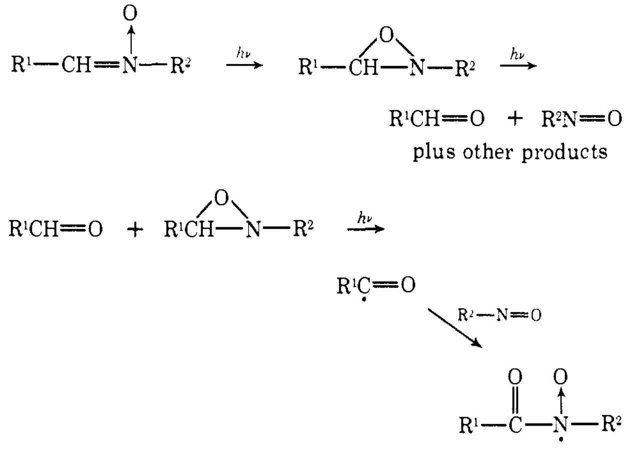
isomeric nitrone. No signal is detected prior to irradiation. In the dark, **6** converts a benzene solution of N-benzoyl-N-phenylhydroxylamine (**5**) to the benzoylnitroxide (**1**). Although this demonstrates further the oxidizing properties of the oxazirane structure, the observation that a benzene solution of **6** does not give **4** in the dark demonstrates that the conversion of oxazirane to benzoylnitroxide is light dependent.

After a brief irradiation of the nitrones in solution we observe that the radical signal continues to grow in intensity when kept in the dark, which would indicate a thermal or chain reaction. Amides are considered to be secondary thermal products arising from the irradiation of nitrones,[12,13] and to explore the possibility that the amide might be a precursor to the nitroxide radicals, we irradiated N-phenylbenzamide in benzene. No esr signal was detected. To simulate conditions where oxazirane might be present, **6** was added to the benzanilide solution. Irradiation did give rise to a signal, but the splittings were not characteristic for **1**.

Apparently an excited form of the oxaziranes is involved initially in the formation of the observed nitroxide radicals. After conversion of the nitrones to oxaziranes by light, photooxidation could lead to the production of benzoylhydroxylamines, such as **5**. The subsequent conversion to the nitroxide radicals could take place in the dark, by the action of residual oxazirane, as shown earlier.

Another scheme might involve fragmentation and recombination as shown below.



The formation of aldehydes and nitroso compounds from the irradiation of nitrones has been reported.[12,14,15] Combination of benzoyl radicals with nitroso compounds has been used to prepare benzoyl nitroxides.[4]

Extended irradiation of the nitrone solutions leads to changes in the esr signals, and in some cases the signals are destroyed. The reaction mechanism which leads to aroylnitroxides is being studied.

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(12) J. S. Splitter and M. Calvin, *Tetrahedron Lett.*, 1445 (1968).
(13) L. S. Kaminsky and M. Lamchen, *J. Chem. Soc.*, *C*, 2295 (1966).
(14) J. S. Splitter and M. Calvin, *J. Org. Chem.*, **30**, 3427 (1965).
(15) H. Shindo and B. Umezawa, *Chem. Pharm. Bull.* (Tokyo), **10**, 492 (1962).

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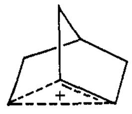
## Gas-Phase Stabilities of Bicyclic Cations

*Sir:*

The long-standing controversy regarding nonclassical carbonium ions in norbornyl systems has focused upon whether the ion I, possessing a three-center bond, is



I

best represented as a transition state between two rapidly equilibrating classical ions or as an intermediate lower in energy than either classical ion.[1,2] An important aspect of the controversy is the intrinsic question of stabilities of ions as a function of their geometry. Spectroscopic,[3] kinetic,[1,4] and stereochemical[5] data related to this problem have been obtained only in solution where solvent effects may and probably do play a significant role. We wish to report the relative stabilities of sets of protonated bicyclic olefins and ketones, free of solvation effects, which establish the presence of $\sigma$ (nonclassical) delocalization in the norbornyl cation.

Limits on heats of formation in the gas phase can be established by observing and identifying ion–molecule reactions.[6] For example, if reactions 1 and 2 are observed, they must be exothermic with respect to the

$$\mathrm{M} + \mathrm{AH}^+ \longrightarrow \mathrm{MH}^+ + \mathrm{A} \qquad (1)$$

$$\mathrm{B} + \mathrm{MH}^+ \longrightarrow \mathrm{BH}^+ + \mathrm{M} \qquad (2)$$

state of the reactants. Therefore, $\Delta H_f(\mathrm{AH}^+ - \mathrm{A}) > \Delta H_f(\mathrm{MH}^+ - \mathrm{M}) > \Delta H_f(\mathrm{BH}^+ - \mathrm{B})$. If M is the compound being studied and A and B are reagents for which $\Delta H_f(\mathrm{AH}^+ - \mathrm{A})$ and $\Delta H_f(\mathrm{BH}^+ - \mathrm{B})$ are known, then limits on $\Delta H_f(\mathrm{MH}^+ - \mathrm{M})$ can be set. Using ion cyclotron resonance techniques[7,8] and available data in the literature, we have studied the gas-phase stabilities of bicyclic cations. The results are summarized in Table I.

