Acknowledgment. Financial support for this research by the Atomic Energy Commission, Grant No. AT-04-3-326, is gratefully acknowledged.

A. Randell Bowen, Henry Taube*
Department of Chemistry, Stanford University
Stanford, California 94305

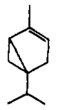
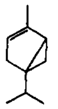
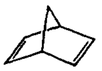
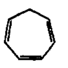
Received March 23, 1971

Linear Relationship between Ultraviolet Absorption Transition Energies and Activation Energies for Thermal Isomerization of Cyclic Olefins[1]

Sir:

We have observed an unusually low-energy ultraviolet transition for bicyclo[2.1.0]pent-2-ene (**1**), $\lambda_{\max}^{\text{gas}}$ 263 nm (ϵ ~440).[2,3] This highly strained bicyclic olefin undergoes facile thermal isomerization to cyclopentadiene (**2**) (E_a = 26.9 kcal mol^{-1})[4] and is the most paramagnetic cyclic olefin yet subjected to molecular rotational Zeeman effect studies: $(2\chi_{cc} - \chi_{aa} - \chi_{bb}) = +3.6 \times 10^{-6}$ erg G^{-2} mol^{-1}.[5,6] 2-Methylbicyclo[2.1.0]pent-2-ene (**3**) has been shown to rearrange thermally to 1-methylcyclopentadiene (**4**), presumably through a symmetry-allowed but rarely encountered $[_\sigma 2_s + {}_\sigma 2_a]$ cycloreaction.[7]

Table I. Ultraviolet Absorption Maxima and Activation Energies for Rearrangement of Cyclic Olefins

Olefin	Product	$\lambda_{\max}$, nm	$\bar{\nu}$, cm^{-1} $\times 10^{-3}$	E_a, kcal mol^{-1}
		300[a]	33.3	~22[a,b]
		263[c]	38.0	26.9[d]
		250[e]	40.0	~31[b,f]
		226[g]	44.2	35.2[h]
		~213[i]	46.9	43.4[j]
		189[k]	52.9	51.6[l]
		175[m]	57.1	57.3[n]

[a] J. Meinwald and H. Tsuruta, *J. Amer. Chem. Soc.*, **91**, 5877 (1969); **92**, 2579 (1970). [b] Estimated from the Arrhenius equation assuming log A = 14. [c] This work and ref 2. [d] Reference 4. [e] J. Meinwald and B. E. Kaplan, *J. Amer. Chem. Soc.*, **89**, 2611 (1967); M. B. Robin, H. Basch, N. A. Kuebler, B. E. Kaplan, and J. Meinwald, *J. Chem. Phys.*, **48**, 5037 (1968). [f] J. Meinwald and D. Schmidt, *J. Amer. Chem. Soc.*, **91**, 5877 (1969). [g] J. Meinwald and F. Uno, *ibid.*, **90**, 800 (1968). [h] H. M. Frey, R. G. Hopkins, H. E. O'Neal, and F. T. Bond, *Chem. Commun.*, 1069 (1969). [i] Unpublished observations on a sample of 6-methylbicyclo[3.1.0]hex-2-ene kindly provided by R. S. Cooke. [j] W. v. E. Doering, Lecture, Twenty-First National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June 18, 1969. [k] K. Stich, G. Rotzler, and T. Reichstein, *Helv. Chim. Acta*, **42**, 1480 (1959). [l] J. H. Birely and J. P. Chesick, *J. Phys. Chem.*, **66**, 568 (1962). [m] C. Heathcock, unpublished observations, private communication, Oct 1970. [n] C. A. Wellington, *J. Phys. Chem.*, **66**, 1671 (1962).

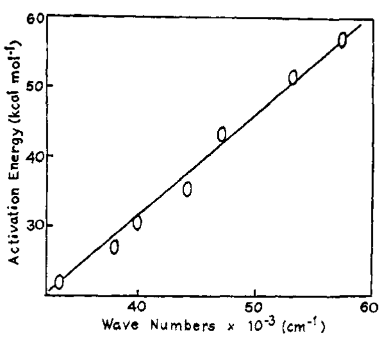
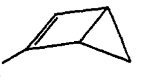
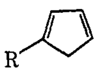


Figure 1. Empirical correlation between Arrhenius activation energy for thermal rearrangement and $\bar{\nu}$ of the $\pi \rightarrow \pi^*$ electronic transition for the cyclic olefins of Table I.



1, R = H
3, R = CH$_3$



2, R = H
4, R = CH$_3$

A number of other cyclic olefins known to suffer formally analogous thermal rearrangements display a linear correlation between ultraviolet absorption transition energies and activation energies. The data are gathered in Table I and plotted in Figure 1; the dimensionless slope of the correlation is 0.5.

