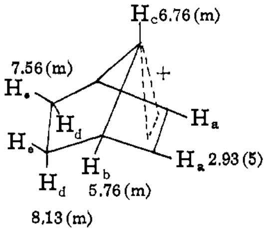
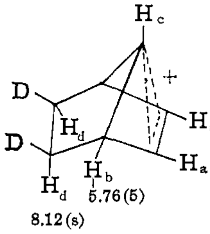
standard for the nmr spectra. These could be recorded at temperatures between −60 and −35°.

The nmr spectrum of ion II is summarized in formula VIII, chemical shifts (relative to internal CH_2Cl_2 taken as τ 4.70) and apparent multiplicities being indicated. Integrations were in good agreement with the expected values, with only a slight disturbance from broad, unresolved signals at τ *ca.* 7 and 8 due to side products formed in amounts varying from run to run. These were even less troublesome with the 5,6-*exo*-dideuterio cation IX, derived from the corresponding labeled I-OH, which in turn was prepared by $LiAlD_4$ reduction of 7-norbornadienyl acetate.[9] For cation IX, the *endo*-H_d proton signal is simplified to a singlet, making easier the separation of the disturbing signal in the integration of the spectrum in the H_d region. Coupling constants were estimated from proton and deuterium decoupling experiments on the deuterated ion at −60° (see IX).[10]

It was possible to store solutions of the cation II salt for long periods of time at liquid nitrogen temperatures. Quenching of such solutions in methanol gave rise to I-OCH_3 in greater than 50% yield. Cation II was also generated from tricyclic V-OCH_3 by the same method employed with I-OH. The same spectrum was obtained as from I-OH, except for somewhat more disturbance from side products. Also, a triplet methyl signal from the generated $CH_3OH_2^+$ species occurs in the region of the bridgehead H_b signal of cation II. This same methyl triplet and an accompanying OH_2 proton quartet are produced in control experiments using CH_3OH as substrate.

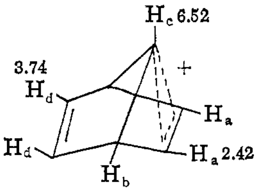


VIII



IX

J_{ac}	J_{bc}	J_{cd}
2.5	2.6	0.8 cps.



X

J_{ac}	J_{bc}	J_{cd}
2.7	2.8	1.0 cps.

As regards chemical shifts and coupling constants, the 7-norbornenyl cation II is quite analogous to the 7-norbornadienyl ion VII, as may be seen from comparing VIII and IX with X[7b] (VII-BF_4 in liquid SO_2, TMS as internal standard). As regards the protons on the three-center bonded carbon atoms, the H_c proton signal occurs at relatively high field relative to that of the H_a protons in both ions. While the nmr spectra alone do not give an unequivocal answer in favor of the nonclassical structures *vs.* equilibrating classical tricyclic ions such as IVab, they are perfectly consistent with nonclassical ions if we view the C_2–C_7–C_3 part of the structure as a distorted electron-deficient cyclopropane-like arrangement with positive charge considerably greater at C_2 and C_3 than at C_7.

Deno has viewed the 7-norbornenyl and 7-norbornadienyl cations as cyclopropylcarbonium ions and has formulated both species as equilibrating tricyclic ions such as IVab. Specifically in the case of the 7-norbornadienyl species, he has considered the C_7 or H_c proton signal to be too far upfield for a nonclassical formulation and in accord with the tricyclic one. However, such a point of view makes too little allowance for the great variation in charge distribution which results from hybridization changes at individual carbon atoms of a bridged ion such as II. As we have discussed elsewhere,[11] the bridging carbon atom in a bridged ion, *e.g.*, C_7 in II, has considerable tendency to rehybridize from sp^2 toward sp^3. Such rehybridization increases the C_7 Coulomb integral as well as C_7–C_2 and C_7–C_3 orbital overlap. This leads to net stabilization of the bridged ion, and these very features of rehybridization at C_7 tend to diminish the charge on this atom.

If one considers the nmr spectra along with all of the chemical and stereochemical evidence discussed in this and the previous communication,[2d] only a nonclassical formulation such as II for the 7-norbornenyl ion and one akin to VII for the 7-norbornadienyl species will account for all of the facts.[12]

Acknowledgment. We are grateful to Professor F. A. L. Anet for advice and assistance with the decoupling experiments.

