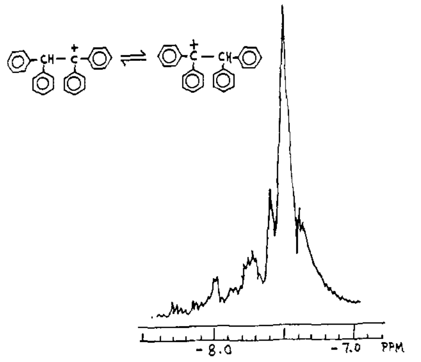
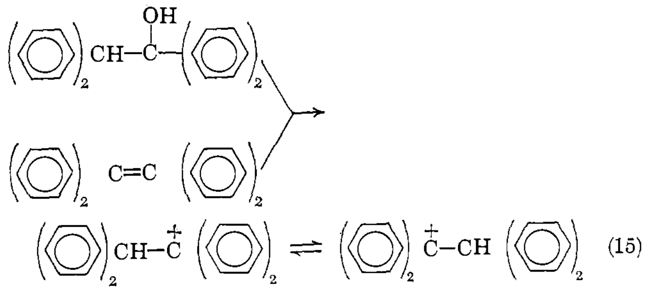


Figure 14.

Similarly to the pentaphenylethyl cation, the tetraphenylethyl cation XV obtained from tetraphenylethyl alcohol (or also tetraphenylethylene) in $FSO_3H-SbF_5$ (eq 15) shows also complete equilibration (Figure 14).

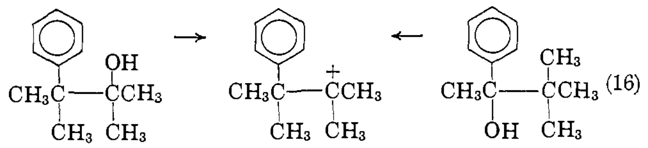


(15)

XV

In this case, rapid 1,2 hydride migration is assumed responsible for equilibration instead of 1,2 phenyl migration. The phenyl protons are all equivalent, whereas the rapidly exchanging methine proton cannot be distinguished (at least at the temperature investigated) in the acidic solvent.

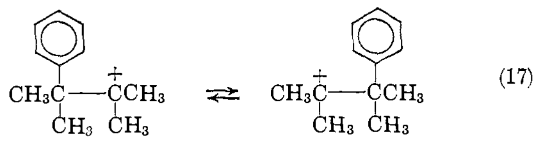
When either 2,3-dimethyl-3-phenyl-2-butanol or 2-phenyl-3,3-dimethyl-2-butanol or a mixture of the two alcohols is dissolved into $SO_2-SbF_5-FSO_3H$ at 60°, the same ion (XVI) is obtained (see eq 16).[32] The pmr spectrum shows all four methyl groups are equivalent and deshielded, with a phenyl ring spectrum and no indication of benzenonium ion nature. The methyl band at $-2.20$ ppm remained sharp even at $-120°$.



(16)

XVI

The spectra indicate a rapid equilibration in XVI and requires that the phenyl shift in the proposed equilibrating ions XVIa and b be extremely fast even at $-120°$ (eq 17, see also Figure 15).



(17)

XVIa XVIb

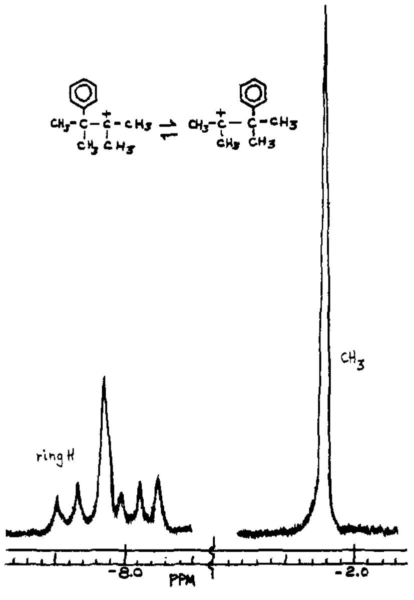
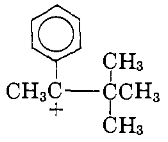


Figure 15.

At first thought it might seem surprising that 2-phenyl-3,3-dimethyl-2-butanol in $FSO_3H-SbF_5$ rearranges to ion XVI instead of the phenylmethyl-*t*-butylcarbonium ion (XVII). However, the steric interaction of the *t*-butyl group with the benzene ring prevents coplanarity, thus hindering overlap of the vacant p orbital and the ring. Also the *t*-butyl group provides no conjugative stability of ion XVII, which must be less stable than ion XVI and rearranges into the latter *via* 1,2 methyl shift.



XVII

These considerations make rapid equilibration through methyl instead of phenyl shifts improbable.

