alcohols the RO–H bond strength is *ca.* 104 ± 1 kcal/mol,[5] the stabilizing effect of the alkyl group manifests itself in the electron affinity of the alkoxy radical. The stabilization observed is consistent with a model in which the alkyl groups, being polarizable, stabilize the charge by an induced dipole.[7] It is to be expected that methyl or methylene groups will be more effective than hydrogen in stabilizing both positive and negative charges and that such stabilization will be of more importance in the gas phase than in solution. The effect of alkyl groups in charge stabilization has been discussed extensively by Schubert.[8] Our observations are consistent with his picture.

The results obtained here are reversed from the "normal" inductive order observed in solution.[9] Thus, in contrast to the solution behavior, *t*-butoxide in the gas phase is less basic than methoxide. This relatively enhanced basicity of *t*-butoxide in solution may be due, in part, to less effective hydrogen bonding and considerable shielding of the negative charge from the bulk solvent by the alkyl groups. Naturally, the bulk properties of the solvent are of great importance, and acidities in *t*-butyl alcohol solvent are not directly comparable with those in methanol. In general, intrinsic acidities may well be expected to differ drastically from solution acidities in which specific solvation, dispersion forces, and steric effects can be large and determining factors.[10] Consequently, solution p*K*'s are complex functions of the medium as well as a reflection of intrinsic acidity.

To explore further the effect of alkyl groups on charges, we have, by ICR and pulsed double-resonance studies, confirmed the results of Munson[11] on the relative basicities of aliphatic amines. The basicities are $Me_3N > Me_2NH > MeNH_2 > NH_3$. Thus, in the gas phase, the "normal" order holds, uncomplicated by solvation and steric effects. In solution, the "intrinsic" basicities are obscured, probably by steric hindrance to solvation. In the gas phase, we assume that the polarizability is an important factor.

Finally, we have found that the acidity of toluene is approximately equal to that of ethanol. Since the bond strength in toluene[12] is *ca.* 19 kcal/mol lower than that in ethanol, the electron affinity of benzyl radical must also be *ca.* 19 kcal/mol lower than that of ethoxy radical. Thus, the increased electronegativity of oxygen enhances the intrinsic acidity of alcohols by its contribution to the electron affinity. Further work will clarify the importance of these effects in a wider range of compounds.

Acknowledgment. We thank Professor J. D. Baldeschwieler for helpful discussions and J. V. Garcia for technical assistance. We gratefully acknowledge support from the National Science Foundation (GP-4924-X; GP-6736), the National Institutes of Health (GM-145752-02), the donors of the Petroleum Research Fund administered by the American Chemical Society (2917-A4), the National Aeronautics and Space Administration (NGR-05-020-250), and the Center for Materials Research, Stanford University.

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[4] A. Streitwieser, Jr., and J. H. Hammons, *Progr. Phys. Org. Chem.*, 3, 41 (1965).

[5] S. W. Benson and R. Shaw in "Oxidation of Organic Compounds-I," Advances in Chemistry Series, No. 75, American Chemical Society, Washington, D. C., 1968. The bond dissociation energy of water is substantially higher.[6] Thus, it is difficult to draw direct comparisons between water and the simple alcohols.

[6] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966); S. W. Benson, *J. Chem. Educ.*, 42, 502 (1965).

[7] E. A. Moelwyn-Hughes, "Physical Chemistry," Pergamon Press, New York N. Y., 1957.

[8] W. M. Schubert, R. B. Murphy, and J. Robins, *Tetrahedron*, 17, 199 (1962). It is particularly interesting to note the effect of neopentyl.

[9] The polar effect of alkyl groups in saturated systems has received considerable attention: F. W. Baker, R. C. Parish, and L. M. Stock, *J. Amer. Chem. Soc.*, **89**, 5677 (1967), and references cited therein; V. W. Laurie and J. S. Muenter, *ibid.*, **88**, 2883 (1966). In general the effect appears to be small.

[10] See C. D. Ritchie and R. E. Uschold, *ibid.*, **90**, 2821 (1968), for relevant comments.

[11] M. S. B. Munson, *ibid.*, 87, 2332 (1965).

[12] R. Walsh, D. M. Golden, and S. W. Benson, *ibid.*, **88**, 650 (1966).

[13] A. P. Sloan Fellow.

