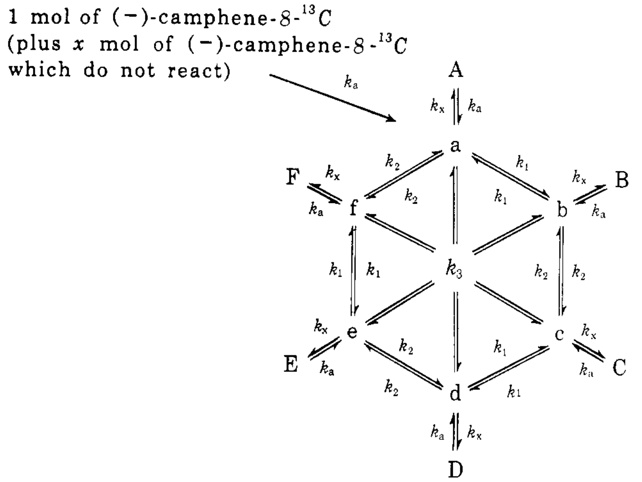
Table I. Comparison of the Observed[2] ^{13}C Distributions on Racemization of (−)-Camphor-*8*-^{13}C with Those Calculated Using Eq 1–5, Neglecting 3,2-*endo*-Methyl Migration (k_1)

Time, hr		Mole fractions: Obsd		Mole fractions: Calcd	
1.5	$m_a + m_f$ (C_8)	0.858 ± 0.01[b]	0.874 ± 0.01[c]	0.869[f,g]	0.875[h,g]
	$m_b + m_e$ (C_9)	0.020 ± 0.002	0.017 ± 0.002	0.017	0.016
	$m_c + m_d$ (C_{10})	0.123 ± 0.007	0.109 ± 0.007	0.114	0.110
	$m_b + m_d + m_f$[a]	0.124 ± 0.012		0.132	0.128
3.0	$m_a + m_f$ (C_8)	0.770 ± 0.008[d]	0.766 ± 0.008[e]	0.767[i]	0.778[i]
	$m_b + m_e$ (C_9)	0.028 ± 0.004	0.032 ± 0.005	0.031	0.028
	$m_c + m_d$ (C_{10})	0.202 ± 0.009	0.202 ± 0.009	0.202	0.194
	$m_b + m_d + m_f$[a]	0.215 ± 0.021		0.235	0.227

[a] Fraction of inversion.[10] [b] Experiment 16.[2] [c] Experiment 17.[2] [d] Experiment 18.[2] [e] Experiment 19.[2] [f] $k_2/k_x = 0.179$; $k_3/k_x = 0.998$.[10] [g] Mole fraction of unreacted (−)-camphene-^{13}C: 0.623. [h] $k_2/k_x = 0.171$; $k_3/k_x = 0.875$. [i] Mole fraction unreacted (−)-camphene-^{13}C: 0.329.

Scheme I



tion process 3,2-*exo*-Me, k_a is the rate constant for protonation of camphene, and k_x is the rate constant for deprotonation of camphene. From the experimental data[8] the sums of the mole fractions of ^{13}C in C_8 ($m_a + m_f$), C_9 ($m_b + m_e$), and C_{10} ($m_c + m_d$) after 1.5 and 3.0 hr of reaction time are available. For each mole of (−)-camphene-*8*-^{13}C which has entered into the reaction after any period of time, it is possible to demonstrate[9] the following relations

$$Ym_b' = k_1m_a' + k_2m_c' + k_3m_e' \quad (1)$$

$$Ym_c' = k_1m_d' + k_2m_b' + k_3m_f' \quad (2)$$

$$Ym_d' = k_1m_c' + k_2m_e' + k_3m_a' \quad (3)$$

$$Ym_e' = k_1m_f' + k_2m_d' + k_3m_b' \quad (4)$$

$$Ym_f' = k_1m_e' + k_2m_a' + k_3m_c' \quad (5)$$

in which $Y = k_1 + k_2 + k_3 + k_x$ and $\Sigma m_i' = 1$. Since k_a is the rate constant for the slow step, it is so much smaller than all the other k's, that the terms containing k_a in the numerator are also insignificant and have been dropped. The mole fractions m_a'–m_f' are related to m_a–m_f in the following way: $(x + m_a')/(1 + x) = m_a$; $m_b'/(1 + x) = m_b$, etc., in which x is the moles of (−)-camphene-*8*-^{13}C which did not enter into the reaction after the given period of time.

