

A Kinetic EPR Study of the Norbornenyl-Nortricyclyl Radical Rearrangement¹

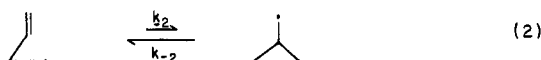
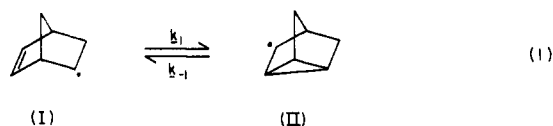
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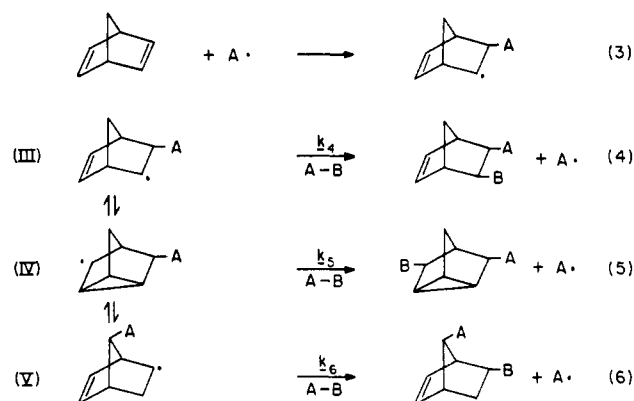
The rate constant, k , for the norbornenyl \rightarrow nortricyclyl radical rearrangement was found to be $6 \times 10^2 \text{ s}^{-1}$ at -130°C , using kinetic EPR spectroscopy. A combination of this result with others derived from product studies gave the Arrhenius expression for the rearrangement, $\log(k/\text{s}^{-1}) = 11.7 - (5.9/\theta)$, where $\theta = 2.30RT \text{ kcal mol}^{-1}$. Comparison of these parameters with those for the related allylcarbinyl \rightarrow cyclopropylcarbinyl rearrangement suggests that less ring strain is developed in the closure which leads to the nortricyclyl radical. Addition of $t\text{-BuS}$, $n\text{-BuS}$, or CF_3O to norbornadiene at temperatures between -60 and -130°C was followed by rapid rearrangement so that only the spectra of the substituted nortricyclyl radicals were detected. A similar experiment using $t\text{-BuO}$ gave the substituted nortricyclyl at -150°C but at -70°C this radical rapidly rearranged to give the 7-substituted norbornenyl. This is the first direct observation of such a rearrangement.

The norbornenyl-nortricyclyl radical rearrangement (eq 1) has been the subject of extensive investigation by organic chemists for many years.^{2,3} Despite this interest, little is known about the kinetics for this reaction. Data based on product yields⁴⁻⁶ for the reductions of norbornenyl or nortricyclyl bromides by trialkyltin hydrides suggest that $k_1 \approx k_{-1}$ at 25°C and that both are greater than 10^6 s^{-1} .⁷ These values are quite different from those for the analogous allylcarbinyl-cyclopropylcarbinyl rearrangements^{8,9} (eq 2) for which $k_2 = 1.0 \times 10^4 \text{ s}^{-1}$ and $k_{-2} = 1.3 \times 10^8 \text{ s}^{-1}$ at 25°C .



While kinetic data for the norbornenyl-nortricyclyl radical rearrangement have been lacking, the reaction has nevertheless been used qualitatively as a "free radical clock",¹⁰ that is, as a timing device to probe the efficiency of chain-transfer reactions. A general scheme for such an experiment is shown in eq 3-6, which describe the radical addition of a molecule A-B to norbornadiene. It is reasonable to assume that $k_4 \approx k_5 \approx k_6$. Hence, the extent to which products are formed from IV and V reflects the competition between chain transfer (i.e., reaction of III, IV, and V with A-B) and radical isomerization (i.e., III \rightleftharpoons IV \rightleftharpoons V).

In this work, we have used EPR spectroscopy to quantify some aspects of the norbornenyl-nortricyclyl radical rearrangement. Kinetics for the rearrangement of I \rightarrow II



were measured and EPR was used to investigate the distribution of isomeric radicals, i.e., III:IV:V, arising out of radical additions to norbornadiene.

Experimental Section

5-Bromonorborn-2-ene¹¹ was prepared by addition of hydrogen bromide to norbornadiene and was purified by distillation followed by preparative VPC (30 ft \times $\frac{3}{8}$ in. 30% Carbowax 20M at 180°C). All other materials were commercially available. 3-Bromonortricyclene, di-*tert*-butyl peroxide, di-*tert*-butyl disulfide, and di-*n*-butyl disulfide were chromatographed through alumina before use. Norbornadiene was purified by distillation. The remaining materials were used as received.