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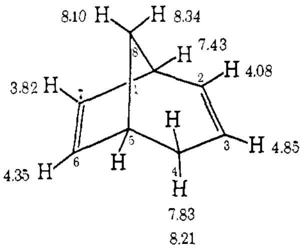
The Bicyclo[3.2.2]nonatrienyl Anion. The Anionic Analog of the Norbornadienyl Cation[1]

Sir:

The successful generation and direct observation of the first homoaromatic carbanion[2,3] (II) prompted us to look for other anions which show evidence of similar electron delocalization. The importance of delocalization in, and the stability of, the norbornadienyl cation[4] suggested that the anionic analog of this cation, the bicyclo[3.2.2]nonatrienyl anion, would be interesting. Recently Goldstein[5] has used MO symmetry arguments to propose that this anion would have enhanced stability. We now wish to report the direct observation of the anion IV and evidence for its homoaromatic character.



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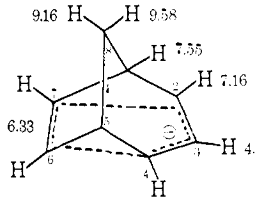

II

Stable solutions of the anion[6] IV are readily prepared by Na–K alloy cleavage of 4-methoxybicyclo[3.2.2]nonatriene-2,6,8 (III-OMe). This ether,[7] bp 31–32° (0.5 mm), was prepared by methylation[8] of the corre-

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[1] Research supported by the National Science Foundation.

[2] S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *J. Am. Chem. Soc.*, **89**, 3656 (1967).

[3] (a) J. M. Brown, *Chem. Commun.*, 639 (1967); (b) J. M. Brown and J. L. Occolowitz, *J. Chem. Soc.*, *B*, 411 (1968).

[4] (a) S. Winstein and C. Ordronneau, *J. Am. Chem. Soc.*, **82**, 2084 (1960); (b) P. R. Story and M. Saunders, *ibid.*, 84, 4876 (1962); (c) M. Brookhart, R. K. Lustgarten, and S. Winstein, *ibid.*, **89**, 6352 (1967).

[5] M. J. Goldstein, *ibid.*, **89**, 6357 (1967).

[6] Only slight signs of decomposition of the anion to yield the hydrocarbon III-H were detectable after 3 weeks at room temperature or 16 hr at 70° in DME.

[7] All new compounds gave satisfactory carbon and hydrogen analyses and/or mass spectra. Structures were assigned on the basis of the usual chemical and spectral criteria.

[8] U. E. Diner, F. Sweet, and R. K. Brown, *Can. J. Chem.*, 44, 1591 (1966).

sponding alcohol[9] III-OH. III-OMe was cleaved in DME to yield IV in the manner previously described.[2] The resulting green carbanion solution is quite stable[6] and is only slightly contaminated with small amounts of the [3.2.2]hydrocarbon III-H. The salt is remarkably insoluble in DME (~1 mg/ml at 25°), but increased temperature increases the solubility. More concentrated solutions can be obtained in diglyme. Part of the spectrum of the anion was obscured by the solvent, but this problem can be largely avoided in DME-d_{10}.

$$\text{III-OH} + \text{MeI} \xrightarrow[\text{DME}\\ 25^\circ]{\text{NaH}} \text{III-OMe} \xrightarrow[\text{DME}\\ -10^\circ]{\text{Na-K}} \text{IV}$$

$$\text{IV} \xrightarrow[25^\circ]{\text{MeOH}} \text{III-H} + \text{III–III}$$

Quenching the carbanion solutions[10] with MeOH gave an essentially quantitative yield of hydrocarbon[11] III-H together with some dimer,[7,12] III–III. The structure of these compounds was shown by ir,[11] nmr, and mass spectra, and vpc confirmed III-H as the only volatile component of the quench (<0.5% barbaralane or indan was detected).

In the nmr spectrum of the anion, the bridgehead protons, H_1 and H_5, appear at τ 7.71 as a septet which arises from a symmetrical quintet (corresponding to the A portion of an A_2X_4 pattern)[13] with a spacing of 3.8 Hz, each line of which is further split into a doublet ($J_{1,2}$ = 7.6 Hz) due to coupling with $H_2(H_4)$. The outermost lines of this multiplet are weak and of comparable intensity to the noise. Each of the lines is broadened by long-range coupling to H_3 ($J_{1,3} \sim 1.0$ Hz). Irradiation at the H_6 frequency collapses the multiplet to a broadened doublet ($J_{1,2}$ = 7.6 Hz).