**C. Investigation of Possible "Phenonium Ion" Systems.** The availability of methods to generate stable phenylethyl cations in strongly acidic systems ($FSO_3H-SbF_5$) offered a possibility to extend the investigations to possible phenonium ion systems. In a brief preliminary report[2] we reported observation of the pmr spectra of 3-phenyl-2-butanol and 1-*p*-tolyl-1-phenyl-2-propanol in $FSO_3H-SbF_5-SO_2$ solution, which seemed to indicate bridged phenonium ions. This conclusion was based primarily on the observation that the spectra indicated no aromatic ring patterns but benzenonium ion type ions, the pmr spectra of which was well known from previous investigations.[21-25] The observation of two methyl doublets in the ion obtained from 3-phenyl-2-butanol was attributed to the presence of both the *cis*- and *trans*-dimethylphenonium ion (XVIII).

XVIII

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[32] This ion was suggested in the work of D. J. Cram and T. D. Knight, *J. Am. Chem. Soc.*, 74, 5839 (1952).

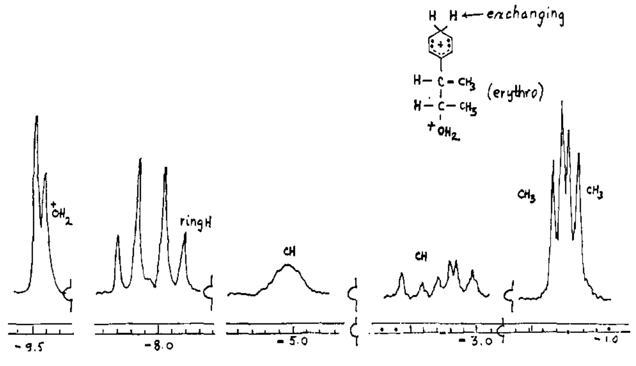


Figure 16.

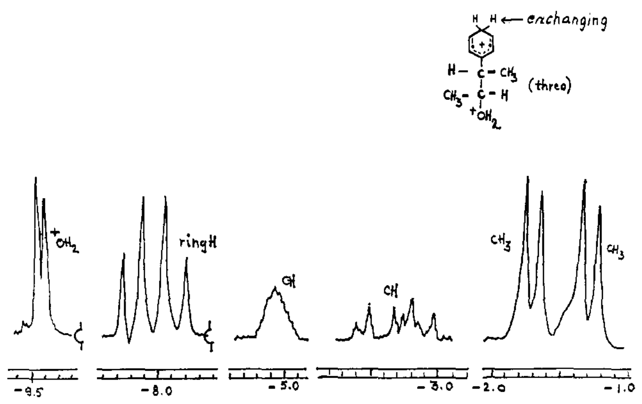
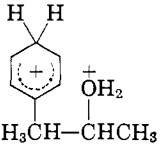


Figure 17.

The ring pattern of ion XVIII was assumed[2] to consist of a quadruplet centered at $-8.02$ ppm and a doublet at $-9.54$ ppm. It was argued that this pattern could be that part of a not entirely resolved, fairly complicated $A_2B_2C$ system, where we are dealing with the mixture of two ions (*cis* and *trans*).

As an alternate possibility, it was suggested[33] that the observed spectrum of 3-phenyl-2-butanol in $FSO_3H$–$SbF_5$–$SO_2$ could be attributed to the diprotonated ion XIX. This ion (XIX) would be a benzenonium ion, but not a bridged phenonium ion.

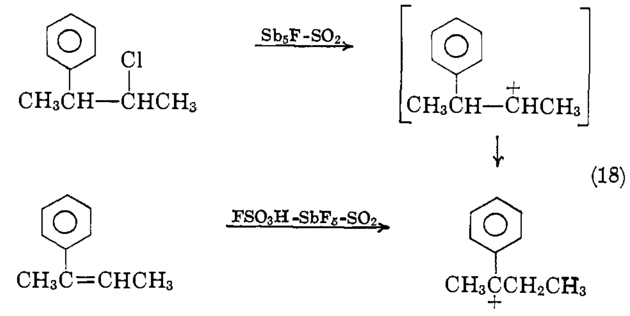


XIX

All the previously discussed phenylethyl cations were generated in $FSO_3H$–$SbF_5$–$SO_2$ solvent system from the corresponding tertiary alcohols, or from *secondary, but benzylic alcohols*, or in specific cases, from *neopentyl type primary alcohols*.

The generation of stable carbonium ions from alcohols as precursors in $FSO_3H$–$SbF_5$ solvent system was originally found to work for tertiary alcohols and certain reactive secondary alcohols (benzylic, or alcohols like 2-*exo*-norborneol). The scope of the reaction was not investigated in detail relating to less reactive secondary alcohols or primary alcohols, other than the neopentyl type.

We have now carried out a comprehensive investigation of the secondary 3-phenyl-2-butanol system in $FSO_3H$–$SbF_5$–$SO_2$ and also investigated the behavior of 3-phenyl-2-chlorobutane in $SbF_5$–$SO_2$, as well as that of 2-phenylbutene-2 in $FSO_3H$–$SbF_5$–$SO_2$.

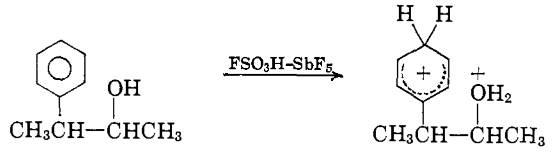


(18)

VI

3-Phenyl-2-chlorobutane and 2-phenylbutene-2 in the strong acid solutions form exclusively the tertiary benzylic phenylmethylethylcarbonium ion (VI) *via* obvious 1,2 hydrogen shift of the intermediate unstable secondary ion (eq 18).