Using standard computer techniques, we solved eq 1–5 for those values of x and k_1/k_x, k_2/k_x, and k_3/k_x which are consistent with the experimentally determined[2] ^{13}C fractions at C_8, C_9, and C_{10}, and with the calculated[10] fractions of inversion at 1.5 and 3.0 hr, respectively. We found that there is a range of values for the three ratios k_1/k_x, k_2/k_x, and k_3/k_x which are reasonably compatible with all four experimental runs. The results,[2] in fact, seem to be quite insensitive to k_1 over a range of contribution by k_1 to the racemizing process of 0–8%. The fit is best when $k_1 = 0$ (that is, leaving *endo*-methyl migration out of the model entirely). For all four experiments of Vaughan and coworkers[2] there are values for k_2/k_x and k_3/k_x which will duplicate the data within experimental error. The range of values (k_2/k_x 0.171–0.179; k_3/k_x 0.875–0.988) which allows us to recalculate the appropriate mole fractions for all four runs with the best overall agreement is shown, together with the results calculated therefrom, in Table I.

Thus the data of Vaughan, *et al.*,[2] can be explained with only two racemizing processes (k_2 and k_3), and offer no evidence whatsoever for *endo*-methyl (k_1) migration.

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(8) Tables I and II, p 1267 of ref 2.

(9) B. M. Benjamin and C. J. Collins, *J. Amer. Chem. Soc.*, **78**, 4329 (1956), discuss the area theorem of J. Z. Hearon which was used in the derivations.

(10) Using $k_{rac} = 5.2 \pm 0.43 \times 10^{-5}$ sec^{-1} as reported by Vaughan, *et al.*,[2] we calculated the fractions of inversion ($m_b + m_d + m_f$) at 1.5 and at 3.0 hr to be 0.124 and 0.215, respectively. The error reported[2] in the rate constant is ±8.3%; the error in these fractions of inversion is certainly greater. Stothers, Vaughan, *et al.*, (ref 2, p 1266) comment on the "lack of precision"... "inherent in the nature of the experimental technique." We estimate a lower limit for the error in the fraction of inversion as ±10%.

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Carbon Scrambling in $C_5H_5^+$, $C_5H_6^+$, and $C_7H_7^+$ Produced by Electron Impact

Sir:

Electron impact decomposition of benzene to extrude a C_2H_2 fragment has been shown[1] to occur with extensive scrambling of both the hydrogen and carbon atoms prior to the extrusion.

We report here on the electron impact fragmentations of cycloheptatriene, cyclopentadiene, and norbornadiene, all doubly labeled with vicinal ^{13}C atoms, to

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(1) (a) C. G. McDonald and J. Shannon, *Aust. J. Chem.*, **15**, 771 (1962); (b) K. R. Jennings, *Z. Naturforsch. A*, **22**, 454 (1967); (c) J. H. Beynon, R. M. Caprioli, W. O. Perry, and W. E. Baitinger, *J. Amer. Chem. Soc.*, **94**, 6828 (1972); (d) R. J. Dickinson and D. Williams, *J. Chem. Soc. B*, 249 (1971); (e) I. Horman, A. N. H. Yeo, and D. H. Williams, *J. Amer. Chem. Soc.*, **92**, 2131 (1970).

make apparent the extent of scrambling which preceded the acetylene extrusion. Scrambling is complete in the C_5H_6 and C_5H_5 cations from cyclopentadiene and in the C_7H_7 cation from cycloheptatriene.

Diels–Alder condensation of 90% ^{13}C enriched acetylene (78.6% $^{13}C_2H_2$, 19.5% $^{13}C^{12}CH_2$) with cyclopentadiene (290–300°) produces norbornadiene-*2,3*-$^{13}C_2$ (77.2% $^{13}C_2$, 19.3% $^{13}C_1$, 3.5% $^{13}C_0$); the reaction under these conditions is not complicated by further dissociation and recombination. Isomerization[2] of this norbornadiene in a flow system (470°, ~3.5 sec contact time) provided cycloheptatriene-$^{13}C_2$ (75.4% $^{13}C_2$, 19.1% $^{13}C_1$, 5.5% $^{13}C_0$). The positions of the ^{13}C labels were determined by examining the C_7 resonance (the methylene carbon) in the noise-decoupled 25-MHz ^{13}C nmr spectrum; a large doublet, J = 38.3 Hz, is found if a second ^{13}C label is at an adjacent position, C_1 or C_6, and little splitting by the second label if at C_2–C_5.[3] Thus, it was determined that 75% of the doubly labeled cycloheptatriene had adjacent labels and 25% had separated labels.