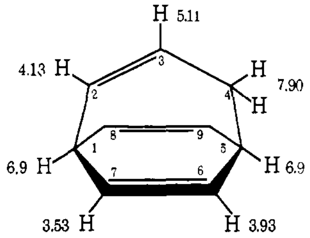
The allylic protons, H_2 and H_4, absorb at τ 6.95 as a triplet arising from equal coupling with H_1 and H_3 ($J_{1,2} = J_{2,3}$ = 7.6 Hz). Irradiation at either H_1 or H_3 collapses this triplet to a doublet. The presence of a small coupling with H_7 ($J_{2,7}$ = 1.5 Hz) was indicated by decoupling experiments.

The central proton, H_3, occurs as a simple triplet at τ 4.76 coupled to H_2 and H_4 ($J_{2,3}$ = 7.6 Hz) with broadening due to long-range coupling with H_1. Irradiation at H_2 reduces this triplet to a broad singlet, while irradiation at H_1 sharpens the triplet.

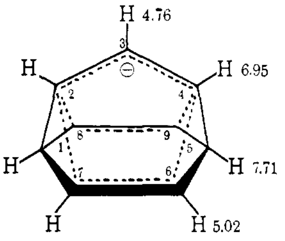
The vinyl protons, H_{6-9}, appear at τ 5.02 as a symmetrical six-line pattern corresponding to the X portion of the A_2X_4 pattern.[13] Irradiation at the H_1 frequency collapses the multiplet to a triplet ($J_{2,7}$ = 1.5 Hz).

The nmr spectrum of the anion is completely consistent with the delocalized, homoaromatic structure IV. The chemical shift differences between the anion IV and the parent hydrocarbon III-H provide strong evidence for substantial delocalization of the negative charge to C_6, C_7, C_8, and C_9. In particular, the considerable upfield shift of the vinyl protons, H_{6-9}, in IV relative to III-H strikingly demonstrates this point. No more than 0.8 ppm of this shift can be attributed to field effects.[15,16] The chemical shifts observed for the allylic protons, H_2 and H_3, are very reminiscent of those reported for these protons in the bishomocyclopentadienyl anion II. The shielding of the bridgehead protons can be ascribed predominantly to field effects.[15]

τ values in DME-d_{10}



III-H



IV

J	1,2	1,3	1,6	1,7	2,3	
Hz	8.0	~1.0	1.6	6.7	10.5	
J	2,4	3,4	4,5	5,6	5,7	6,7
Hz	<1	3.0	2.5	6.3	1.6	7.8

J	1,2	1,3	1,5	1,6
Hz	7.6	~1.0	~0.7	1.8
J	1,7	2,3	2,7	6,7
Hz	6.4	7.6	~1.5	7.5

The question still remains as to whether IV exists as a symmetrical structure or whether it is undergoing a rapid (on the nmr time scale) "bridge flip" similar to that observed for the norbornadienyl cation.[4c] The nmr spectrum of IV in diglyme shows no detectable change over the range −35 to 100°. So, if "bridge flipping" is occurring in IV, the free-energy barrier for the process must be ⩽11.8 kcal/mol (*cf.* norbornadienyl cation barrier,[4c] ⩾19.6 kcal/mol).

Until we investigate additional anions we do not know the quantitative influence of the second vinyl bridge on the bishomocyclopentadienyl system in IV. This is of interest with regard to Goldstein's designation[5] of IV as a bicycloaromatic ion. This term was proposed to describe a bicyclic ion with three π bridges which possesses enhanced thermodynamic stability (measured or predicted) when compared with a suitably chosen isoelectronic bicyclic ion with two π bridges as a reference. In Goldstein's system the bicycloaromatic ions are all bishomoaromatic in two of the three π bridges, and the corresponding reference ions are all antibishomoaromatic.[17] It seems to us that the most interesting question has to do with the effect of the additional π bridge which converts a bishomoaromatic ion to a bicycloaromatic one.