Radicals were generated by direct UV photolysis of samples placed in the cavity of a Varian E104 spectrometer. The photolyzing light was filtered through an aqueous cobalt-nickel solution so as to remove much of the visible and most of the infrared radiation. After filtration, the heating effect at the samples due to the photolysis beam was less than 1°C . The sectorized disk experiment for measuring rate constants for radical self-reactions and the method of measuring radical concentrations have been described in detail elsewhere.¹²

Results and Discussion

Kinetics for the Norbornenyl-Nortricyclyl Rearrangement. Photolysis of a cyclopropane-propane solution (3:7 v/v) containing 3-bromonortricyclene, trimethylsilane, and di-*tert*-butyl peroxide (each 5% v/v) at -130°C gave the EPR spectrum of the nortricyclyl radical (II). The EPR parameters were the same, within experimental error, as those previously reported¹³ (see Table I).

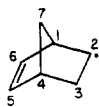

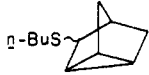
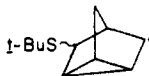
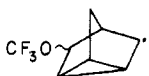
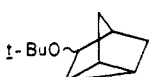
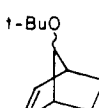
(11) Schmerling, L.; Luvisi, J. P.; Welch, R. W. *J. Am. Chem. Soc.* 1956, 78, 2819-2821.

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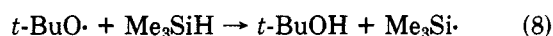
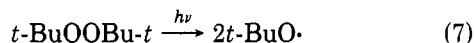
(1) Issued as NRCC publication no. 19328.
 (2) Davies, D. I. *Chem. Soc. Spec. Publ.-Chem. Soc.* 1970, No. 24, 201-237.
 (3) Wilt, J. W. *Free Radicals* 1973, 1, 333-501.
 (4) Warner, C. R.; Strunk, R. J.; Kuivila, H. G. *J. Org. Chem.* 1966, 31, 3381-3384.
 (5) Halgren, T. A.; Firkins, J. L.; Fujimoto, T. A.; Suzukawa, H. H.; Roberts, J. D. *Proc. Natl. Acad. Sci. U.S.A.* 1971, 68, 3216-3218.
 (6) See also; Wilt, J. W.; Levin, A. A. *J. Org. Chem.* 1962, 27, 2319-2322; Trecker, D. J.; Henry, J. P. *J. Am. Chem. Soc.* 1963, 85, 3204-3212; Davies, D. I.; Done, J. N.; Hey, D. H. *Chem. Commun.* 1966, 725.
 (7) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* 1968, 90, 7047-7055.
 (8) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* 1976, 98, 7024-7026.
 (9) Effio, A.; Griller, D.; Ingold, K. U.; Beckwith, A. L. J.; Serelis, A. *K. J. Am. Chem. Soc.* 1980, 102, 1734-1736.
 (10) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* 1980, 13, 317-323.

Table I. EPR Parameters for Norbornenyl and Nortricyclyl Radicals

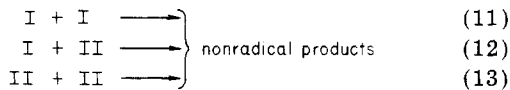
radical	g	hyperfine splittings, G
	2.002 68 ^a	a^{H_2} (19.42), a^{H_3} (exo, 30.49), a^{H_3} (endo, 23.27), a^{H_1} (3.75); others 2.18 (1 H, 1.23 (1 H), 0.77 (1 H), 0.44 (1 H)) ^a
	2.002 69 ^a	a^{H_2} (18.16); others 0.27 (1 H), 0.14 (1 H), 0.98 (2 H), 0.56 (2 H) ^a
		a^{H_2} (18.19); others 0.75 (m)
	2.002 74	a^{H_2} (18.06); others 0.81 (m)
		a^{H_2} (18.88); others 0.88 (m)
	2.002 85	a^{H_2} (18.38); others 0.25 (m)
	2.002 83	a^{H_2} (20.00), a^{H_3} (exo, 30.10), a^{H_3} (endo, 23.90), a^{H_1} (3.75); others 1.80 (1 H), 0.50 (2 H)

^a See ref 13.

Radical II did not isomerize to give a detectable EPR signal of I over the temperature range -60 to -150 °C (eq 7-9).



Photolysis of a similar solution in which the 3-bromonortricyclene was replaced by 5-bromonorborn-2-ene gave the spectrum of the norbornenyl radical (I) at -145 °C. This spectrum is particularly difficult to detect since it consists of a large number of easily saturated lines. Again the EPR parameters for I were the same, within experimental error, as the literature data¹³ (see Table I). As the sample temperature was raised from -145 to -100 °C the concentration of I diminished and the spectrum of II appeared. Since II is not converted to I in this temperature range, the reactions can be described as in eq 10-13.