The relative stabilities of bicyclic cations can be evaluated by comparing differences in the heats of formation of an ion and its saturated hydrocarbon (Table I, lines 5 and 6). The bicyclo[2.2.1]heptyl cation compared to its saturated system is approximately 6 kcal/mol more stable than the bicyclo[2.2.2]octyl cation compared to its hydrocarbon. Changes in angle strain, nonbonded interactions, torsional strain, and bond deformation which includes $\sigma$ delocalization in going from the hydrocarbon to the ion in the two bicyclic systems account for this difference. A greater increase in angle strain in the bicyclo[2.2.1]heptyl system and comparable changes in nonbonded interactions and torsional strain in the two bicyclic systems would be expected.[1] This would predict greater stability for

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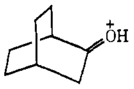
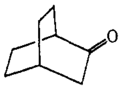
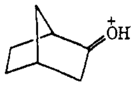
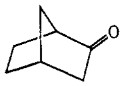
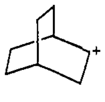
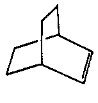
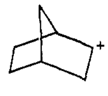
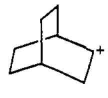
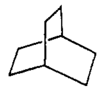
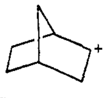
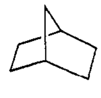
(1) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).
(2) H. C. Brown, *Chem. Brit.*, 199 (1966); H. C. Brown, *Chem. Eng. News*, **45** (7), 85 (1967).
(3) G. Olah and A. White, *J. Am. Chem. Soc.*, **91**, 3954, 3956 (1969), and references therein.
(4) J. Schaefer, M. Dagani and D. Weinberg, *ibid.*, **89**, 6939 (1967); C. Collins and M. Lietzke, *ibid.*, **89**, 6565 (1967), and references therein.
(5) H. Goering and C. Schewene, *ibid.*, **87**, 3517 (1965).
(6) F. Lampe, J. Franklin, and F. Field, *Progr. Reaction Kinetics*, **1**, 68 (1961).
(7) J. D. Baldeschwieler, *Science*, **159**, 263 (1968).
(8) J. Beauchamp and S. Buttrill, *J. Chem. Phys.*, **48**, 1783 (1968).

Table I. Heats of Formation of Bicyclic Species

| Line | Species A | Species B | $\Delta H_f(A - B)$,[a,b] kcal/mol |
|---|---|---|---|
| 1 |  |  | 159 |
| 2 |  |  | 161 |
| 3 |  |  | 171.5 ± 1.5 |
| 4 |  |  | 160 ± 1 |
| 5 |  |  | 199.5 ± 1.5[c] |
| 6 |  |  | 193 ± 1[c] |

[a] The following scales of relative $\Delta H_f$'s were used to place limits on $\Delta H_f(A - B)$: $\Delta H_f[(CH_3)(C_2H_5)OH^+ - (CH_3)(C_2H_5)O] >$ $\Delta H_f$[bicyclo[2.2.2]octyl cation − bicyclo[2.2.2]octene] > $\Delta H_f[(CH_3)(C_2H_5)COH^+ - (CH_3)(C_2H_5)CO]$; $\Delta H_f$[cyclohexanone-H$^+$ − cyclohexanone] ≅ $\Delta H_f$[2-bicyclo[2.2.1]heptanone-H$^+$ − 2-bicyclo[2.2.1]heptanone] > $\Delta H_f$[bicyclo[2.2.1]heptene-H$^+$ − bicyclo[2.2.1]heptene] > $\Delta H_f$[2-bicyclo[2.2.2]octanone-H$^+$ − 2-bicyclo[2.2.2]octanone] ≅ $\Delta H_f[((CH_3)_2CH)_2OH^+ - ((CH_3)_2CH)_2O]$. Heats of formation not listed in the table were taken from J. Beauchamp, Ph.D. Thesis, Harvard University, 1968. [b] The listed errors represent differences between bracketing reagents. [c] Value obtained using the heat of hydrogenation of the olefin: R. B. Turner, W. Meador, and R. Winkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957).