Electron impact fragmentation of cycloheptatriene (70 eV, 160° source temperature) yields $C_5H_5^+$ as a major product. High-resolution analysis of this ion (Table I)[5] shows that *it is derived from a pool of seven carbon atoms which have no memory of their relative positions in the cycloheptatriene.*

Table I. High-Resolution Analysis of $C_5H_5^+$ from Cycloheptatriene-$^{13}C_2{}^{a-e}$

Composition	Abundance[d]	Calcd abundance: Scrambling	Calcd abundance: Retention
C_5H_5	0.045	0.048 (1/21)	0.143 (1/7)
$^{13}CC_4H_5$	0.446	0.476 (10/21)	0.286 (2/7)
$^{13}C_2C_3H_5$	0.509	0.476 (10/21)	0.572 (4/7)

[a] Average of seven–ten spectra obtained at 70 eV, AEI MS9 spectrometer. [b] Σ = 1.000. [c] Corrected for naturally abundant ^{13}C. [d] Abundance for the pure doubly labeled compound, obtained by correction for incomplete labeling employing the composition analysis and the required statistical loss of C_2H_2–$^{13}CCH_2$ from the monolabeled component. [e] Resolution 20,000.

$$\begin{tikzcd} C_7H_8 \arrow[r, "-e"] & C_7H_8{}^{\cdot+} \arrow[r, "-H\cdot"] & C_7H_7{}^{+} \arrow[r, "-C_2H_2"] & C_5H_5{}^{+} \\ \text{vicinally labeled carbons} & & \text{labels scrambled} & \end{tikzcd}$$

The pyrolysis of norbornadiene, described above, produces the doubly labeled cycloheptatriene and, by reversal of the Diels–Alder, doubly labeled cyclopentadiene (42.9% $^{13}C_2$, 11.0% $^{13}C_1$, 46.1% $^{13}C_0$), presumably with exclusively vicinal labeling.[6] Electron impact data for the cyclopentadiene fragments $C_3H_4{}^{\cdot+}$ and $C_3H_3{}^+$ are shown in Table II. The origin of these ions is established from the [M − C_2H_2] and [(M − H) − C_2H_2] metastable transitions. Both ions derive from highly scrambled precursors, indicating the following mechanism for cyclopentadiene.[7]

Table II. High-Resolution Analysis of $C_3H_3{}^+$ and $C_3H_4{}^{\cdot+}$ from Cyclopentadiene-$^{13}C_2{}^{a,b}$

Composition	Abundance[b]	Calcd abundance: Scrambling	Calcd abundance: Retention
C_3H_3	0.073	0.100	0.200
C_3H_4	0.117		
$^{13}CC_2H_3$	0.592	0.600	0.400
$^{13}CC_2H_4$	0.563		
$^{13}C_2CH_3$	0.334	0.300	0.400
$^{13}C_2CH_4$	0.320		

[a] See footnotes *a–c* of Table I. [b] See footnote *d* of Table I.

$$\begin{tikzcd} & & C_5H_5{}^{+} \arrow[r, "-C_2H_2"] & C_3H_3{}^{+} \\ C_5H_6 \arrow[r, "-e"] & C_5H_6{}^{\cdot+} \arrow[ur, "-H\cdot"] \arrow[dr, "-C_2H_2"'] & & \\ \text{vicinally labeled carbons} & \text{labels scrambled} & C_3H_4{}^{\cdot+} & \end{tikzcd}$$

The formation of C_nH_n cations (n = 5–7) by electron impact, with sufficient energy to eliminate C_2H_2, occurs with complete scrambling of the carbon atoms; with C_6H_6 it has even been demonstrated that the hydrogens scramble independently of carbon.[1c,d] A "statistical mechanism" appears to operate for each of these cations.

