In other media and at somewhat higher temperatures, nonexponential decay has been reported.[3]

We have studied triplet-state lifetimes also in random matrix but under conditions in which the temperature could be varied from *ca.* 100°K down to 3.0°K.[4] For simple aromatic molecules the lifetimes vary with temperature in generally the same way. At 80°K the nonradiative processes predominate and the emission is small; at 60° or so, the emission process becomes increasingly important at the expense of viscosity-related quenching processes[5] and, finally, at about 15°K the rates of decay do not change with temperature. These "adiabatic" rates are the subject of this communication and will be referred to simply as the triplet-state lifetimes. The compounds investigated were toluene, *p*-xylene, *p*-diethylbenzene, anisole, diphenyl ether, *p*-ethyltoluene, and ethylbenzene. Approximately 10^{-3} *M* solutions in a 9:1 mixture of methylcyclohexane–isopentane were studied over the temperature range of 3 to 110°K.

The triplet-state lifetime, as defined above, is dependent on at least two terms, the rate of emissive decay and the rate of an "internal quenching" process. The latter type of decay has been discussed by various authors,[6,7] and the relative magnitudes of the two in different types of molecules will probably continue to be debated for some time. Both processes are undoubtedly dependent on molecular structure and matrix interactions and most probably on such minor factors as intermolecular association, some ordering of the matrix liquid structure, and, perhaps, even "surface ordering" of the molecules receiving the largest amounts of exciting radiation. Of these, molecular structure seems to play the most important role, but little is known experimentally about which molecular parameters are of great influence—excepting the effects of large spin–orbit coupling atoms. We are now able to report an empirical relationship between the triplet-state lifetime and the electronic polarizability of the molecules indicated above. A plot of these two parameters is shown in Figure 1.

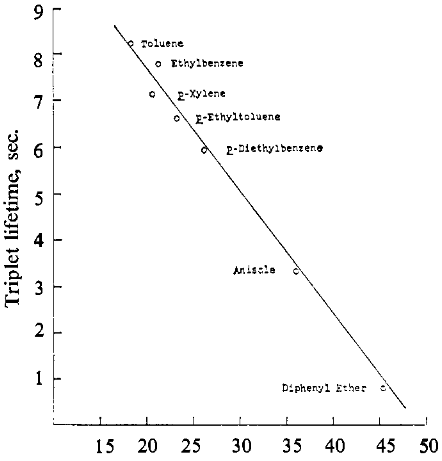

Figure 1. Electronic polarization *vs.* triplet lifetime.

Even though Figure 1 indicates a definite correlation between electronic polarizability and triplet lifetime, these terms are probably not independently related. How a measure of ground-state orbital distortion under the influence of an electric field can be directly related to the "forbiddenness" of a triplet–singlet transition has thus far escaped us. Intuitively, one suspects that both may be related to orbital mixing terms, but no uncontestable arguments can be presented.

These preliminary results suggest that future studies should include examination of other types of molecules with various functional groups, as well as an examination of the effects of heavy atoms, such as the halogens, which have rather large spin–orbit coupling factors, to determine the generality of this correlation.[8]

Acknowledgment. The authors wish to acknowledge the financial support (Grant P-058) of the Robert A. Welch Foundation and helpful discussion with R. G. Parr, W. H. Watson, and H. F. Hameka.

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(4) Employing an Air Products Helium Cryotip refrigeration device.

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(7) M. Gouterman, *ibid.*, **36**, 2846 (1962).

(8) A detailed description of our experimental procedures and theoretical speculations are available on request.

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Stable Carbonium Ions. XXX.[1] The *p*-Anisonium and 2,4,6-Trimethylphenonium Ions

Sir:

No direct observation of phenonium ion formation *via* phenyl participation from phenylethyl[2] or related systems (anthrylethyl[3]) in strong acid solutions has been achieved so far.

Phenylethyl cations, like the 3-phenyl-2-butyl cation, rearrange in strong acid systems (SbF_5–SO_2, FSO_3H–SbF_5–SO_2) to the more stable benzylic cations, with no evidence of bridged phenonium ion formation.[2]

The observation by Eberson and Winstein[3] 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 phenonium ion formation *via* aryl participation, that of the *p*-anisonium (I) and 2,4,6-trimethylphenonium (II) ions. Whereas our previous attempts to this effect[4] proved to be unsuccessful on closer reinvestigation,[2] we feel that evidence presented in this communication will stand up to any scrutiny and will provide conclusive evidence for phenonium ion formation *via* phenyl participation in strong acid solution.