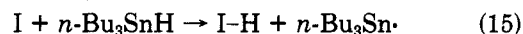
We can assume that reactions 11-13 are diffusion controlled. Since both I and II have similar structures and identical molecular weights, we can further assume that $2k_{11} = k_{12} = 2k_{13}$. Then, under the steady-state condition attained by continuous photolysis of the sample, eq 14 applies.¹²

$$\frac{1}{[\text{II}]} = \frac{2k_{13}}{k_1} \left(\frac{[\text{II}]}{[\text{I}]} + 1 \right) \quad (14)$$

It was possible only to measure the concentrations of the norbornenyl and nortricyclyl radicals at -130 °C because of the complexity of the spectrum of I, line overlap, and poor spectral signal to noise. At this temperature $[\text{I}] = 8.10 \times 10^{-8}$ M, $[\text{II}] = 7.39 \times 10^{-8}$ M, and, therefore,

$2k_{13}/k_1 = 7.0 \times 10^6$. A value for $\log(2k_{13}/M^{-1} \text{ s}^{-1}) = (9.6 \pm 0.3)$ was obtained in a time-resolved experiment using the standard sector-disk arrangement.¹² Hence, $k_1 = 6 \times 10^2 \text{ s}^{-1}$ at -130 °C.

An estimate of the Arrhenius parameters for reaction 1 can be obtained by combining the above data with those obtained for the reduction of norbornenyl bromide by tri-*n*-butyltin hydride at -10 °C. In the latter work, yields of norbornene and nortricyclene were measured as a function of tin hydride concentration and led to the result $k_{15}/k_1 = 0.12 \text{ M}^{-1}$, where k_{15} is the rate constant for the reduction of I (eq 15). Rate constants for reduction of



alkyls by tri-*n*-butyltin hydride are quite insensitive to the nature of the alkyl.^{7,14} We can therefore apply the rate constant for reduction of cyclohexyl as a satisfactory estimate of k_{15} ; i.e., $k_{15} = 8.9 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at -10 °C.¹⁴ Hence, $k_1 = 7.4 \times 10^6 \text{ s}^{-1}$ at -10 °C and when combined with the kinetic EPR result yields the Arrhenius equation shown in eq 16, where $\theta = 2.30RT \text{ kcal mol}^{-1}$. The error

$$\log(k_1/\text{s}^{-1}) = 11.7 - (5.9/\theta) \quad (16)$$

in the *A* factor could be as much as ± 1.0 while that in the activation energy is probably 1 kcal mol⁻¹. This estimate allows for an error of a factor of 2 on each of the measured rate constants.

This result can be compared with that for the allyl-carbinyl ring closure⁹ (reaction 2) for which $\log(A_2/\text{s}^{-1}) = 10.4$ and $E_2 = 9.1 \text{ kcal mol}^{-1}$. Thus, the energy required for closure to give the nortricyclyl radical is ca. 3.2 kcal mol⁻¹ less than that for closure to cyclopropylcarbinyl.¹⁵ That is, less ring strain is developed in the closure which leads to the nortricyclyl radical. The Arrhenius *A* factor for reaction 1 is expected to be somewhat greater than that

(14) Chatgililoglu, C., unpublished results.

(15) For recent studies of enthalpy differences in norbornenyl and nortricyclyl radicals, see: Giese, B.; Jay, K. *Chem. Ber.* 1977, 110, 1364-1367; *Ibid.* 1979, 112, 298-303.

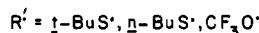
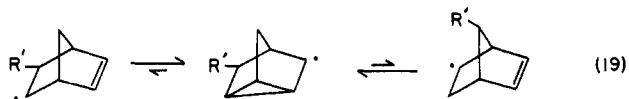
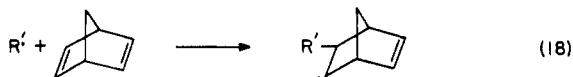
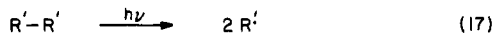
for the allylcarbonyl radical ring closure, since the latter involves the loss of a rotational degree of freedom not available in the norbornenyl case. While the raw data support this view, the experimental errors are such that a firm conclusion cannot be drawn.

The EPR data obtained at $-130\text{ }^\circ\text{C}$ suggest that at this temperature $k_1 \geq 10k_{-1}$, while at $-10\text{ }^\circ\text{C}$ the tin hydride reduction experiments give $k_{-1} = 1.26k_1$. Hence, both the Arrhenius A factor and activation energy for the radical rearrangement of nortricyclyl to norbornenyl must be greater than those for reaction 1 (see eq 16).

