and the other through the energy minimum ($\phi = 115°$).

It is evident from Figure 1 that one structure is clearly favored. This structure corresponds to a pyramidal carbanion with the electron pair on carbon directed along the acute bisector of the OSO angle, *i.e.*, **1**. Figure 2 shows this more clearly. *The case II conformation is more stable than the case I conformation, but neither planar conformation is as stable as the pyramidal carbanion with the lone pair directed along the bisector of the OSO angle.*

A set of six GTF were used in the calculations to describe the d orbitals of sulfur, and for each of the molecular orbitals this set of functions could be transformed to a single 3s-type and a set of five 3d-type orbitals. The 3s-type orbital appears as an s-type function in the sulfur 1s and 2s cores, and the five d-type functions appear as a set of five nearly degenerate *antibonding* molecular orbitals. Thus, as in the earlier calculations,[10] and in contrast to the semiempirical results,[9] the nonempirical calculations appear to show no significant contribution to the structure of the carbanion from the d orbitals of sulfur. It must be noted, however, that ours is a *minimal* basis set calculation. Further work is now under way with improved (near Hartree–Fock) basis sets.

The present calculations suggest that the asymmetry of α-sulfinyl and α-sulfonyl carbanions need not be related to a possible existence of 3d-orbital conjugation. Rather, we now believe that the two species adopt an asymmetric structure as a consequence of the stereochemical requirements of two adjacent electron pairs or an electron pair and an adjacent dipole. This concept, which appears to have broad implications, will be examined in more detail in a forthcoming communication.[14]

Acknowledgments. The authors thank Professor D. J. LeRoy for his encouragement and the National Research Council of Canada for continuous financial support of this work and for the award of a special grant. Grateful acknowledgment is also made to the Institute of Computer Science of the University of Toronto and to the Department of Computing and Information Science of Queen's University for generous allocation of computing time.

(14) S. Wolfe, A. Rauk, and I. G. Csizmadia, in preparation.

(15) Holder of National Research Council Studentships, 1966–1968.

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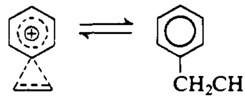
Static Bridged Carbonium Ions. Direct Nuclear Magnetic Resonance Observation of Stereochemically Distinct Ions

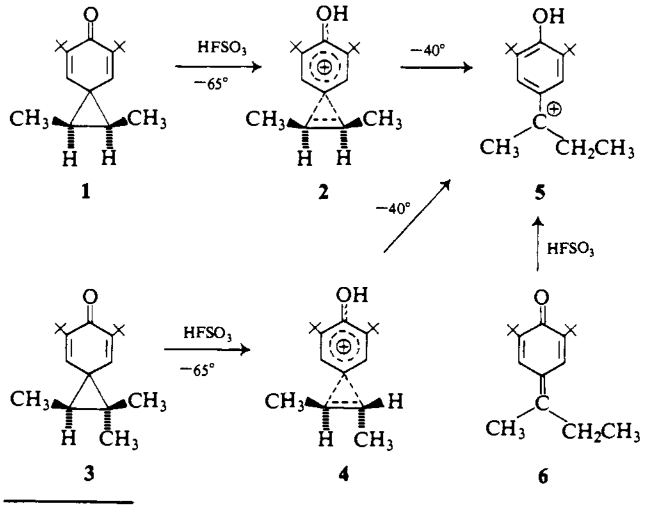
Sir:

Although substituted "ethylenephenonium" cations have now been directly observed under specialized conditions, the existing reports[1,2] of nmr observations of these cations provide no evidence with regard to the question of whether these bridged ions are static or are in rapid equilibrium with the corresponding open ions (see, *e.g.*, eq 1).[3] We wish to report the observation of two stereochemically distinct "ethylenephenonium" cations which could in principle interconvert *via* a nonbridged ion but which in actuality fail to do so.