---

[9] (a) B. Franzus and E. I. Snyder, *J. Am. Chem. Soc.*, **87**, 3423 (1965); (b) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

[10] Irradiation of H_b reduced the H_a signal to a doublet (J_{ac} = 2.5 cps) and the H_c signal to an ill-resolved triplet; irradiation of H_a also simplified the H_c signal to an ill-resolved triplet and the H_b signal became a doublet (J_{bc} = 2.6 cps); irradiation of H_d simplifies the H_c signal to a pentuplet; with deuterium decoupling the H_d signal becomes a doublet with J_{cd} = 0.8 cps, and irradiation of the H_c proton gives the H_a signal an A_2X_2 pattern with the separation between the two outer intense lines equal to 8.7 cps ($J_{ab} + J_{ab'}$).

[11] R. J. Piccolini and S. Winstein, *Tetrahedron*, **19**, 423 (1963).

[12] Further support for a symmetrical disposition of C_7 with respect to C_2 and C_3 is provided by extended Hückel calculations [R. Hoffman, *J. Am. Chem. Soc.*, **86**, 1259 (1964)]. A symmetrical structure II is also suggested by comparison with its 7-benzonorbornenyl analog. With the latter system, Tanida has shown the accelerating effects of 4′- and 5′-methoxyl groups to be additive. This indicates a symmetrical ionization transition state and, presumably, therefore, a symmetrical intermediate [H. Tanida, private communication; see *J. Am. Chem. Soc.*, **86**, 4904 (1964)].

[13] National Institutes of Health Predoctoral Fellow, 1965–1966.

M. Brookhart,[13] Arthur Diaz, S. Winstein
Contribution No. 1934, Department of Chemistry
University of California, Los Angeles, California 90024

Received April 4, 1966

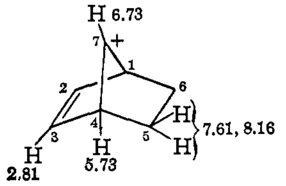
Direct Observation of Norbornenyl Cations

Sir:

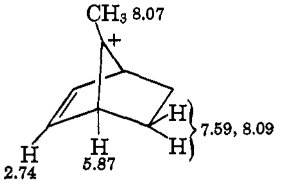
This communication reports the nmr spectra of the unsubstituted 7-norbornenyl cation (**1**), the 7-methyl (**2**) and 7-hydroxy (**3**) 7-norbornenyl cations, and the 2-hydroxy-2-norbornenyl cation (**4**). The importance of "homoallylic"[1] interactions in bicyclic systems such as **1**, **5**, and **6** has been evident from studies of rates and

---

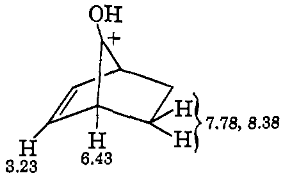
[1] This word was coined [S. Winstein, H. M. Walborsky, and K. Schreiber, *J. Am. Chem. Soc.*, **72**, 5795 (1950)] to describe interaction between a double bond and a center separated by an intervening carbon atom.



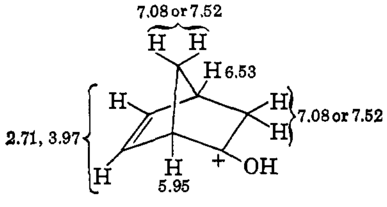
1



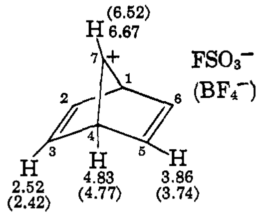
2



3



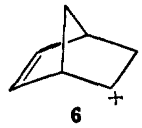
4



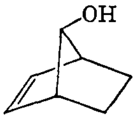
5

of products of solvolysis reactions that would be expected to form these ions as intermediates.[2] Nmr[3,4] and ultraviolet[5] spectra attributed to the norbornadienyl cation (**5**) are the only previously reported direct observations of such ions.

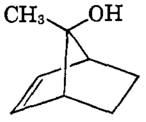
The cations were prepared by dissolving sulfur dioxide solutions of precursors in fluorosulfonic acid at −78° and the nmr spectra were observed at −60°. Ions **1** and **2** were prepared from **7** and **8**, respectively, **3** and **4** from the corresponding ketones, and **5** from 7-methoxynorbornadiene.[6] Chemical shifts are expressed in parts per million relative to tetramethylsilane as 10.0; tetramethylammonium chloride, used as an internal reference, was assumed to absorb at 6.90. The chemical shifts indicated on the structures are the approximate centers of absorptions that generally were complex multiplets, but in all cases had appropriate areas.