3-Phenyl-2-butanol on the other hand forms in $FSO_3H$–$SbF_5$ the diprotonated cation XIX (eq 19) but not a phenonium ion.[33a] Figures 16 and 17 show the pmr spectra of the diprotonated ions (XIXa and



(19)

XIX

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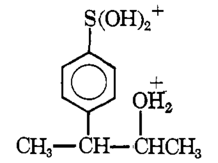
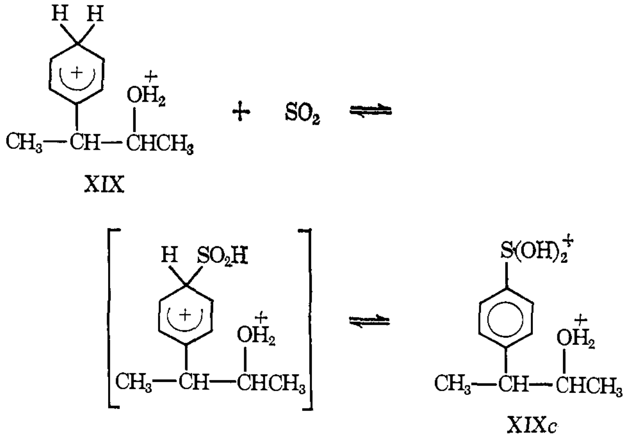
(33) Suggestion was originally made by Professor F. A. L. Anet, as communicated to us by Professor S. Winstein.

(33a) Note Added in Proof. Professors F. A. L. Anet and S. Winstein, investigating the same system, informed us that they have also obtained evidence of formation of a diprotonated ion, which they, however, consider to be protonated alcohol-protonated sulfinic acid (XIXc). We feel that there is no discrepancy between their findings and ours, because there is an obvious equilibrium between the ring protonated cation XIX and the protonated sulfinic acid XIXc. The diprotonated ion XIX can be obtained without interference from XIXc in the absence of $SO_2$ in $FSO_3H$–$SbF_6$ solvent system. The sulfination reaction of benzenonium ions seems to be limited to weakly basic hydrocarbons (benzene, monoalkylbenzenes).

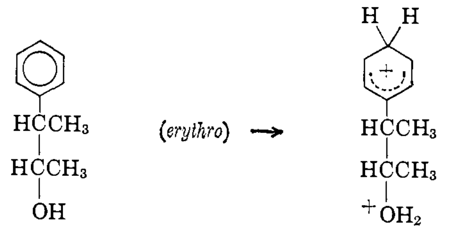




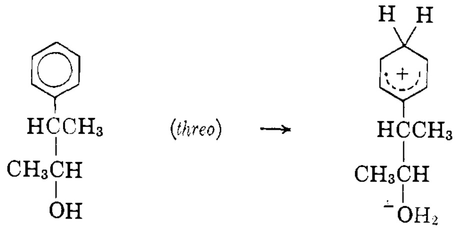
XIX

XIXc

b) obtained from *erythro*- and *threo*-3-phenyl-2-butanol in $FSO_3H–SbF_5–SO_2$ solution at −60°.



XIXa



XIXb

We can offer the following experimental evidence for the structural proof of the unusual dictations XIXa and b.

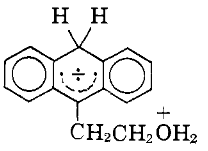
a. Whereas hydrolysis experiments of solutions of 3-phenyl-2-butanols in $FSO_3H–SbF_5$ gave a 73% recovery of the starting alcohols, methanolysis[34] using excess methanol and no base gave a product of which 10% was the methyl ether of the alcohols and 90% of the starting alcohol.

As experiments were carried out under anhydrous conditions we must conclude that ion XIX can not be the phenonium ion, because the latter should form only the methyl ethers if the structure of the ion is that of XIX. Formation of some methyl ethers besides deprotonation to the starting alcohols is not unexpected under the acidic reaction conditions.

b. The methylene protons exchange readily in strong acid solvents and the peak can broaden substantially making accurate peak integration or even observation difficult.

c. The $A_2B_2$ quartet observed in spectra can be assigned to the protonated benzenonium ions. This is in agreement with the observations on protonated toluene[21] which serves as a model of the benzenonium ion part of XIX. Exchange of benzenonium ions in $FSO_3H–SbF_5$ is quite fast even at −60°, more so than in $HF–SbF_5–SO_2$.

d. In $FSO_3H–SbF_5–SO_2$ solution at low temperature protonated primary and even secondary alcohols show surprisingly low exchange rates allowing observations of well-resolved spectra. Illustrative are protonated methyl alcohol, ethyl alcohol, normal and isopropyl alcohol, and *n*-butyl alcohol.[35] Based on these observations, the low-field doublet in the spectrum of XIX can be assigned to $^+OH_2$. The inability of Eberson and Winstein[20] to obtain the bridged anthrylethyl cation from 9-anthrylethanol also can be explained by the fact that a strong acid solution a diprotonated arenonium ion (XX) but not phenonium ion is formed.