(1)

Protonation of *cis*-1,2-dimethyl-5,7-di-*t*-butylspiro[2.5]octa-4,7-dien-6-one (**1**)[4] with fluorosulfonic acid at −65° affords a species whose nmr spectrum[5] (see Figure 1) is in accord with that expected for the *cis* ion **2**. The most significant features in the spectrum occur at low field where three one-proton singlets are observed at δ 8.30, 8.04, and 7.80. In deuterated fluorosulfonic acid, the resonance at δ 8.30 is absent from the spectrum of **2**. These resonances are ascribed to the hydroxyl proton and to the two nonequivalent vinyl protons, respectively.[6] Additionally, resonances at δ 4.60 (2 H), 1.88 (6 H), and 1.45 (18 H) are observed and ascribed to the methine, methyl, and *t*-butyl protons, respectively, in cation **2**. The spectrum persists unchanged for at least 1 hr at −65°, and no resonances attributable to the *trans* cation **4** are detectable. However, protonation of *trans*-1,2-dimethyl-5,7-di-*t*-butylspiro[2.5]octa-4,7-dien-6-one[4] (**3**) with fluorosulfonic acid at −65° does afford a species which has an nmr spectrum[5,7] (see Figure 2) in accord with that expected for the *trans* ion **4**. In particular, a singlet at δ 8.30 (1 H), a singlet at 7.95 (2 H), a broad singlet at 4.57 (2 H), a broad singlet at 1.79 (6 H), and a



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(1) L. Eberson and S. Winstein, *J. Amer. Chem. Soc.*, **87**, 3506 (1965).

(2) G. A. Olah, M. B. Comisarow, E. Namanworth, and B. Ramsey, *ibid.*, **89**, 5259 (1967).

(3) On the basis the chemical shifts observed for these cations, it is clear that they spend the greater fraction of their time bridged. However, one cannot infer from chemical shift measurements whether or not the ions are static or are opening and reclosing rapidly.

(4) G. F. Koser and W. H. Pirkle, *J. Org. Chem.*, **32**, 1992 (1967).

(5) Spectra were recorded on a Varian HA-100 nmr spectrometer and overlapping resonances were resolved and integrated by means of a DuPont 310 curve resolver. Chemical shifts are referenced to tetramethylsilane, using methylene chloride as a secondary internal standard.

(6) The weak coupling which is observed[4] between the nonequivalent vinyl protons in dienone 1 is not clearly resolved in the spectrum of ion **2**.

(7) Since a 3:1 mixture of the *trans* and *cis* dienones was actually used, the resonances previously ascribed to the *cis* cation **2** were observed as well as those of the *trans* cation 4. The relative ratio of the two ions is the same as the ratio of the two isomeric dienones prior to protonation.

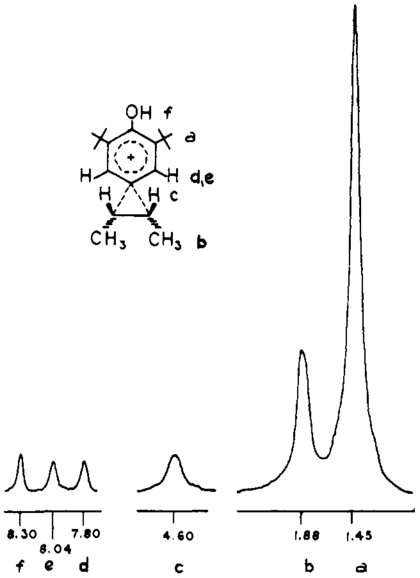

Figure 1. Nmr spectrum of cation **2** in FSO_3H, recorded at −65°. Relative areas[5] a:b:c:(d + e + f) = 18.0:6.0:2.4:2.8.