6



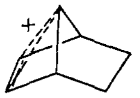
7



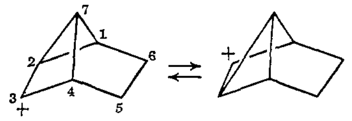
8

Comparison of the spectra of **1** and **2** indicates that introduction of a methyl group at C-7 leads to little alteration in the chemical shifts exhibited by hydrogens elsewhere in the ion and suggests that relatively little positive charge resides at C-7. In other carbonium ions, replacement of H by a methyl at a site where significant positive charge resides results in upfield shifts of absorptions of other hydrogens since less of the charge now is located in other positions. The upfield position of the absorption of the H at C-7 in the spectrum of the 7-norbornenyl cation is another indication that, contrary to the implication of structure **1**, relatively little charge is present at C-7.

Structures **9** and **10** represent two proposals[2] for the structure of the 7-norbornenyl cation.[7] In **10**, C-7 is assumed to be bonded more strongly to C-2 than to C-3.



9



10 11

If **10** is correct, then it must be in rapid equilibrium with **11**, since the nmr spectrum of each of the 7-norbornenyl cations (**1**–**3**) shows identical absorptions for hydrogens at C-2 and C-3 (and identical absorptions for hydrogens at C-1 and C-4 and for hydrogens at C-5 and C-6). The nmr observations do not indicate whether **9** or **10** ⇄ **11** is of lowest energy. However, even if **10** and **11** are more stable, their equilibration must involve passing through symmetrical geometry **9**. The energy barrier between **10** and **11** would be low since even at −60° equilibration would have to be rapid, and **9** therefore could not be of much higher energy than **10** and **11**.

The spectrum observed in fluorosulfonic acid for the 7-norbornadienyl cation is the same as that reported by Story for this ion generated from the reaction of 7-chloronorbornadiene and silver fluoroborate in sulfur dioxide (values in parentheses on structure **5**).[4] Story noted that C-7 must bond more strongly to one "double bond," since the hydrogens at C-2 and C-3 show a different nmr absorption than exhibited by the hydrogens at C-5 and C-6, though some bonding might also take place to the other double bond.[8] The similarity[9] in chemical shifts of comparable hydrogens (at C-2, C-3, and C-7) in **1** and **5** now suggests that C-7 does not bond strongly to C-5 and C-6 in **5**.

Solutions of the 7-norbornadienyl cation are stable for hours at room temperature in fluorosulfonic acid as evidenced by the nmr spectra of *1 M* solutions. More dilute solutions in fluorosulfonic acid exhibit a strong absorption at 352 mμ (ϵ ~11,000). This absorption could be attributed to the cation, though it has been reported[3] that there is no absorption above 330 mμ) in solutions of the cation in sulfur dioxide. An absorption at 350 mμ (ϵ ~5,000) has been observed[5] for sulfuric acid solutions, but the nmr spectrum of the ion has not been observed in the more concentrated solutions in sulfuric acid needed for nmr spectral observations.

Acknowledgments. We are grateful for support of this research by the National Science Foundation and by funds made available by the Alfred P. Sloan Foundation. The National Science Foundation provided funds to aid in the purchase of the Varian A-60 nmr spectrometer used in this research. We thank Arthur

---

[2] Reviewed by P. R. Story in a chapter prepared for "Carbonium Ions," G. A. Olah and P. von R. Schleyer, Ed., to be published by John Wiley and Sons, Inc., New York, N. Y.

[3] P. R. Story and M. Saunders, *J. Am. Chem. Soc.*, **82**, 6199 (1960); **84**, 4876 (1962).

[4] P. R. Story, L. C. Snyder, D. C. Douglass, E. W. Anderson, and R. L. Kornegay, *ibid.*, **85**, 3630 (1963).

[5] S. Winstein and C. Ordronneau, *ibid.*, **82**, 2084 (1960); see also H. G. Richey, Jr., and N. C. Buckley, *ibid.*, **85**, 3057 (1963).

[6] Though solvolysis reactions of derivatives of 2-norbornenol and nortricyclanol lead to **6**,[2] these alcohols apparently undergo other reactions in acids. *syn*-7-Norbornenol does not form **1** in acid. The reactions of these alcohols (H. G. Richey, A. S. Kushner, and R. K. Lustgarten, unpublished work) will be described later.

[7] Other structures with more extensive charge delocalization that have been considered involve the same symmetry problem.