the classical bicyclo[2.2.2]octyl cation compared to its hydrocarbon than for the corresponding species in the bicyclo[2.2.1]heptyl system. The experimental results are in direct opposition to this. The 6-kcal/mol energy difference is explicable in terms of σ delocalization, a method for dispersing charge, which would be expected to be of considerable importance in the absence of any compensating solvation phenomena. The experimental results do not negate σ participation in the bicyclo[2.2.2]octyl cation but indicate that it is at least 6 kcal/mol greater in the bicyclo[2.2.1]heptyl cation where the geometry is more favorable.[9]

Any unforseen effects in the bicyclo[2.2.1]heptyl or bicyclo[2.2.2]octyl system can be evaluated by examining 2-keto compounds. The results are summarized in lines 1 and 2 of Table I. The difference in heat of formation of protonated 2-bicyclo[2.2.2]octanone and its ketone is 2 kcal/mol less than the difference in heat of formation of protonated 2-bicyclo[2.2.1]heptanone and its ketone. This corresponds to the same difference observed for protonated cyclohexanone and cyclohexanone when compared to protonated cyclopentanone and cyclopentanone.[10] Thus the bicyclo[2.2.1]heptyl and bicyclo[2.2.2]octyl systems appear to exhibit no unique stabilization of protonated carbonyls.[11] The localization of charge on the oxygen at the 2 position in the bicyclic systems is competitive with and more favorable than σ participation.

Finally, using −17[12] and −14[13] kcal/mol as the heats of formation of bicyclo[2.2.2]octane and bicylo[2.2.1]heptane, respectively, one may calculate a $\Delta H_f$ value of 182 kcal/mol for the bicyclo[2.2.2]octyl cation and 179 kcal/mol for the bicyclo[2.2.1]heptyl cation. The latter value is approximately 20 kcal/mol lower than one obtained by a quantum mechanical approach.[14]

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[9] A choice of an appropriate model, in which σ participation does not occur, will be the subject of a forthcoming publication.

[10] J. Beauchamp, Ph.D. Thesis, Harvard University, 1968.

[11] The use of protonated bicyclic ketones as models is discussed in D. Farnum and G. Mehta, *J. Am. Chem. Soc.*, **91**, 3256 (1969).

[12] N. Allinger, J. Hirsch, M. Miller, I. Tyminski, and F. Van-Catledge, *ibid.*, **90**, 1199 (1968).

[13] A. Bedford, A. Beezer, C. Mortimer, and D. Springall, *J. Chem. Soc.*, 3823 (1963). The heats of fusion and vaporization were assumed to be 8.0 kcal/mol.

[14] G. Klopman, *J. Am. Chem. Soc.*, **91**, 89 (1969).

[15] Public Health Service Special Fellow on sabbatical leave at Stanford University, 1967–1968.

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*Received September 29, 1969*

## Thermal and Photodecarboxylation of Pyridylacetic Acids and Photocleavage of Some 2-Substituted Pyridines[1]

*Sir:*

Our discovery[1,2] of a facile photocleavage of 2-substituted quinolines led us to consider establishing the generality of the reaction. Some substituted pyridines similar to the quinolines were available as well as the 2-, 3-, and 4-pyridylacetic acids. The thermal decarboxylation of 2-pyridylacetic acid has been studied[3] and a mechanism similar to our proposal for the quinoline cleavage was considered. Photodecarboxylation of 2-, 3-, and 4-nitrophenylacetate ions was recently thoroughly studied[4] and it was of interest to learn if the similarities observed between pyridyl and nitrophenyl reactivities in some chemical reactions could be extended to a photoreaction.

Irradiation[5] of the 2-, 3-, and 4-pyridylacetic acids in aqueous solutions did indeed yield the corresponding 2-, 3-, and 4-methylpyridines and $CO_2$. The initial rate of decarboxylation of each acid was a maximum at or near the isoelectric point (pH 4.0–4.2) and at this point the following quantum yields for conversion of the acid to the methylpyridine were found: 2-pyridyl, 0.49; 3-pyridyl, 0.46; 4-pyridyl, 0.20. At pH values higher

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[1] Photochemistry of N-Heterocycles. VI. Previous paper: F. R. Stermitz, C. C. Wei, and C. M. O'Donnell, *J. Amer. Chem. Soc.*, in press. This work was supported in part by Grant No. GM-15425 from the National Institute of General Medical Sciences, U. S. Public Health Service.

[2] F. R. Stermitz and C. C. Wei, *ibid.*, **91**, 3103 (1969).

[3] W. von E. Doering and V. Z. Pasternak, *ibid.*, **72**, 143 (1950).

[4] J. D. Margerum and C. T. Petrusis, *ibid.*, **91**, 2467 (1969).

[5] Irradiations were carried out on 0.01 *M* solutions in a Rayonet reactor employing 2537-Å lamps. They were accomplished under $N_2$ although the presence of air did not appear to affect the reaction. Quantum yields were determined by nmr analysis at about 9% reaction on degassed samples using a "merry-go-round" apparatus and ferrioxalate actinometry.