Taking advantage of the known powerful participating effect of the *p*-anisyl[5] and mesityl group, we were

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(1) Part XXIX: G. A. Olah, N. Friedman, J. M. Bollinger, and J. Lukas, *J. Am. Chem. Soc.*, **88**, 5329 (1966).

(2) G. A. Olah, C. U. Pittman, E. Namanworth, and M. B. Comisarow, *ibid.*, **88**, 5571 (1966).

(3) L. Eberson and S. Winstein, *ibid.*, **87**, 3506 (1965).

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

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

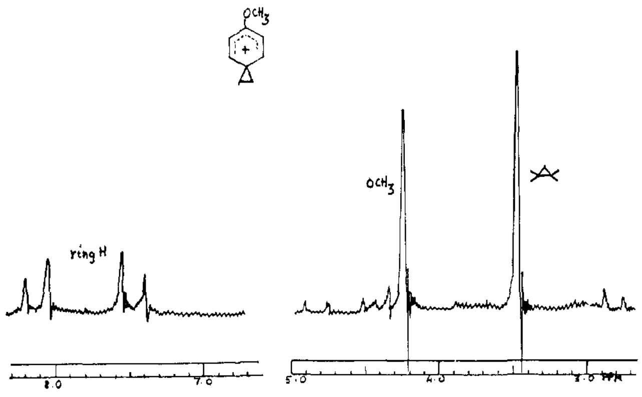
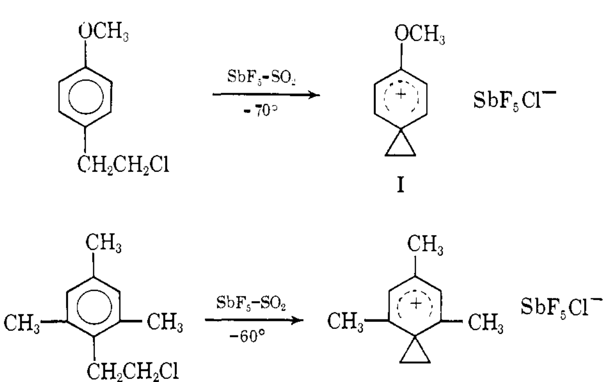


Figure 1.

able to observe the *p*-anisonium and 2,4,6-trimethylphenonium ions upon ionizing β-*p*-anisylethyl and β-mesityl ethyl chloride in SbF_5–SO_2 at −70°.



I

II

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.

The pmr spectrum of ion II (Figure 2) shows the 2- and 6-methyl protons at −2.38 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 5-ring protons at −7.66 ppm.

Attempts to generate the *p*-anisonium ion from β-anisylethanol in FSO_3H–SbF_5–SO_2 were unsuccessful because a stable diprotonated dication, III, is formed $((CH_3OH^+)C_6H_4CH_2CH_2O^+H_2)$.

In some preparations of the *p*-anisonium ion from β-*p*-anisylethyl chloride and SbF_5–SO_2 at higher temperatures, besides the anisonium ion there was present also smaller amounts of the benzylic *p*-anisylmethylcarbonium ion IV formed *via* obvious hydride shift from the open-chain primary carbonium ion in competition with bridging. The *p*-anisylmethylcarbonium ion (*p*-methoxystyryl cation) was observed in pure form from α-*p*-anisylethanol in FSO_3H–SbF_5–SO_2 or through its chlorosulfite in $SOCl_2$–SbF_5–SO_2.

Attempts to generate ion II from β-2,4,6-trimethylphenylethyl alcohol in excess FSO_3H–SbF_5–SO_2 resulted also only in a diprotonated ion (O and ring-C protonation). With 1 equiv of acid only the monoprotonated alcohol is formed.