[8] The problem of differentiating between symmetrical and unsymmetrical bonding of C-7 to C-2 and C-3 that was discussed for **1** exists also for **5**.

[9] Carbon charge distributions were predicted for **2** and **5** on the basis of extended Hückel calculations [R. Hoffmann, *J. Am. Chem. Soc.*, **86**, 1259 (1964)].

S. Kushner for assistance in obtaining the nmr spectra and Dr. W. C. Baird, Jr., for a sample of *syn*-7-norbornenol. We are grateful to Professor S. Winstein for delaying the publication of his study (see adjoining communication) of the 7-norbornenyl cation so that our work could be published at the same time.

[10] Alfred P. Sloan Foundation Research Fellow.

[11] Supported (1964–1966) by a Fellowship (5-F1-GM, 23-26-302) from the National Institute of General Medical Sciences.

Herman G. Richey, Jr.,[10] Ronald K. Lustgarten[11]
Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802

Received April 30, 1966

Mechanisms of Thermal Racemization of Sulfoxides[1]

Sir:

It has long been known that sulfoxides suffer stereomutation on heating at elevated temperatures.[2] We now wish to report preliminary results of a study aimed at correlating the rates of racemization of optically active sulfoxides with their structures. We restricted our investigation to sulfoxides which are incapable of β elimination.[3] Salient results are collected in Table I.

Table I. Thermal Racemization of Sulfoxides, $RSOC_6H_4CH_3$-*p*[a]

R	Compd no.	Temp range, °C	k_R/k_{Ph}[b]	ΔH^*, kcal/mole	ΔS^*, eu
CH_3	**1**	240–260	0.24[c]	43	+3
p-$CH_3OC_6H_4$	**2**	210	0.60		
C_6H_5	**3**	200–220	1.0	39	0
p-$CF_3C_6H_4$	**4**	210	1.9		
o-$CH_3C_6H_4$	**5**	200–220	2.2	37	−2
α-$C_{10}H_7$	**6**	210	2.3		
2,4,6-$(CH_3)_3C_6H_2$	**7**	180–200	53.0[d]	34	−3
$C_6H_5CH_2$	**8**	135–155	2.8×10^3 [e]	43	+24
$CH_2{=}CHCH_2$	**9**	50–70	5.6×10^5 [f]	22	−9

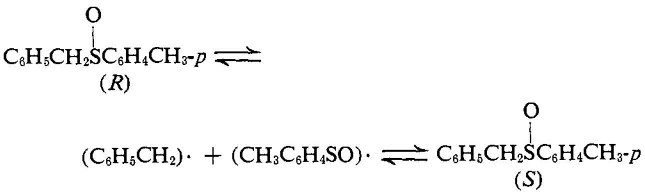
[a] In *p*-xylene or benzene. [b] First-order rate constant, k_R, of $RSOC_6H_4CH_3$-*p*, relative to that of phenyl *p*-tolyl sulfoxide, k_{Ph}, at 210° ($k_{Ph}^{210} = 3.19 \times 10^{-5}$ sec^{-1}); k_R^{210} values for **1** and **7–9** were obtained by extrapolation. [c] $k_R^{250} = 6.7 \times 10^{-5}$ sec^{-1}. [d] $k_R^{190} = 3.7 \times 10^{-4}$ sec^{-1}. [e] $k_R^{145} = 7.3 \times 10^{-5}$ sec^{-1} corrected for decomposition. [f] $k_R^{60} = 4.0 \times 10^{-4}$ sec^{-1}.

The rates of racemization of **1–7** are cleanly first order, and the racemized products are structurally identical with the starting materials.[4] While the rates are relatively insensitive to electronic effects, a steric factor appears to be operative, for the attachment of bulky groups to the sulfur atom leads to an increase in the rate of racemization. In the thermal racemization of sulfoxides the steric factor operates in the reverse direction from that observed[7] in the hydrogen chloride catalyzed racemization.

As the simplest working hypothesis, we assume that racemization of **1–7** proceeds by a *pyramidal inversion mechanism* and does not involve bond breaking. According to this model, the nonbonded repulsive interaction between the groups attached to the sulfur atom will be more important in the ground state than in the planar or near-planar transition state. This interpretation has its analogy in the B-strain hypothesis which has been invoked to account for the acceleration of solvolysis rates of tertiary halides.[8]

The thousandfold enhancement in rate of racemization of **8** over sulfoxides **1–7** is not accommodated within the framework of the above mechanism. It had previously been noted[9] that **8** was "more thermolabile" than the stereoisomeric 4-*t*-butylthiane 1-oxides, but no explanation for the accelerated rate of racemization was offered other than the comment that "conjugation between the tolyl and sulphoxide groups is possible" in **8**. However, as indicated above, such conjugation is incapable of accounting for the results since in **1–7** temperatures in excess of 180° are required to effect convenient measurements of racemization rates.