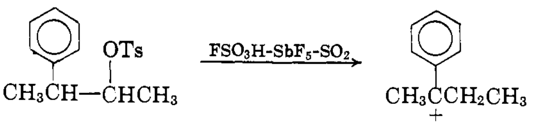


XX

e. The ultraviolet absorption of ion XIX shows $\lambda_{max}$ 329 m$\mu$ ($\epsilon$ 23,500) characteristic of a benzenonium ion. The position of the 329-m$\mu$ absorption is close to the reported position of the cyclohexadienyl cation (331 m$\mu$).[36]

The spectra of ions XIXa and b obtained from *erythro*- or *threo*-3-phenyl-2-butanol, if obtained immediately after making up the strong acid solutions, show no isomerization and upon hydrolysis the starting alcohols can be regained. (After standing for 2 hr, isomerization is observed upon hydrolysis with formation of phenylmethylethylcarbinol.)

In contrast to the behavior of 3-phenyl-2-butanol in strong acid, its esters (like the phthalic or *p*-toluenesulfonic ester) in $FSO_3H–SbF_5$ give the tertiaryl phenylmethylethylcarbonium ion.

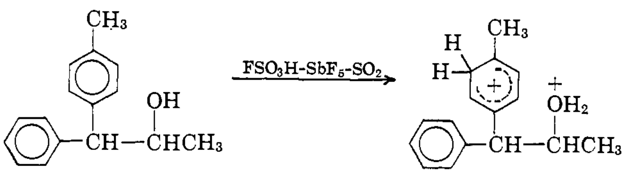


VI

Ionization of the esters must consequently yield the open-chain secondary carbonium ion which then rearranges *via* 1,2 hydrogen shift to ion VI.

The marked difference between the behavior of 3-phenyl-2-butanol and its esters in $FSO_3H–SbF_5$ further indicates the difficulties to try to extrapolate the results observed in strong acid systems to the behavior in solvolysis systems. In the strong acids, $FSO_3H–SbF_5$ or $SbF_5$, precursors (halide, esters) which ionize directly to the open-chain secondary 3-phenylbutyl-2 cation, consequently rearrange *via* 1,2 hydrogen shift to the more stable tertiary and benzylic phenylmethylethylcarbonium ion. 3-Phenyl-2-butanol is, however, only protonated, but does not dehydrate to the open-chain carbonium ion. The ability of the open-chain carbonium ion to undergo 1,2 hydride shift must be a consequence of its relative stability in the strongly acidic medium. If such a medium is absent, as for example in solvolysis systems, the open-chain secondary ion can be quenched very rapidly and no rearrangement to the phenylmethylethylcarbonium ion is observed.

The spectrum of 1-*p*-tolyl-1-phenyl-2-propanol (mixture of the isomers) in $FSO_3H–SbF_5–SO_2$ solution (Figure 18) can also be best interpreted as that of a diprotonated ion XXI, keeping in mind that protonation of available ring positions may result in a mixture of benzenonium ions. The possibility of simulta-



XXI

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[34] This experiment was carried out at the suggestions of Professor H. C. Brown. We are grateful for his many comments and suggestions in connection with this work.

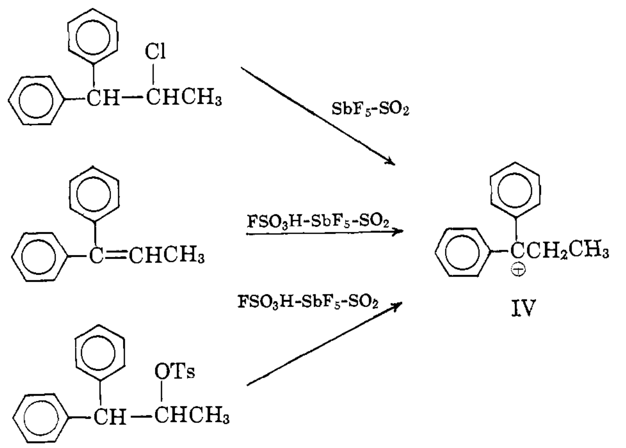
[35] G. A. Olah and E. Namanworth, *J. Am. Chem. Soc.*, **88**, 5327 (1966). A similar observation in $HF–SbF_5$ for protonated ethanol was previously made by C. McLean and E. L. Mackor, *Discussions Faraday Soc.*, **34**, 165 (1962).

[36] H. Luther and G. Pickels, *Ber. Bunsenges. Physik. Chem.*, **59**, 159 (1958).

neous protonation of both phenyl rings was, so far, not closer investigated, primarily because of the complex nature of the ring's nmr pattern.

The structure of ion XXI is further substantiated by investigation of model compounds like *p*-tolylethanol in $FSO_3H-SbF_5$, showing diprotonated benzenonium ion structure.