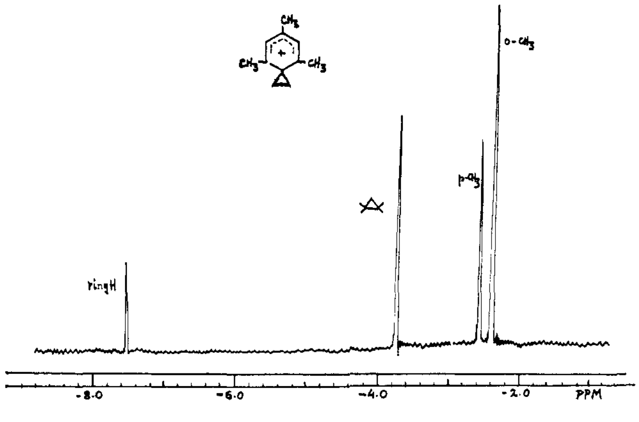
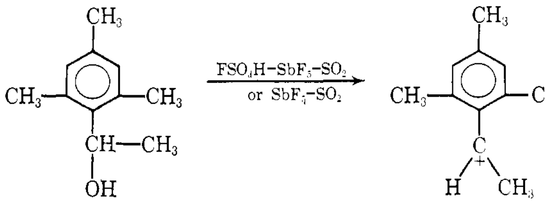


Figure 2.

In preparations of ion II at higher temperatures there was formed, besides the bridged 2,4,6-trimethylphenonium ion II, also smaller amounts of the benzylic 2,4,6-trimethylphenylmethylcarbonium ion (V). Ion V was obtained in pure form from α-2,4,6-trimethylphenylethyl alcohol in FSO_3H–SbF_5–SO_2 or SbF_5–SO_2 solution at −60°. The pmr spectrum of V 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.

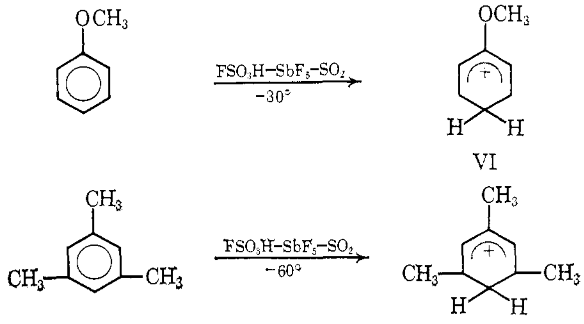


V

Quenching of the solutions I and II with methanol at −80° gives, in better that 80% yield, the β-methyl ethers $p\text{-}CH_3OC_6H_4CH_2CH_2OCH_3$ and $2,4,6\text{-}(CH_3)_3\text{-}C_6H_2CH_2CH_2OCH_3$, with some α-methyl ethers (and some styrene and polymer) as by-products.

Protonation of anisol[6–8] and mesitylene[9] with strong acids is well known.

The *p*-methoxybenzenonium ion (VI) and the 2,4,6-trimethylbenzenonium ion (VII) provide good models for the anisonium and 2,4,6-trimethylphenonium ions.



VI

VII

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The close correlation of spectra of I and II with VI and VII further substantiates the assignment of I and II as phenonium ions. The methoxy group is more deshielded in VI than in I because, in the latter, charge is delocalized also into the cyclopropane ring. This may also explain that even at $-70°$ in I rotation of the methoxy group is relatively free (less C–O double bond character than in ion VI), and the *ortho* ring protons are equivalent.

The AB quartets are well separated, indicating the benzenonium ion character of the ions and substantial differences in the shieldings of A and B. (This excludes Brown's suggested rapidly equilibrating π-bridged ions,[5b] because these should have phenyl, but not benzenonium character.) Further, the cyclopropyl protons in spiro[2.5]octa-1,4-dien-3-one were found by Baird and Winstein[10] as a sharp singlet. Eberson and Winstein observed the cyclopropyl protons in the bridged anthryethyl ion at -3.44 ppm.[3] Comparing these data with those of the *p*-anisonium ion I provides a strong case of direct analogy and further strengthens the assignment of I as a bridged phenonium ion.

All spectra (if otherwise not shown) were obtained at $-60°$ with external TMS as reference (sealed capillary tube). Acid peaks have been deleted, to simplify spectra.

From all data, we must conclude that we observed in SbF_5–SO_2 solution of β-*p*-anisylethyl and β-mesitylethyl chloride at $-60°$ the bridged *p*-anisonium and 2,4,6-trimethylphenonium ions, the first phenonium ion to be observed formed by direct aryl participation.