Expressions for the diagonal matrix elements in the diamagnetic and paramagnetic molecular magnetic susceptibility tensors are available.[8,9]

$$\chi^{d}_{aa} = -\frac{e^2}{4mc^2}\langle 0|\sum_i (b_i^2 + c_i^2)|0\rangle \qquad (1)$$

$$\chi^{p}_{aa} = -\frac{\beta^2}{2\hbar^2}\sum_{k>0}\frac{|\langle 0|L_a|k\rangle|^2}{E_0 - E_k} \qquad (2)$$

$$\chi_{\text{total}} = \chi^{d} + \chi^{p} \qquad (3)$$

In eq 1 and 2, b_i and c_i are the coordinates of electron i, and L_a is the projection of electronic angular momentum along the a axis.

The diamagnetic contribution, χ^d, depends solely upon the electron density of the ground state, while the paramagnetic contribution to χ_{total} depends on mixing of ground and excited states by the electronic orbital magnetic moment operator. Thus, as noted by

---

(1) This work was supported by National Science Foundation Grant No. GP 9259, the Cities Service Oil Co., and the Du Pont Co.

(2) Initially reported in conjunction with the microwave spectroscopic studies of **1**: A. H. Andrist, S. L. Hsu, T. D. Gierke, R. C. Benson, W. H. Flygare, and J. E. Baldwin, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, No. PHYS 184.

(3) This observation has been corroborated by an independent study: J. I. Brauman, private communication, March 1970.

(4) D. M. Golden and J. I. Brauman, *Trans. Faraday Soc.*, **65**, 464 (1969).

(5) S. L. Hsu, A. H. Andrist, T. D. Gierke, R. C. Benson, W. H. Flygare, and J. E. Baldwin, *J Amer. Chem. Soc.*, **92**, 5250 (1970).

(6) Compare this value with those presented in Table V of R. C. Benson and W. H. Flygare, *ibid.*, **92**, 7523 (1970).

(7) J. E. Baldwin and A. H. Andrist, *Chem. Commun.*, 1561 (1970).

(8) J. R. Eshbach and M. W. P. Strandberg, *Phys. Rev.*, **85**, 24 (1952).

(9) W. H. Flygare and R. L. Shoemaker, *Symp. Faraday Soc.*, No. 3, 119 (1970).

Longuet-Higgins,[10] low-lying excited states enhance molecular paramagnetism, and the relatively high paramagnetism of bicyclopentene is as expected[10,11] for a homo[4*n*]annulene.

Might the lowest excited state of **1** be involved in its thermal isomerization through a nonadiabatic transition, as has been suggested[12] for certain triatomic molecules?

The different activation energies for $[_\sigma 2_s + {}_\sigma 2_a]$ reactions of bicyclopentene and bicyclo[1.1.0]butane (**5**), 26.9 and 41 kcal mol^{-1},[13] may be compared with the different magnetic susceptibilities: $+3.6 \times 10^{-6}$ (**1**) and -15.3×10^{-6} (**5**) erg G^{-2} mol^{-1}.[14] Thus the lack of low-lying excited states in bicyclobutane is reflected in its diamagnetism and its high activation energy for thermal isomerization.

5

The correlation observed in Figure 1 makes labeling experiments testing whether the other hydrocarbons, like bicyclopentene (**1**), may rearrange according to the $[_\sigma 2_s + {}_\sigma 2_a]$ mechanistic template seem very worthwhile. The magnetic properties of **1** suggest the possibility of systematic magnetic field effects on thermolysis rates. Low-lying excited states having energies proportionate to the $\pi \rightarrow \pi^*$ spectroscopically accessible singlet state (Figure 1) may be important to the thermal chemistry of [4*n*]- and homo[4*n*]annulenes.[10] Experiments designed to probe for further examples of $[_\sigma 2_s + {}_\sigma 2_a]$ thermal rearrangements and to gauge the importance of low-lying excited states on unimolecular isomerizations are in progress.

(10) H. C. Longuet-Higgins, *Chem. Soc. Spec. Publ.*, No. 21, 109 (1967).

(11) J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.*, **88**, 4811 (1966).

(12) E. E. Nikitin, "Theory of Thermally Induced Gas Phase Reactions," Indiana University Press, Bloomington, Ind., 1966, pp 65–67.

(13) H. M. Frey and I. D. R. Stevens, *Trans. Faraday Soc.*, **61**, 90 (1965); R. Srinivasan, A. A. Levi, and I. Haller, *J. Phys. Chem.*, **69**, 1775 (1965).