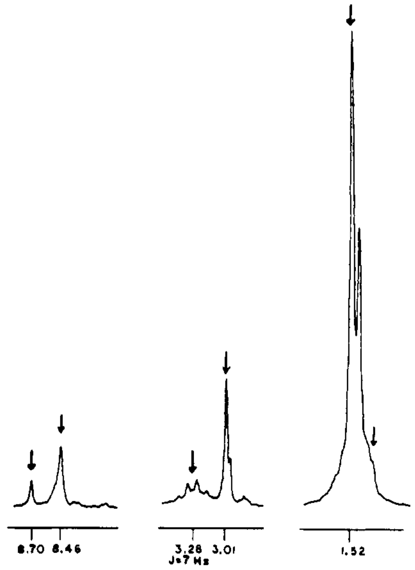

Figure 3. Nmr spectrum of the mixture obtained upon warming FSO_3H solutions of ion **2** or **4**, recorded at −25°. The marked resonances are assigned to benzylic cation **5**.

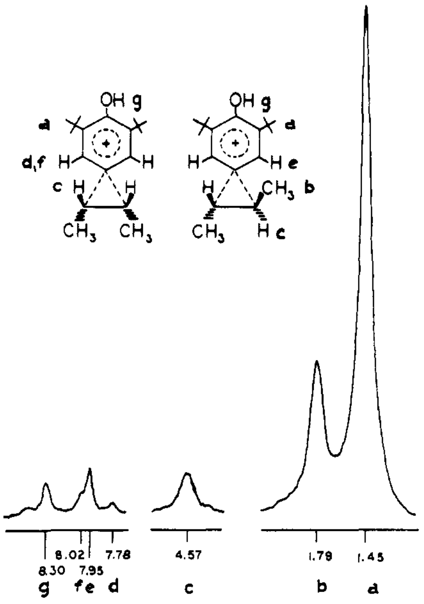

Figure 2. Nmr spectrum of a 3:1 mixture of cations **4** and **2** in FSO_3H, recorded at −65°. Relative areas[5] d:e:f:g = 0.24:1.5:0.30:0.93.

singlet at 1.45 (18 H) are observed. These resonances are presumed to arise from the hydroxyl, vinyl, methine, methyl, and *t*-butyl protons, respectively, in *trans* ion **4**. As required, the δ 8.30 resonance is absent in deuterated fluorosulfonic acid solvent.

Neither cation **2** nor cation **4** is observed to interconvert as the probe temperature is raised from −65 to −40°, although both slowly rearrange at −40° to afford the benzyl cation **5** as the major (>70%) product. Cation **5** is independently generated by fluorosulfonic acid protonation of quinone methide **6**[8] and, at −40°, exhibits singlets at δ 8.70 (1 H) and 8.46 (2 H), a quartet at 3.28 (2 H), a singlet at 3.01 (3 H), and a multiplet at *ca.* 1.5 (21 H). These signals are assigned to the hydroxyl, aryl, methylene, α-methyl, and overlapping *t*-butyl and methyl proton resonances, respectively. When the solution is brought to -25°, the spectra obtained from **1** and from **3** are identical (see Figure 3) but showed several resonances in addition to those originating from cation **5**. These unidentified resonances may come from a fraction (<30%) of the material in which *t*-butyl group loss or migration has occurred. During the warming process, a transient sharp singlet resonance is observed at δ 3.80 and is presumed to arise from the presence of free *t*-butyl cations since fluorosulfuric acid solutions of isobutylene give rise to a similar resonance (along with broad lines assumed to come from polymer).

The stereochemical integrity of cations **2** and **4** clearly requires that any nonbridged cation in equilibrium with **2** or with **4** must have a lifetime shorter than that required for rotation about a σ bond. This finding suggests strongly that cations **2** and **4** are static under the present conditions. Moreover, the observation that cations **2** and **4** do not interconvert at −40°, although both ions rearrange to benzyl cation **5** at this temperature, is consistent with (but does not require) the notion that benzyl cation **5** arises *via* a ring-opened (*i.e.*, a β-phenylethyl) cation.[9] In this event, the rearrangement would have to be appreciably faster than rotation about the σ bond and reclosure to a bridged cation.

