the usual molybdenum blue method.[35]

Isomerization of 4-Allylanisole with Polymer-Bound $RuCl_2(PPh_3)_3$ (7a). In a typical experiment, a 20-mL Schlenk tube equipped with a neoprene seal was purged with 99.9% pure argon and charged with 107 mg of **7a** (1.6×10^{-2} mequiv of Ru). The reaction vessel was cooled to 0 °C, and into it there was injected a solution of 236 mg (1.6 mmol) of 4-allylanisole in 1.9 mL of mesitylene and 0.1 mL of 1-methylnaphthalene (internal standard). The tube was immersed at once into an oil bath regulated at 140 ± 0.2 °C. Samples (1–2 μL) were withdrawn periodically from the mixture and immediately frozen at −78 °C. GLC analysis was performed on a 6.32 × 2000 mm copper column packed with 20% DC 200 on 80–100-mesh Chromosorb P at 150 °C. After 90 min the liquid was decanted off (under argon), and the solid beads were washed three times with 10 mL of degassed benzene, dried under argon at 70 °C for 15 h, and then carried through an identical reaction procedure again.

Similar procedures were applied for the isomerization of the other allylic compounds by the three supported catalysts.

Acknowledgment. We thank Professor Milton Orchin for useful discussions and the United-States-Israel Binational Science Foundation for financial support of this study.

Registry No. **1** (Ar = C_6H_5), 300-57-2; **1** (Ar = 4-$CH_3OC_6H_4$), 140-67-0; **1** (Ar = 4-ClC_6H_4), 1745-18-2; **1** (Ar = $CH_3C_6H_4$), 3333-13-9; **1** (Ar = 3,4-$OCH_2OC_6H_3$), 94-59-7; **2** (Ar = C_6H_5), 766-90-5; **2** (Ar = 4-ClC_6H_4), 1879-52-3; **2** (Ar = 4-$CH_3C_6H_4$), 2077-29-4; **2** (Ar = 4-$CH_3OC_6H_4$), 25679-28-1; **3** (Ar = C_6H_5), 873-66-5; **3** (Ar = 4-ClC_6H_4), 1879-53-4; **3** (Ar = 4-$CH_3C_6H_4$), 2077-30-7; **3** (Ar = 4-$CH_3OC_6H_4$), 4180-23-8; **4** (R = $CH_3(CH_2)_4$), 3391-86-4; **4** (R = $CH_3(CH_2)_6$), 51100-54-0; **4** (R = C_6H_5), 4393-06-0; **5** (R = $CH_3(CH_2)_6$), 928-80-3; $RuCl_2(PPh_3)_3$, 15529-49-4; $RhCl(PPh_3)_3$, 14694-95-2; $IrCl(CO)(PPh_3)_2$, 15318-31-7.

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[35] Chalmers, R. A.; Thomson, D. A. *Anal. Chim. Acta* **1958**, *18*, 575.

Kinetic Properties of Caged Ambident Radicals Formed in the Thermolyses of Nitrones[1,2]

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Thermal decompositions of *N*-benzhydryl-α,α-diphenylnitrone (1) and the para-tetradeuterated analogue 1-d_4 in several solvents are reported. Mass spectral analyses of recovered nitrones and/or *O*-benzhydryl ethers were performed. These data are combined with previously reported spectroscopic rate constants for the decomposition of 1 to evaluate the true carbon-nitrogen homolysis rate constant and the relative rate constants for (a) geminate radical recombination at the iminoxy nitrogen, (b) irreversible recombination at oxygen, and (c) diffusion of the solvent-caged radicals.

Introduction

The thermal decomposition of *N*-benzhydryl-α,α-diarylnitrones in several different solvents involves the homolysis of a carbon–nitrogen bond forming iminoxy and benzhydryl radicals.[3] The lifetime of the initially formed caged radical pair is limited primarily by the occurrence of three competitive processes, namely, recombination at nitrogen to regenerate nitrone, irreversible recombination at oxygen to form *O*-benzhydryloxime, and diffusion from the cage.[4] The present study describes experiments which provide a measure of the true homolysis rate constant and of relative rates of destruction of the caged radical pair via the three paths mentioned above.

An understanding of the kinetic properties of these caged radical pairs can be derived from measurements of isotopic compositions of products formed from the thermal decompositions of mixtures of *N*-benzhydryl-α,α-diphenylnitrone (1) and its tetra-*p*-deuterated analogue 1-d_4.

Results

The synthesis of 1-d_4 has been recently described.[4,5] For the crossover experiments, mixtures of the deuterated and undeuterated nitrones 1 and 1-d_4 were decomposed in degassed solutions prepared from either diethylcarbitol (diethylene glycol diethyl ether), *tert*-butyl alcohol, or *N*,*N*-dimethylacetamide. In one run the mixture of nitrones was decomposed as a melt at 173 °C. The products were separated chromatographically and the isotopic composition of the *O*-benzhydryloxime and/or the recovered nitrone was then determined mass spectroscopically.[6] Control experiments (employing mass spectral analyses) with nitrones and *O*-ethers of known isotopic composition demonstrated that neither isotopic scrambing nor structural isomerization occurred during the isolation and separations following partial or total decompositions of nitrone mixtures. Table I summarizes the product analyses for decompositions of mixtures of 1 and 1-d_4.