The related 1,1-diphenyl-2-chloropropane and esters of 1,1-diphenyl-2-propanol (as well as 1,1-diphenylpropene-2) in strong acid solution give, *via* apparent 1,2 hydrogen shift rearrangement, the tertiary diphenylethylcarbonium ion IV. The behavior is thus identical with that observed in the 3-phenyl-2-butyl systems.



IV

## Conclusions

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.[4] On the other hand, Brown argued that the reaction of the open-chain carbonium ions might be the faster; thus the actual reaction might proceed through the classical ion.[4]

In the course of our investigations, we were able to show that a substantial number of stable phenylethyl cations can be observed in strongly acidic solution ($FSO_3H-SbF_5$). All these ions have classical carbonium ion structures (using Bartlett's definition[37] they do not have delocalized bonding, $\sigma$ electrons in the ground state).

No example of bridged phenonium ions was found in the strong acid solutions,[37a] although a number of rapidly equilibrating phenylethyl cations were observed (pentaphenylethyl, tetraphenylethyl, and tetramethylphenylethyl cations) (Table I).

It must be stressed that one cannot extrapolate these results to conventional solvolysis reaction systems. For instance, it has been demonstrated by isotopic labeling experiments that $\beta$-phenylethyl[38] and pentamethylethyl[39] systems can be solvolyzed without the equilibration of the carbon atoms which either bridged or rapidly equilibrating structures require. On the other hand, it has been observed in the present work that all the phenyl groups of the stable pentaphenylethyl and tetraphenylethyl cations are in very rapid equilibrium even at −110° in $SbF_5-FSO_3H-SO_2F_2$ solution. A similar observation relating the methyl groups in the tetramethylphenylethyl cation was also made.

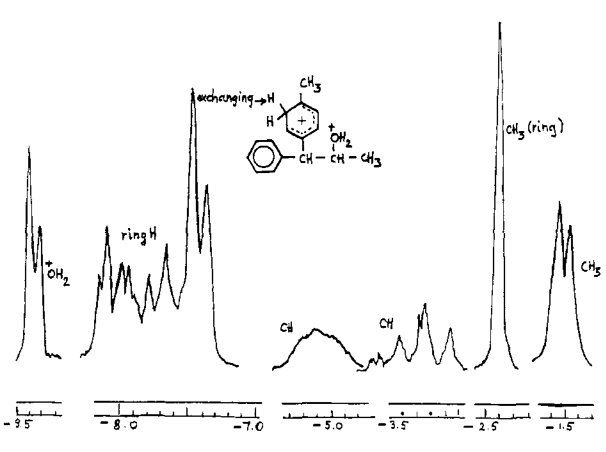
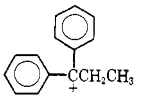
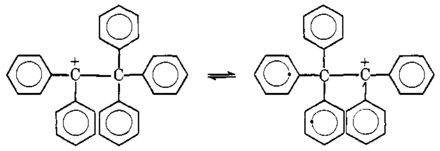
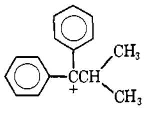
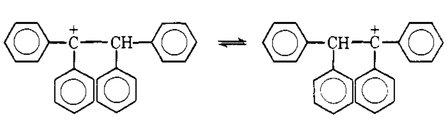
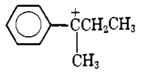
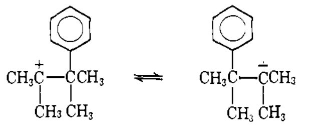
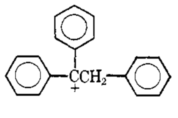
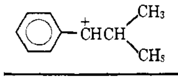


Figure 18.

Table I. Examples of Static and Rapidly Equilibrating Phenylethyl Cations in $FSO_3H-SbF_5-SO_2$ at Low Temperature

| Static | Rapidly equilibrating |
|---|---|
|  |  |
|  |  |
|  |  |
|  | |
|  | |

Although rapid reaction of the initially formed carbonium ion with solvent in the solvolysis systems might preclude equilibration, it has been claimed that intramolecular rearrangements can occur within a carbonium ion with rates in excess of solvent and ion-pair relaxations.[40] These results, however, were obtained assuming that quenching was diffusion controlled, an assumption which may not always be valid and the absence of which could invalidate the data. Another example of the different behavior ions might exhibit

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

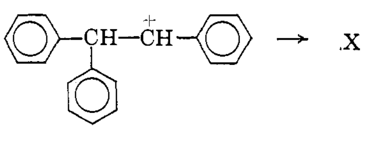
(37a) NOTE ADDED IN PROOF. Recently we succeeded, by taking advantage of substantially enhanced phenyl participation, to generate the bridged *p*-anisonium and 2,4,6-trimethylphenonium ions from the corresponding $\beta$-ethyl chlorides in $SbF_5-SO_2$ solution at low temperatures: G. A. Olah, *et al.*, *J. Am. Chem. Soc.*, in press.

(38) J. D. Roberts and C. M. Regan, *J. Am. Chem. Soc.*, **75**, 2609 (1953).

(39) J. D. Roberts and J. A. Yancey, *ibid.*, **77**, 5558 (1955).