Acknowledgment. This work has been supported by unrestricted grants in aid from the E. I. du Pont de

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(8) W. H. Pirkle and G. F. Koser, *Tetrahedron Lett.*, 129 (1968).

(9) The view that β-arylalkylcarbonium ions rearrange to benzylic cations whereas the corresponding bridged cations do not seems implicit in arguments advanced by prior workers in the field. However, we are aware of no data which require that this be so. For example, the kinetic deuterium isotope effects recently observed by workers at the University of California at Los Angeles and explained on the preceding basis [see M. Brookhart, F. A. L. Anet, D. J. Cram, and S. Winstein, *J. Amer. Chem. Soc.* **88**, 5659 (1966)] can also be rationalized by a mechanism involving concomitant migration and ring opening.

Nemours and Rohm and Haas Corporations, and technically assisted by R. L. Thrift and L. Brodsky.

(10) National Science Foundation Predoctoral Fellow, 1966–1968; Public Health Service Predoctoral Fellow, 1968–1969.

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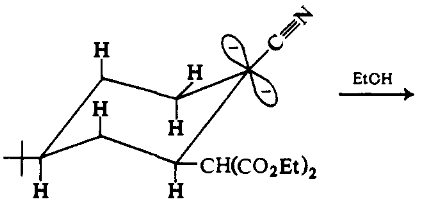
The Stereochemistry of Protonation of 2-Substituted Cyclohexyl Anions

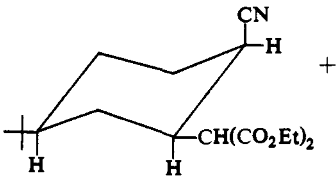
Sir:

There has been much discussion recently concerning the stereochemistry of C-protonation of nitronates and nitronic acids and of the ketonization of exocyclic enolates derived from ketones and esters,[1–4] but no concensus has been reached. We report some results in this area which throw light on the subject.

The addition of diethyl sodiomalonate in ethanol to 4-*t*-butyl-1-cyanocyclohexene *under conditions of kinetic control* gives mainly the *cis* product II together with some of the thermodynamically more stable *trans* isomer III.[5] Protonation of the intermediate delocalized anion I has, therefore, taken place from the equatorial side which, according to Zimmerman,[6] is the least hindered. It should be pointed out that, the nitrile group being linear, it would not be likely to give rise to any appreciable $A^{(1,3)}$ strain[1] in I, and that, in any event, the presence of the equatorial 4-*t*-butyl group in addition to the equatorial malonate group ensures that no chair–chair interconversion[1] can occur.

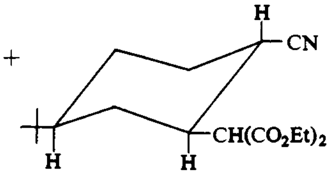


I



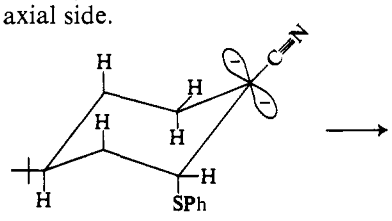
II

+

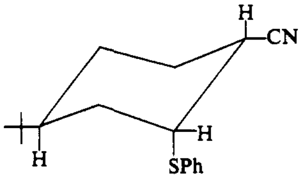


III

The addition of thiophenoxide ion to 4-*t*-butyl-1-cyanocyclohexene in ethanol gave a mixture of adducts: IV, mp 55–55.5°, and V,[7] bp 138–140° (0.1 mm), in which the thiophenoxy group was axial.[8] Under conditions of thermodynamic control (90 hr) the equilibrium mixture contained IV and V in the ratio 1.97:1. Under conditions of kinetic control (16 hr) the adducts were formed in the ratio of IV:V = 52.5:1; *i.e.*, IV was the main product of kinetic control of the protonation as well as the thermodynamically more stable isomer. Clearly, protonation of the intermediate anion VI in this case takes place more readily from the axial side, which is readily understood, as pointed out by Johnson and Malhotra,[1] in terms of the greater steric hindrance by the axial 2 substituent to the approach of the proton donor from the equatorial side than by the 3 and 5 axial protons to its approach from the axial side.