Preliminary experiments have indicated the occurrence of a degenerate nine-carbon rearrangement process in anion IV. A MeOH quench of the anion generated from 4-D-III-OMe after 2 days yielded hydrocarbon III-H and dimer III–III with the deuterium essentially completely scrambled. On the other hand, the spectrum of the anion solution immediately after preparation showed essentially no scrambling. A degenerate nine-carbon scrambling process could be formulated as proceeding *via* a series of 1,2 shifts or

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(9) M. J. Goldstein and B. G. Odell, *J. Am. Chem. Soc.*, **89**, 6356 (1967).

(10) The anion was also present as a precipitate in the solutions which were quenched.

(11) M. Jones and S. D. Reich, *J. Am. Chem. Soc.*, **89**, 3935 (1967).

(12) This dimer had a broad melting point range (88–120°), but good analysis and spectra, which suggest that it is a mixture of *meso* and *dl* diastereomers.

(13) The H_1 and H_6 patterns were satisfactorily simulated by the spin-spin coupling program of Bothner-By[14] (LAOCN3). The calculation assumed that these six protons formed an AA'XX'X''X''' system with the chemical shifts and coupling constants given.

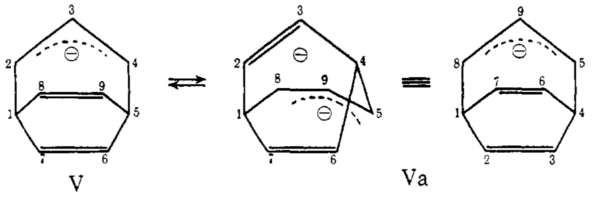
(14) A. A. Bothner-By and S. Castellano, *J. Chem. Phys.*, **41**, 3863 (1964).

(15) (a) The through-space electric field effects arising from the excess negative charge were estimated from a semiempirical equation developed by J. B. Grutzner and L. M. Jackman; (b) J. B. Grutzner, Ph.D. Thesis, Melbourne, 1967.

(16) It is interesting to note that in the norbornadienyl cation[4c] the protons on the "bound" vinyl group are shifted to about the same extent as the vinyl protons in anion IV.

(17) S. Winstein, Special Publication No. 21, The Chemical Society, London, 1967, p 5.

equivalently *via* a barbaralyl intermediate (V ⇌ Va ⇌ etc.). This matter, together with the synthesis of metal complexes of IV, is presently under investigation.



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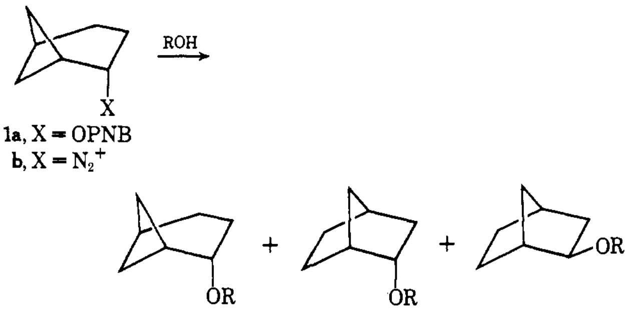
A Novel σ Route to the Norbornyl Cation

Sir:

We have investigated the formation of norbornyl cations by rearrangement of various norpinyl (bicyclo[3.1.1]heptyl) precursors.

Tosylation (TsCl, pyridine, 0°) of norpinan-2-ol (**2a**)[1] afforded *endo*-norbornan-2-yl tosylate, indistinguishable by melting point and ir from an authentic sample.[2,3] The *p*-nitrobenzoate of norpinan-2-ol (**1a**), mp 89–90°, was solvolyzed in 66.7% aqueous acetone (sealed tube, 120°, 240 hr, *ca.* 30% conversion) to give **2a** (3.5%), **3a** (34%), and **4a** (62.5%). Attempts to separate the recovered mixture of *p*-nitrobenzoates by tlc failed, but reduction with $LiAlH_4$ afforded **2a** (58.2%), **3a** (36.5%), and **4a** (5.3%).

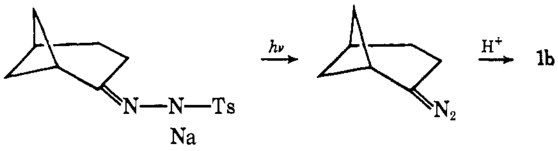


1a, X = OPNB
b, X = N_2^+

2 **3** **4**
a, R = H; **b**, R = CH_2CH_3; **c**, R = CH_2CF_3;

Rearrangement with internal return, producing *endo*-norbornan-2-yl *p*-nitrobenzoate, appears to be a major primary step in the solvolysis of **1a**.[4] Under the conditions specified above, *endo*-norbornan-2-yl *p*-nitrobenzoate solvolyzes to the extent of 1.4% to give **4a**. Obviously most of the **4a** produced in the solvolysis of **1a** is *not* formed by way of an *endo*-2-norbornyl intermediate.