(40) P. S. Skell and R. J. Maxwell, *ibid.*, **84**, 3963 (1962).

in strongly acidic solvent systems, compared to previous solvolytic reaction conditions, is found in the solvolysis studies of the tosylate and acetate of 1,2,2-triphenylethanol and as well as in the deamination of the corresponding amines.[41-44] These studies as well as isotope labeling experiments carried out by Collins, *et al.*,[45] have demonstrated that the 1,2,2-triphenylethyl cation does not need to involve phenonium ion nature to explain the experimental results, but can be an equilibrating ion where extensive and sometimes complete phenyl equilibration occurs in solvolysis reactions. In contrast in $SbF_5$–$FSO_3H$ solvent systems we have observed the stable diphenylbenzylcarbonium ion (X) as the static stable species which is generated from 1,2,2-triphenyl-1-ethanol *via* the 1,2,2-triphenyl-1-ethyl cation (XXI). However, no phenyl equilibration prior to the 1,2 hydride shift was observed. This was demonstrated by the methyl labeling experiment shown in eq 13, indicating no phenyl scrambling. The initially formed benzhydrylphenylcarbonium ion XXI is far more stable in the acidic solvent system than in a solvolysis reaction.



XXI

In fact, the phenylisopropylcarbonium ion (IX), also a secondary benzylic cation, exists for days in $FSO_3H$–$SbF_5$ at −60°.

The experimental evidence that no phenonium ion formation takes place from 3-phenyl-2-butanol or 1-*p*-tolyl-1-phenyl-2-propanol in strong acid solutions is of particular interest. Phenonium ions with spirocyclopropylbenzenonium ion structures must be considered as relatively stable species, which under proper conditions can even be synthesized.[20] Their intermediacy in the present strongly acidic systems was proved, on the other hand, to be absent, and all data were in accordance with static or rapidly equilibrating classical carbonium ions.

It must be concluded that in the extremely strong acid systems used in present studies, thermodynamic and not kinetic control prevails. The most stable carbonium ions are formed and are present as stable intermediates (represented by definition by energy minima). In the systems which under solvolysis conditions indicate phenonium ion formation (3-phenyl-2-butyl, 1-phenyl-1-*p*-tolyl-2-propyl) in the strong acid systems, different behavior is observed. There can be still visualized a rapid kinetically controlled equilibrium between the secondary open-chain carbonium ions first formed from ionizing precursors (halides, esters) involving a low-energy transition state, as suggested by Brown,[4] or a phenonium ion type of intermediate, as suggested by Cram[3] (see Figure 1). Available data do not allow any differentiation in this regard, because the open-chain carbonium ions also are in equilibrium with the tertiary benzylic carbonium ions, formed *via* slower 1,2 hydrogen shifts. As the tertiary benzylic carbonium ions obviously represent a much lower energy as either the equilibrating open-chain secondary ions or the phenonium ions, once formed they are not any more reversing. Thus the equilibria soon shift to the most stable tertiary benzylic ions and, by the time the nmr spectra are observed, these are the only cations present in detectable concentrations. Thermodynamic control giving the stable carbonium ion intermediates sharply contrasts kinetic control under solvolysis conditions where phenonium ion formation must be considered.

## Experimental Section

**1,1-Diphenyl-1-propanol.** Benzophenone was treated in the usual manner with ethylmagnesium iodide to form 1,1-diphenyl-1-propanol. 1,1-Diphenylpropanol was purified by recrystallization from alcohol and was obtained in 78% yield, mp 72°.[46-48] Its pmr spectrum showed the main phenyl band at −7.11 ppm (area 10.2), $CH_2$ (quartet, $^3J_{H-H} = 7$ cps) at −2.15 ppm (2), $CH_3$ (triplet, $^3J_{H-H} = 7$ cps) at 0.78 ppm (3.0), OH (singlet) at −1.99 ppm (1.2).

**1-Phenyl-2-methyl-2-propanol.** Methyl phenylacetate was added to excess methyllithium (Foote Mineral Co.) in diethyl ether solution in the usual manner. The resulting crude product contained a significant amount (~30%) of ketone (mono adduct). The entire crude product was treated with excess methylmagnesium bromide in ether solution. After the usual work-up and distillation, 10.2 g (68% yield) of 1-phenyl-2-methyl-2-propanol was collected at 112–114° (12 mm).[47,49] The pmr spectrum showed phenyl protons (main peak) at −7.1 ppm (relative area 5), benzylic methylene protons (singlet) at −2.64 ppm (2), hydroxyl proton at −1.96 ppm (1), and methyl protons (singlet) at −1.11 ppm (6).

Subsequent preparations showed the reaction of methyl phenylacetate with methylmagnesium iodide is far cleaner than with the use of methyllithium.

**1-*p*-Anisyl-1-phenyl-1-propanol.** *p*-Anisylmagnesium bromide was added to phenyl ethyl ketone in the usual way giving the title alcohol, bp 200° (13–14 mm).[50] The pmr spectrum showed phenyl protons (main peaks) at −6.8 to −7.5 ppm (relative area 9.4), methoxyl protons (singlet) at 3.69 ppm (3), methylene (quartet, $^3J_{H-H} = 8$ cps) at −2.19 ppm (2), methyl protons (triplet, $^3J_{H-H} = 8$ cps ) at −0.79 ppm (3).