Radical Additions to Norbornadiene. A number of experiments were carried out to measure the distribution of type III, IV, and V isomers resulting from radical additions to norbornadiene. The methods for radical generation have been described in detail elsewhere.¹⁶ All samples were made up in cyclopropane-propane solvent (3:7 v/v) containing ca. 5% by volume of the various substrates.

Attempts were made to generate a series of radicals, $R\cdot$ ($R = \text{Me}_3\text{Si}\cdot$, $(\text{EtO})_2\text{P}\cdot\text{O}$, $\text{Cl}_3\text{C}\cdot$), by hydrogen abstraction from RH using *tert*-butoxyl as reagent. However, in the presence of norbornadiene only the products of *tert*-butoxyl addition were observed (see below). That is, in the temperature range of the experiments (-80 to $-150\text{ }^\circ\text{C}$) addition of *tert*-butoxyl to norbornadiene must be more rapid than abstraction at RH.

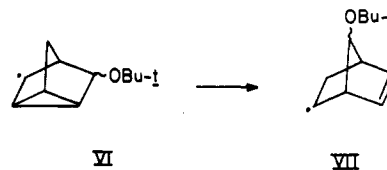
Photolysis of solutions containing norbornadiene and di-*tert*-butyl disulfide, di-*n*-butyl disulfide, or bis(trifluoromethyl) peroxide gave the spectra of the corresponding nortricyclyl adducts (eq 17–19). No other rad-



icals were detected in the temperature range -130 to $-60\text{ }^\circ\text{C}$. The hyperfine splittings for these radicals are reported in Table I. While it may be difficult to detect the norbornenyl-type radicals if the spectral line widths are large, one can, at a minimum, say that the nortricyclyl radical

predominates at these temperatures.

Photolysis of a solution containing di-*tert*-butyl peroxide and norbornadiene at $-150\text{ }^\circ\text{C}$ gave the spectrum of the nortricyclyl-type radical ($R' = t\text{-BuO}\cdot$). As the sample was heated to $-70\text{ }^\circ\text{C}$ the spectrum of this radical weakened and was gradually replaced by a spectrum similar to that of I except that one of the smallest hyperfine splittings present in I was absent in this spectrum. We assign this spectrum to radical VII. Its spectral parameters are re-



ported in Table I. The spectrum cannot be due to a radical of type III since the spectrum of such a radical would lack a major hyperfine splitting (i.e., $a^H \approx 23\text{ G}$) found in I.

Ring openings of nortricyclyl radicals to give 7-substituted norbornenyls have been detected in product studies^{2,3,17} and are relatively rare. This is the first direct observation of such a rearrangement. Presumably the distribution of isomeric radicals depends on a subtle balance of steric and electronic effects.¹⁸

It should be noted that the spectral data obtained in this work do not allow us to identify the stereochemistry of radical addition. However, product studies² indicate that exo attack on norbornadiene is generally preferred.

Summary

In this work, kinetics for the radical rearrangement of norbornenyl to nortricyclyl has been measured. The difference in Arrhenius parameters for this reaction and those for the related allylcarbonyl-cyclopropylcarbonyl radical rearrangement is ascribed to the fact that less ring strain is developed in the closure which leads to the nortricyclyl radical.

Radical additions to norbornadiene in the temperature range -70 to $-130\text{ }^\circ\text{C}$ lead predominantly to the substituted nortricyclyl radicals. However, in the case of *tert*-butoxyl addition, the nortricyclyl ring opens to give the 7-substituted norbornenyl.

Registry No. 5-(Butylthio)tricyclo[2.2.1.0^{2,6}]hept-3-yl, 77028-03-6; 5-(*tert*-butylthio)tricyclo[2.2.1.0^{2,6}]hept-3-yl, 77028-04-7; 5-[(trifluoromethyl)oxy]tricyclo[2.2.1.0^{2,6}]hept-3-yl, 77028-05-8; 5-*tert*-butoxytricyclo[2.2.1.0^{2,6}]hept-3-yl, 77028-06-9; 7-*tert*-butoxybicyclo[2.2.1]hept-5-en-2-yl, 77028-07-0.

(17) See also: Story, P. R. *J. Org. Chem.* 1961, 26, 287–290.

(18) This seems to be a general characteristic of cyclopropylcarbonyl ring opening reactions. See: Mariano, P. S.; Bay, E. *J. Org. Chem.* 1980, 45, 1763–1769 and references cited therein.

(16) Griller, D. *Magn. Reson. Rev.* 1979, 5, 1–23.