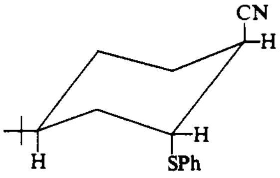


VI



IV

+



V

The situation in which the 1 substituent can give rise to $A^{(1,3)}$ strain with an equatorial 2 substituent, *but in which relief of such a strain by chair–chair interconversion is not possible*, was examined next. The addition of diethyl sodiomalonate in alcohol solution to ethyl 4-*t*-butylcyclohexene-1-carboxylate gave the intermediate enolate anion VII which, under conditions of kinetic control, gave VIII, mp 50.5–51.5°, and IX, bp 128° (0.05 mm), with VIII predominating.[9] Under thermodynamic control IX was the main product, as expected. Once again, approach from the equatorial side at C-1 appears to be the least hindered for the small proton donors (EtOH or CH_3CO_2H)[10] used in this work in spite of the presence of a bulky equatorial group at C-2.[11]

(1) F. Johnson and S. K. Malhotra, *J. Am. Chem. Soc.*, **87**, 5495 (1965); S. K. Malhotra and F. J. Johnson, *ibid.*, **87**, 5493 (1965); F. Johnson, *Chem. Rev.*, **68**, 375 (1968).

(2) F. G. Bordwell and M. M. Vestling, *J. Am. Chem. Soc.*, **89**, 3906 (1967).

(3) H. E. Zimmerman and P. S. Mariano, *ibid.*, **90**, 6091 (1968), and references cited therein.

(4) R. J. Sundberg and P. A. Bukowick, *J. Org. Chem.*, **33**, 4098 (1968).

(5) R. A. Abramovitch and D. L. Struble, *Tetrahedron*, **24**, 357 (1968); *Tetrahedron Letters*, 289 (1966).

(6) H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955).

(7) Satisfactory analyses and infrared, nmr, and mass spectral data were obtained for all the new compounds reported.

(8) R. A. Abramovitch, M. M. Rogić, and N. Venkateswaran, in preparation.

(9) When a solution of diethyl malonate (2 mol), ethyl 4-*t*-butylcyclohexene-1-carboxylate (2 mol), and sodium ethoxide (1 mol) in ethanol was kept at room temperature for 2 weeks only VIII was formed. When a relatively smaller amount of olefin was used (1.36 mol) the ratio of VIII to IX was 2.2:1. Equilibration of either VIII or IX with NaOEt in boiling EtOH gave a mixture of VIII and IX in the ratio of 1:5.2–7 (a considerable amount of reversal of the Michael addition was also observed with both isomers). The structures of VIII and IX were confirmed by their conversion under mild conditions to the corresponding known[5] *cis*- and *trans*-4-*t*-butyl-2-carboxymethylcyclohexanecarboxylic acids.

(10) A direct proton transfer from the equatorial malonate residue in I and VII is stereochemically unlikely. A referee has pointed out, however, that a solvent-mediated transfer of a proton from the malonate residue involving a six-membered-ring transition state may take place. It has been previously shown that ethanol is a much better proton donor than diethyl malonate in this reaction.[5]

(11) Any flattening of the cyclohexane ring from the chair conformation would tend to make approach from the axial side easier and from the equatorial side more difficult since it would increase the dihedral angle between the group at C-1 and the axial protons at C-3 and C-5 but decrease the angle between the carbethoxyl group and the axial protons at C-2 and C-6.