(14) T. D. Gierke and W. H. Flygare, unpublished observations.

John E. Baldwin,* A. Harry Andrist
Department of Chemistry, University of Oregon
Eugene, Oregon 97403

Received February 26, 1971

Reactions of Aromatic Nitrile *N*-Oxides with Organic Radicals. A New Type of Spin-Trapping Reagent

Sir:

Both nitroso compounds and nitrones react readily with organic radicals to form relatively stable nitroxide radicals.[1,2] This "spin-trapping" technique enables esr spectroscopy to be applied successfully in the diagnosis of free-radical intermediates and is especially valuable when the initial radical is too short lived to reach concentrations detectable by the esr method; the scope of this technique and the relative merits of nitroso compounds and nitrones as spin traps have been summarized.[2] We now report on the utility of aromatic nitrile *N*-oxides (RCNO) as spin-trapping reagents and certain advantages of these compounds compared with nitroso compounds and nitrones; reactions with radicals (R′·) lead to iminoxy radicals (RR′C=NO·) which are usually sufficiently long lived for esr observation in a static system.[3]

In most of our studies the *N*-oxides of benzonitrile or *p*-chlorobenzonitrile have been employed. The latter is thermally the more stable compound and may therefore be preferred; the iminoxy radicals from each have very similar esr spectra (see below), in accord with the observation that para substituents do not significantly affect the hyperfine splitting constants or *g* factors of aryl-containing iminoxy radicals.[3] The *N*-oxide was prepared either separately[4] or *in situ* in a suitable solvent; concentrations of 0.1–0.5 *M* were usually employed, and all solutions were deoxygenated before irradiation.

In control experiments, there was no esr absorption when solutions of nitrile *N*-oxides, in a variety of solvents, were irradiated with ultraviolet light in the cavity of an esr spectrometer. However, when dibenzoyl peroxide was included, esr signals were detected soon after irradiation began. With benzonitrile *N*-oxide, in benzene, chloroform, diethyl ether, or dichloromethane, the spectrum was the same as that obtained by the one-electron oxidation of benzophenone oxime,[3,5] indicating that the phenyl radical had been trapped. An identical spectrum was obtained by the use of *p*-chlorobenzonitrile oxide, and in neither case was there an appreciable dependence of a^H or a^N on solvent.

The following results illustrate some typical applications of this spin-trapping technique; esr data for some of the radicals observed are in Table I. Mixtures of a nitrile *N*-oxide and di-*tert*-butyl peroxide or *tert*-butyl perbenzoate did not yield a detectable concentration of radicals on irradiation in the absence of a solvent, but esr signals were obtained when either methanol or chloroform was present. In methanol with benzonitrile *N*-oxide, the spectrum showed the presence of the radicals resulting from the addition of both $\cdot CH_3$ and $\cdot CH_2OH$ to the trap; the same signals were obtained when a mixture of the oximes of acetophenone and phenacyl alcohol was oxidized by lead tetraacetate or was irradiated in the presence of di-*tert*-butyl peroxide in various solvents. In chloroform, the spectrum observed showed partially resolved splitting (0.05 mT) from three nuclei of $I = {}^3/_2$, which is typical of iminoxy radicals with the group CCl_3 syn to the N–O bond (*cf.* ref 5): it is accordingly assigned to the species **1** derived from the radical $\cdot CCl_3$.

When a mixture of the nitrile *N*-oxide and di-*tert*-butyl peroxide or *tert*-butyl perbenzoate in benzene, chloroform, or diethyl ether containing a small amount of an aldehyde was irradiated, radicals derived from oxidation of the aldehyde were observed. The spec-

---

(1) A. Mackor, Th. A. J. W. Wajer, and Th. J. de Boer, *Tetrahedron*, **24**, 1623 (1968), and references therein; G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Amer. Chem. Soc.*, **90**, 7141 (1968), and *J. Chem. Soc. B*, 401 (1970); S. Forshult, C. Lagercrantz, and K. Torssell, *Acta Chem. Scand.*, **23**, 522 (1969); K. Torssell, *Tetrahedron*, **26**, 2759 (1970); E. G. Janzen and B. J. Blackburn, *J. Amer. Chem. Soc.*, **90**, 5909 (1968); **91**, 4481 (1969); J. G. Pacifici and H. L. Browning, Jr., *ibid.*, **92**, 5231 (1970).

(2) E. G. Janzen, *Accounts Chem. Res.*, **4**, 31 (1971).

(3) B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc. B*, 86 (1966).

(4) R. Huisgen and W. Mack, *Tetrahedron Lett.*, 583 (1961).

(5) R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, **71**, 14 (1967).