In contrast to the racemization of **1–7**, the racemization of **8** is accompanied by decomposition. Three of the decomposition products have been identified as dibenzyl, *p*-tolyl *p*-toluenethiolsulfonate, and benzyl *p*-tolyl sulfide. The first two products arise from radical dimerization: it is known that arenesulfinyl radicals (ArSO) couple and rearrange to give thiolsulfonates.[10] The rate of racemization at 145° is about four times the rate of decomposition and in xylene a greater variety of pyrolysis products is noted than in benzene. These observations argue for the presence of radicals and suggest that **8** suffers racemization by a *homolytic dissociation mechanism.*



$$\underset{(R)}{C_6H_5CH_2\overset{\overset{\displaystyle O}{|}}{S}C_6H_4CH_3\text{-}p} \rightleftharpoons (C_6H_5CH_2)\cdot + (CH_3C_6H_4SO)\cdot \rightleftharpoons \underset{(S)}{C_6H_5CH_2\overset{\overset{\displaystyle O}{|}}{S}C_6H_4CH_3\text{-}p}$$

The activation parameters for the racemization of **8** support this conclusion. The low value of the bond dissociation energy of the carbon–sulfur bond, whose upper limit is 43 kcal/mole, is related to the stability of the two radicals, the one because it is a benzyl radical,[11] and the other because it is a *p*-toluenesulfinyl radical.[10,12] That the $ArCH_2$–S bond in sulfoxides of structure type **8** is notably weak had previously been

[1] This work was supported by the National Science Foundation under Grants No. GP-757 and GP-3375.

[2] K. Fries and W. Vogt, *Ber.*, **44**, 756 (1911); H. Baw, G. M. Bennett, and P. Dearns, *J. Chem. Soc.*, 680 (1934); G. Farina, F. Montanari, and A. Negrini, *Gazz. Chim. Ital.*, **89**, 1548 (1959); H. B. Henbest and S. A. Khan, *Proc. Chem. Soc.*, 56 (1964); K. Mislow, P. Schneider, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **86**, 2957 (1964); C. R. Johnson and D. McCants, Jr., *ibid.*, **86**, 2935 (1964); **87**, 1109 (1965).

[3] C. A. Kingsbury and D. J. Cram, *ibid.*, **82**, 1810 (1960); V. E. Cates and C. E. Meloan, *Anal. Chem.*, **35**, 658 (1963); C. Walling and L. Bollyky, *J. Org. Chem.*, **29**, 2699 (1964); T. J. Wallace, *J. Am. Chem. Soc.*, **86**, 2018 (1964); D. N. Jones and M. A. Saeed, *Proc. Chem. Soc.*, 81 (1964); S. I. Goldberg and M. S. Sahli, *Tetrahedron Letters*, **No. 49**, 4441 (1965); I. D. Entwhistle and R. A. W. Johnstone, *Chem. Commun.*, 29 (1965); D. G. Barnard-Smith and J. F. Ford, *ibid.*, 120 (1965).

[4] These compounds were prepared by the Grignard synthesis.[5,6] All new compounds gave satisfactory elemental analyses.

[5] K. K. Andersen, W. Gaffield, N. E. Papanikolaou, J. W. Foley, and R. I. Perkins, *J. Am. Chem. Soc.*, **86**, 5637 (1964).

[6] K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *ibid.*, **87**, 1958 (1965).

[7] K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *ibid.*, **86**, 1452 (1964).

[8] H. C. Brown, *Science*, **103**, 385 (1946).

[9] H. B. Henbest and S. A. Khan, *Proc. Chem. Soc.*, 56 (1964).

[10] D. Barnard, *J. Chem. Soc.*, 4673 (1957); D. Barnard and E. J. Percy, *Chem. Ind.* (London), 1332 (1960); R. M. Topping and N. Kharasch, *J. Org. Chem.*, **27**, 4353 (1962).

[11] T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publications, London, 2nd ed, 1958, p 60.

[12] J. L. Kice and N. E. Pawlowski, *J. Am. Chem. Soc.*, **86**, 4898 (1964).