This conclusion is supported by the decomposition of 2-norpinyldiazonium ions (**1b**), where internal return of the leaving group should not occur. A convenient method of generating **1b** is the photolysis of norpinan-2-one[1] tosylhydrazone, mp 200–202°, in alkaline solution. Photolysis of tosylhydrazone salts is known to give diazoalkanes.[5] Diazolakanes are sufficiently basic for protonation even in alkaline aqueous or alcoholic solutions.[6] This deamination procedure ensures kinetic control and permits variation of the attacking nucleophile.



5

Photolyses of **5** have been carried out in water–dimethoxyethane, ethanol, and trifluoroethanol (Table I). In the H_2O–DME experiments, variation of the alkali concentration from 2 to 10 equiv had only a small effect on the product distribution. The *exo*/*endo* ratio of the norbornane derivatives depended markedly on the nucleophilicity of the solvent. Trifluoroethanol, a poor nucleophile,[7] afforded predominantly *exo*-2-norbornyl trifluoroethyl ether (**4c**).

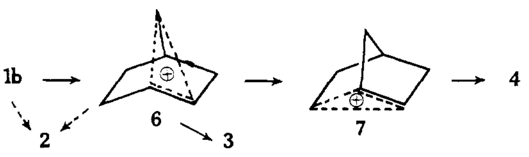
Table I. Product Distribution (%) in the Photolysis[a] of **5**

Solvent	Equiv of base	Hydrocarbons[b]	2	3	4
H_2O–DME (6:4)	1.9	4.7	2.6	40.0	52.7
	10.0	13.4	2.5	36.2	47.9
CH_3CH_2OH	2.5	42.6	11.4	24.3	20.7
CF_3CH_2OH	6.4	34.0	4.6	10.3	51.1

[a] Water-cooled medium-pressure mercury arc (Hanau), quartz vessels, 20°. [b] Major components were nortricylcene, norpinene-2, and tricyclo[3.2.0.0^{2,7}]heptane, identified by comparison with authentic samples.

Photolysis of **5** in D_2O–DONa–DME led to the incorporation of 0.91 atm of D in **3a** and **4a**. Quantitative nmr analysis revealed that **3a**-*d* did not contain deuterium in position 2 (α to OH). The simplified H-2 signal of **3a**-*d* (approximately a doublet of doublets), as compared with **3a**, indicates that most of the deuterium in **3a**-*d* occupies the bridgehead position. In contrast, **4a**-*d* contained 43 ± 5% of its D in position 2.

Obviously, most of the **4a** comes from the well-known bridged (or rapidly equilibrating) norbornyl cation **7**, which reacts with high *exo* stereospecificity. In our reaction sequence, **7** appears to be preceded by a norbornyl cation of high *endo* stereospecificity which may be pictured as the bridged species **6**.[8] Clearly, our



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[1] H. Musso, K. Naumann, and K. Grychtol, *Chem. Ber.*, **100**, 3614 (1967), and unpublished results.

[2] S. Winstein and D. Trifan, *J. Amer. Chem. Soc.*, 74, 1147 (1952).

[3] Related observations have been made in the brosylation of the nopinols by P. von R. Schleyer, W. E. Watts, and C. Cupas, *ibid.*, **86**, 2722 (1964); *cf.* also ref 4.

[4] Our results resemble those of E. C. Friedrich and S. Winstein, *ibid.*, **86**, 2720 (1964), in the nopinyl (6,6-dimethylbicyclo[3.1.1]heptyl) series.

[5] W. G. Dauben and F. G. Willey, *ibid.*, **84**, 1497 (1962).

[6] W. Kirmse and H. A. Rinkler, *Ann.*, 707, 57 (1967).

[7] F. L. Scott, *Chem. Ind.* (London), 224 (1959); W. S. Trahanovsky and M. P. Doyle, *Tetrahedron Lett.*, 2155 (1968).

[8] Formation of the norpinane derivatives 2 may proceed *via* 6, but direct displacement on 1a,b is also a possible path.