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

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

(11) National Science Foundation Postdoctoral Research Investigator, 1965–1966.

(12) National Science Foundation Predoctoral Research Investigator.

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Hindered Rotation around the S–S Bond in the Anomeric Di-5-(2′-deoxyuridilyl) Disulfides[1]

Sir:

We recently reported the synthesis of the anomeric 5-mercapto-2′-deoxyuridines.[2] These compounds readily undergo autoxidation[3] to the corresponding disulfides, I(α) and II(β). We found that the latter compounds show surprisingly large optical rotations compared to the original thiols or to their S-methyl derivatives,[4] III(α) and IV(β), respectively (see Figure 1).

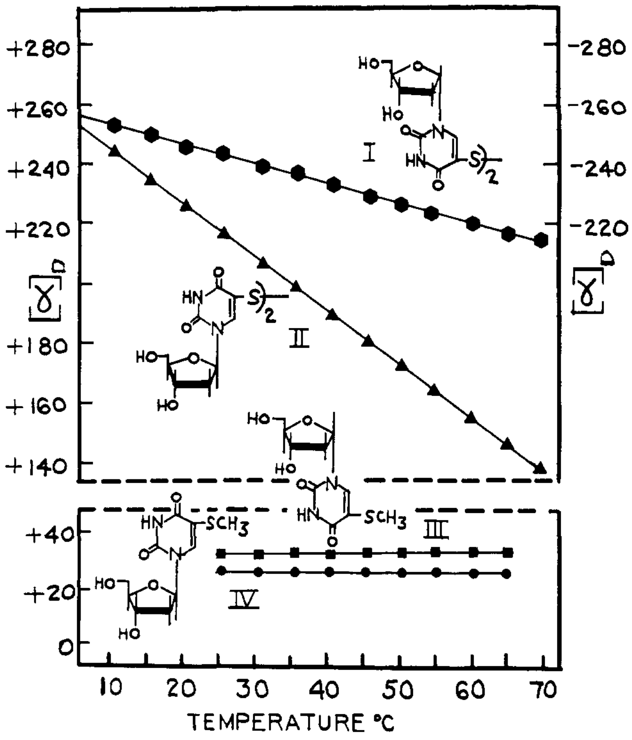

Figure 1. Temperature dependence of optical rotations: ⬢-⬢-⬢, compound I, negative $[\alpha]_D$ values (ordinate, scale at the right); ▲-▲-▲, compound II, positive $[\alpha]_D$ values (ordinate, scale at the left); ■-■-■ compound III, and ●-●-●, compound IV, low positive $[\alpha]_D$ values (ordinate, scale at the left).

The high optical rotatory power of cystine was noted by van't Hoff. Fieser[5] explained this apparent anomaly with the proposed formation of a system of three ten-membered rings with stable hydrogen bonds, while Fredga[6] attributed it to the proximity of the S–S bond to an asymmetric carbon atom. The latter view was also expressed by Balenovic, *et al.*,[7] who found that β-homocystine had a much higher specific rotation than homocystine; in the latter, the S–S bond is removed from the asymmetric carbon by one more methylene group. However, neither of these explanations seems to be satisfactory in the case of the title compounds in which the S–S bond is removed from the nearest asymmetric center of the molecule by three atoms of the pyrimidine ring.

More recently, Strem, *et al.*,[8] studied the optical rotatory dispersion of amino acids and suggested that the unusually large rotation and Cotton effect of cystine may be due to the asymmetric configuration of the S–S bond.[9] It has been suggested,[10] and demonstrated in the case of a number of disulfides,[11] that the valencies of two bonded sulfur atoms form a dihedral angle of about 90–100° (between the two S–S–C planes), resulting in two symmetrical energy minima for rotations around an S–S linkage.[12] The rotational barrier has been calculated for a few simple disulfides from spec-

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(1) This investigation was supported by Grant CA-06695 from the National Cancer Institute, U. S. Public Health Service, Bethesda, Md.

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(3) T. I. Kalman and T. J. Bardos, *J. Am. Chem. Soc.*, in press.

(4) The synthesis and properties of these compounds will be reported.

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