**2-Phenyl-2-butanol.** Acetophenone was added to excess ethylmagnesium iodide to give 2-phenyl-2-butanol, bp 100–103° (15 mm).[51,52] The pmr spectrum showed phenyl protons (main peak) at −7.31 ppm (relative area 5.4), OH (singlet) at −3.06 ppm (1), $CH_3$ (singlet) at −1.44 (3), $CH_2$ (quartet, $^3J_{H-H} = 6$ cps) at −1.73 ppm (2), $CH_3$ (triplet, $^3J_{H-H} = 7$ cps) at −0.73 ppm (3).

**2,3-Dimethyl-3-phenyl-2-butanol.** a. Attempts to prepare the title alcohol by adding α-cumylmagnesium chloride to acetone led only to the coupling product, 2,3-dimethyl-2,3-diphenylbutane, mp 118°.[53]

b. Methyl 2-methyl-2-phenylpropionate (prepared from the acid with diazomethane) was treated with an excess of methylmagnesium bromide in ether solution. The reaction mixture was worked up in the usual way and gave a 61% yield of the title alcohol, bp 96–102° (6 mm).[54]

The pmr spectrum exhibited phenyl protons (main peak) at −7.4 ppm (relative area 5.2), methyl protons at −1.4 (6) and at −1.1 ppm (6).

c. An easier method of preparing the alcohols was the addition of 2-methyl-2-phenylpropionic acid to an excess of methyllithium.

**3,3-Dimethyl-2-phenyl-2-butanol.** Attempted synthesis of the alcohol by action of *t*-butylmagnesium chloride[55] on acetophenone

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(41) W. A. Bonner and C. J. Collins, *J. Am. Chem. Soc.*, **75**, 5372 (1953).

(42) C. J. Collins and W. A. Bonner, *ibid.*, **77**, 92 (1955).

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(46) A. Klages, *Ber.*, **35**, 2646 (1902).

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(48) H. Gilman, R. E. Fothergill, and H. H. Parker, *Rec. Trav. Chim.*, **48**, 748 (1929).

(49) A. Klages, *Ber.*, **37**, 1723 (1904), gave 127–128° (14 mm).

(50) J. Levy, P. Gallais, and D. Abragam, *Bull. Soc. Chim. France*, [4] **43**, 875 (1923).

(51) A. Klages, *Ber.*, **35**, 3508 (1902).

(52) H. Wienhaus and W. Treibs, *ibid.*, **56**, 1651 (1923).

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(54) Reference 4 gave bp 81–82° (1 mm).

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gave only 10% of the title alcohol. The method of Brown and co-workers[4] was therefore used by addition of phenylmagnesium bromide to methyl *t*-butyl ketone (pivalone). A 41% yield of crude 3,3-dimethyl-2-phenyl-2-butanol was obtained, bp 90–94° (5 mm). The alcohol was purified by converting the traces of residual ketone to its oxime. The pmr spectrum of the pure alcohol shows the phenyl protons at −7.1 to −7.55 ppm (relative area 5.1) and the methyl protons at −1.50 (3) and −0.87 ppm (9). The infrared spectrum showed no carbonyl absorption.

**Pentaphenylethanol.** a. To an excess (0.2 mole) of a commercial (Foote Mineral Co.) solution of phenyllithium was added an ethereal solution of 10 g of triphenylacetic acid. The usual $N_2$ atmospheric dry conditions were observed. After refluxing for 1 hr, the reaction mixture was hydrolyzed with water, followed by aspiration of the ether layer to give a yellow oil which on recrystallization from petroleum ether gave 1.1 g of white crystals, mp 142–144°. After several recrystallizations, the melting point did not increase above 145°. The infrared spectrum gave an intense OH band at 3585 $cm^{-1}$. The nmr spectrum gave phenyl protons centering at −7.27 ppm and a hydroxyl proton (singlet) at −2.47 ppm. When calibrated with a known amount of TMS, integration of the nmr spectrum showed ~25 phenyl hydrogens.

b. Methyl triphenylacetate was prepared from triphenylacetic acid and diazomethane in the usual manner. The ester was obtained in 85% yield with mp 181–183°.[56] Its pmr spectrum contained phenyl protons (main peak) at −7.19 ppm (relative area 16) and methyl protons (singlet) at −3.76 ppm (3). The ester (4.5 g) was then slowly added to a 4-mole excess of phenyllithium in ether–benzene solution, refluxed for 2 hr, and worked up in the usual way. Trituration with petroleum ether gave white crystals of pentaphenylethanol (17% yield), mp 143–144°. *Anal.* Calcd for $C_{32}H_{26}O$: C, 90.10; H, 6.11. Found: C, 89.72; H, 6.26. An ebullioscopic molecular weight determination in THF gave mol wt 409 (calcd 426).