The classical studies of Meyerson and coworkers[8] indicated that the seven carbon atoms of toluene become equivalent under electron impact conditions which result in the formation of $C_5H_5^+$. Rinehart, *et al.*,[9] and Siegel[10] could not detect other than fully scrambled fragmentation products from toluene-$^{13}C_2$ labeled α,1 and 2,6, respectively. From this certain of the pathways for the transformation of toluene to the crucial tropylium intermediate were excluded. It has been demonstrated here that the tropylium cation is scrambled even if one starts with vicinally labeled cycloheptatriene. This observation leaves in total obscurity the mechanism of carbon scrambling in toluene; it could occur during or after the ring expansion.[11]

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(2) (a) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958); (b) W. M. Halper, G. Gaertner, E. W. Swift, and G. E. Pollard, *Ind. Eng. Chem.*, **50**, 1131 (1958); (c) J. H. Birely and J. P. Chesick, *J. Phys. Chem.*, **66**, 568 (1962); (d) W. C. Herndon and L. L. Lowry, *J. Amer. Chem. Soc.*, **86**, 1922 (1964); (e) K. N. Klump and J. P. Chesick, *ibid.*, **85**, 130 (1963).

(3) $^1J_{7,1}$ = 44.2,[4a,b] 39.7 Hz[4c] for toluene, 45.1 Hz for 1-methylcyclohexene;[4c] $^2J_{7,2}$ = 3.1 Hz, $^3J_{7,3}$ = 3.8 Hz for toluene.[4b]

(4) (a) K. Frei and H. J. Bernstein, *J. Chem. Phys.*, **38**, 1216 (1963), (b) A. M. Ihrig and J. L. Marshall, *J. Amer. Chem. Soc.*, **94**, 1756 (1972); (c) A. C. Buchholz, Ph.D. Thesis, University of Illinois, 1967.

(5) In the analyses of Tables I–III whatever discrepancy may exist between observed and model distributions may reflect the overall uncertainty of high-resolution intensities, which we estimate to be 4%. If the differences are taken to be meaningful, interpolation at the most sensitive abundance for each system indicates operation of a dominant mechanism to an extent of 80–90%.

(6) Thermal isomerization in this system is unfavorable on both thermodynamic and electronic grounds, in contrast to cycloheptatriene. Disrotatory closure to bicyclo[2.1.0]pentene is symmetry forbidden, while 1,3-sigmatropic shift of a vinyl group to 3-vinylcyclopropene must be antarafacial.

(7) The label distribution of $C_3H_4{}^{\cdot+}$ from cyclopentadiene directly indicts the molecular ion as a scrambled species and, with the observations for benzene, suggests this may be true for cycloheptatriene, also. However, it is possible that $C_nH_n{}^+$ forms with label integrity by rapid H dissociation, randomization occurring in all cases only in those particular ions which can proceed directly to acetylene.

(8) (a) P. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Amer. Chem. Soc.*, **79**, 842 (1957); (b) H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 10; (c) S. Meyerson, *Rec. Chem. Progr.*, **26**, 257 (1965).

(9) K. L. Rinehart, Jr., A. C. Buchholz, G. E. Van Lear, and H. L. Cantrill, *J. Amer. Chem. Soc.*, **90**, 2983 (1968).

(10) A. S. Siegel, *ibid.*, **92**, 5277 (1970).

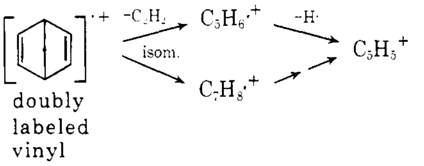
(11) A detailed examination of hydrogen scrambling in both toluene and cycloheptatriene has been reported: I. Howe and F. W. McLafferty, *ibid.*, **93**, 99 (1971).

The decomposition of unlabeled norbornadiene has been reported upon by Meyerson[12] and exhibits, in competition with the characteristic C_7H_8 fragmentation, an intense $C_5H_6\cdot^+$ ion ascribed to the electron impact reverse Diels–Alder (EIRDA) process. The splitting of acetylene from norbornadiene-*2,3*-$^{13}C_2$ (70 eV, 160° source temperature) is shown to occur with at most minor scrambling (Table III) and therefore before isomerization. The $C_5H_6\cdot^+$ ion from norbornadiene has substantially the same composition as C_5H_6 formed in the 470° pyrolysis. A significant difference is found between the $C_5H_5^+$ distributions from the norbornadiene and cycloheptatriene. This difference in behavior is attributed in whole or in part to the presence of an additional pathway to $C_5H_5^+$ in the case of norbornadiene, namely through the $C_5H_6\cdot^+$ intermediate.

Table III. High-Resolution Analysis of $C_5H_6\cdot^+$ from Norbornadiene-$^{13}C_2$ Mixture[a,b]

Composition	Abundance[b]	Calcd abundance: Scrambling	Calcd abundance: EIRDA
C_5H_6	0.467	0.128	0.518
$^{13}CC_4H_6$	0.139	0.505	0.096
$^{13}C_2C_3H_6$	0.394	0.367	0.386

[a] See footnotes *a–c* and *e* of Table I. [b] Mixture composition 77.2% $^{13}C_2$, 19.3% $^{13}C_1$, 3.5% $^{13}C_0$; independent data for pure norbornadiene-*2*-^{13}C not available.