**2,2,2-Triphenylethanol.** Methyl triphenylacetate was reduced with ethereal $LiAlH_4$. A 63% yield of 2,2,2-triphenylethanol was obtained, mp 103–104°.[57] The pmr spectrum showed the phenyl protons (main peak) at −7.17 ppm (relative area 15.2), methylene protons (singlet) at −4.52 ppm (2.0), and the OH proton (singlet) at −1.38 ppm (1.0).

**1,1-Diphenyl-2-methyl-2-propanol.** Attempts to prepare the alcohol by addition of methyllithium directly to diphenylacetic acid gave poor results; therefore methyl diphenylacetate[58] was added to excess methyllithium in diethyl ether. An 18% yield of the title alcohol was obtained on usual work-up (product separated by column chromatography on silica gel).

A more convenient synthesis proved to be the addition of excess methylmagnesium bromide to 1,1-diphenyl-2-propanone in diethyl ether. Using this method an 85% yield of 1,1-diphenyl-2-methyl-2-propanol was obtained, bp 136–138° (4 mm). The pmr spectrum shows phenyl protons (main peak) at −7.30 ppm (relative area 10.3), the benzylic proton at −5.02 ppm (1), hydroxyl proton at −3.75 ppm (1), and the methyl protons at −1.15 ppm (6).

**2-*p*-Tolyl-2-butanol.** The alcohol was prepared in 54% yield by the addition of excess ethylmagnesium iodide to *p*-tolyl methyl ketone, bp 110–112° (11 mm).[59] The pmr spectra showed the aromatic protons ($A_2B_2$ quartet) at −7.25 ppm (relative area 4.2), OH at −3.08 ppm (1), methylene protons (quartet) at −2.73 ppm (2), methyl (singlet) at −2.31 ppm (3.1), methyl (singlet) at −1.42 ppm (3), methyl (triplet) at −0.63 ppm (2.9).

**Preparation of Phenylethyl Cation Complexes and Their Spectroscopic Investigation.** The samples of the carbonium ions were prepared by dissolving the precursor alcohol in $SO_2$ (or in pentane) at low temperature (~−60°) and adding this solution to a vigorously stirred 1:1 molar mixture of $FSO_3H$ and $SbF_5$ at −60°. The ratio of $FSO_3H$ to $SbF_5$ was increased when working at −78° where the solutions could become more viscous or start to solidify. Generally a large excess of $SO_2$ has to be used to prepare the solution. The solution was then concentrated by pumping off $SO_2$ at −78° to give a 5–8% concentration of ion complex in $FSO_3H–SbF_5–SO_2$.

The pmr spectra were taken on Varian Model A-60, A56-60A, and HA60IL spectrometers equipped with variable low-temperature probes operating generally at −60°. All spectra were obtained in 1:1 molar composition of $FSO_3H–SbF_5$ diluted with some $SO_2$ and using external TMS as reference (compared to a separate sample of TMS in chloroform; if compared to capillary reference TMS, all chemical shifts should be shifted by approximately 0.5 ppm to less shielding). The alcohol spectra themselves were run in $CCl_4$ solution with 5% internal TMS added as reference.

Ultraviolet spectra were taken on a Cary Model 15 spectrometer equipped with a low-temperature cell described previously.[1,60] Solutions of $10^{-1}$ to $10^{-3}$ *M* were used. These were prepared by adding a cold ethanol solution of the precursor alcohol to a solution of $FSO_3H–SbF_5$ at −60°. It has been shown that carbonium ions coexist with protonated ethanol in $FSO_3H–SbF_5$ solution at −60°.

**Hydrolysis of Phenylethyl Cations.** A typical procedure, as used in the case of the carbonium ion obtained from 3-phenyl-2-butanol, is the following. A solution of (30 ml) of fluorosulfonic acid and antimony pentafluoride was cooled to −70°. Then a solution of ~0.6 g of *erythro*- (*threo*-) 3-phenyl-2-butanol in about 20 ml of pentane was added from a syringe to the rapidly stirring acid solution. During addition of the pentane solution, the mixture (which is very pale straw yellow in color) was kept at −70° and was then hydrolyzed. The acid solution (separated from the pentane layer) was added to a rapidly stirring suspension of 150 g of powdered KOH, 200 g ice, and 500 ml $SO_2$ kept at −60°. Stirring was continued for 1 hr. The mixture was then extracted four times with 150 ml of pentane. Sulfur dioxide was distilled off, the solution was neutralized, and dried ($NaHCO_3$ and $Na_2SO_4$). After distilling off pentane, the hydrolysis-product alcohols were isolated (0.57 g, 78%) and analyzed by gas–liquid partition chromatography, infrared and nmr spectroscopy. The infrared and nmr spectra showed only 3-phenyl-2-butanols (and phenylmethylethylcarbinol), when compared with spectra of the pure starting materials. Resolving the recovered alcohols in $FSO_3H–SbF_5–SO_2$ gave identical spectra with those obtained from pure 3-phenyl-2-butanol.

In glpc analysis, using open tubular (capillary) columns, products were identified by comparison of glpc retention times and peak enhancement with authentic materials. In the case of packed column glpc analysis, products were also trapped and identified by comparison of infrared and nmr spectra with those of authentic materials.

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