Acknowledgment. The financial support of the Air Force Office of Scientific Research (1983) is acknowledged with gratitude.

(12) S. Meyerson, J. D. McCollum, and P. Rylander, *J. Amer. Chem. Soc.*, **83**, 1401 (1961).

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Photochemical Reaction of Oximes with Quinones. A New Method for the Preparation of Iminoxy Radicals

Sir:

There has been considerable interest in the preparation and properties of iminoxy radicals,[1] RR′C═NO·. We have recently found that such radicals are readily produced from oximes using photoexcited quinones as hydrogen abstractors. This method suffers from none of the limitations encountered in previously reported methods for the generation of iminoxy radicals.[1] High concentrations of radical and consequently clean electron paramagnetic resonance spectra can be obtained for all types of radicals, small amounts of oxime are required since radicals are produced in a "static" system, and radicals can be obtained at low temperatures and in rigid media. We describe here the technique used and also propose mechanisms for radical production and decay in these systems.

Experimentally, solutions containing approximately 50 mg of oxime and 20 mg of quinone in 1 ml of dichloromethane or benzene were prepared in 4-mm Pyrex tubing. Good spectra could be obtained without deoxygenation, but solutions were generally degassed by the freeze–thaw technique. Radicals were generated by irradiating the samples with a 150-W Varian EIMAC high-pressure xenon lamp in a Varian rectangular cavity with a 0.25-in. hole in the front plate. Spectra were obtained with a Varian E-3 spectrometer.

Supercooled liquid benzophenone has also been used as both solvent and hydrogen abstractor to generate diaryl- or arylalkyliminoxy radicals. Spectra from dialkyloximes have been observed under these conditions, but the iminoxy signals initially produced are rapidly replaced by the spectra of secondary nitroxide products in these cases. We have also obtained the spectrum of oriented diphenyliminoxy radicals in a benzophenone single crystal by this technique; analysis of the results is in progress.

Since irradiations were carried out at long wavelengths (λ_{ex} > 300 nm), precluding direct photodecomposition of oxime,[2,3] we presume that iminoxy radicals are produced as the result of hydrogen abstraction by the quinone $^3n\pi^*$ state.[4] It is therefore expected that efficiency of radical production will be independent of temperature as there should be no thermal activation barrier to hydrogen abstraction,[4] in contrast to the case of hydrogen abstraction by photolytically generated *tert*-butoxy radicals.[1] This is indeed what we have observed. For diphenyliminoxy there is a threefold increase in signal intensity for a 35° decrease in temperature. This increase in intensity is caused by a corresponding threefold increase in radical lifetime, from 0.67 sec at +10° to 2.1 sec at −25°, assuming that iminoxy decay is pseudo first order, as shown below.

For benzophenone another mechanism, involving triplet energy (E_T = 68.5 kcal/mol)[5] transfer[6] followed by oxime O–H bond rupture, should be considered in addition to hydrogen abstraction by the $^3n\pi^*$ state.[7] However the radical signals obtained in benzene solution using the isoenergetic but nonhydrogen abstracting sensitizers triphenylene (E_T = 66.6 kcal/mol)[5] and triphenylamine (E_T = 70.1 kcal/mol)[5] are at least two orders of magnitude less intense than those obtained using benzophenone under similar conditions and are probably due to direct light absorption by oxime.[2] This rules out the sensitization process.

In contrast to the second-order decay previously reported for aryl-substituted iminoxy radicals,[1] we have observed clean first-order decay in our systems (Figure 1). This decay presumably occurs by radical addition to quinone. This assumption is supported by the pronounced effect of quinone structure on the lifetime of the iminoxy radical, as well as by the appearance of nitroxide radicals concurrent with iminoxy

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(1) J. L. Brokenshire, J. R. Roberts, and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 7040 (1972), and references therein.

(2) P. P. Gaspar and C. T. Ho, unpublished results.

(3) H. Muto and M. Iwasaki, *J. Chem. Phys.*, **58**, 2454 (1973).

(4) J. M. Bruce, *Quart. Rev., Chem. Soc.*, **21**, 405 (1967).

(5) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(6) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 348.

(7) Reference 6, p 532.