The degree of intramolecularity, α, was determined by comparing the mole fraction of dideuterated species (*m*/*e* 365) found in the *O*-ether or nitrone with that expected from a purely statistical recombination of benzhydryl and iminoxy radicals. The degree of intramolecularity is defined in eq 1, where X_{365} is the mole fraction of di-

$$\alpha = (X_{365} - D_{365})/(C_{365} - D_{365}) \qquad (1)$$

deuterated species in the isolated nitrone or *O*-ether, D_{365} is the mole fraction of dideuterated species which would be formed from a completely statistical recombination of radicals, and C_{365} is the mole fraction of dideuterated species in the starting mixture of nitrones 1 and 1-d_4. The general methods and discussion of approximations for

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[1] Abstracted from the Thesis of J. A. Villarreal, University of California, San Diego, and San Diego State University. A preliminary report of this study has been published.[2]

[2] Villarreal, J. A.; Grubbs, E. J. *J. Am. Chem. Soc.* **1974**, *96*, 7594.

[3] See: (a) Villarreal, J. A.; Dobashi, T. S.; Grubbs, E. J. *J. Org. Chem.* **1978**, *43* 1890; (b) Grubbs, E. J.; Villarreal, J. A.; McCullough, J. D., Jr.; Vincent, J. S. *J. Am. Chem. Soc.* **1967**, *89*, 2234; (c) Vincent, J. S.; Grubbs, E. J. *Ibid.* **1969**, *91*, 2022; (d) Dobashi, T. S.; Parker, D. R.; Grubbs, E. J. *Ibid.* **1977**, *99*, 5382; Morris, D. G. *J. Chem. Soc. D* **1971**, 221.

[4] Villarreal, J. A.; Grubbs, E. J. *J. Org. Chem.* **1978**, *43*, 1896.

[5] The samples employed in these studies were comprised of 81.33% tetra-, 17.56% tri-, and 1.11% dideuterated species.

[6] The isotopic compositions of isolated tetraphenylethane samples were not determined. Neither was any attempt made to isolate benzophenone oxime from the decomposition products.

0022-3263/81/1946-0260$01.00/0

Table I. Product Analyses of Mixtures of 1 and 1-d_4 Decomposed at 144.0 °C

run	wt of 1, 1-d_4, mg	solvent (mL)	% reacn[l]	O-ether,[a] mg	nitrone,[b] mg	tetraphenylethane,[c] mg
1	10.0, 10.2	DEC[d] (20)	50		9.8	
2	10.2, 10.4	DEC (20)	99.9	9.8		3.5
3	10.1, 10.1	DEC (3)	99.9	12.2		2.5
4	20.3, 20.2	DEC (1[e])	99.9	29.6		3.5
5	33.1, 33.5	DEC (10)	10	4.6[f]	57.6	
6	15.9, 17.3	DEC (5)	20	4.0[g]	26.9	
7	10.6, 10.5	DEC (3)	30		15.4	
8	9.9, 10.1	t-BuOH (20)	50		9.8	
9	10.2, 9.9	t-BuOH (20)	99.9	17.0		0.2
10	10.0, 10.2	t-BuOH (3)	99.9	19.3		0.1
11	20.1, 20.2	t-BuOH (1[h])	99.9	37.4		0.5
12	9.9, 10.1	DMA[i] (20)	50		10.5	
13	10.0, 10.1	DMA (20)	99.9	8.6		3.9
14	20.3, 20.3	DMA (1[j])	99.9	26.6		4.5
15	13.6, 13.6	none[k]	99.9	23.3		

[a] Weight of O-benzhydryloxime isolated. [b] Weight of nitrone recovered. [c] Weight of 1,1,2,2-tetraphenylethane isolated. [d] Diethyl carbitol. [e] 1.0130 g. [f] 0.01208 mmol by UV analysis. [g] 0.01063 mmol by UV analysis. [h] 0.9203 g. [i] *N,N*-Dimethylacetamide. [j] 1.1301 g. [k] Decomposed in melt at 173 °C. [l] Based upon kinetic data.

Table II. Degree of Intramolecularity (α) for Nitrones[a] and O-Benzhydryloximes and Yields of O-Benzhydryloximes and Tetraphenylethane Isolated from Crossover Experiments at 144 °C

run	solvent	nitrone concn, M[b]	% reacn[c]	compd	α[d]	standard error of α	total O-ether yield[e]	yield of intramol O-ether[f]	yield of intermol O-ether[g]	yield of coupling product[h]
5	DEC[i]	0.0183	10	N[j]	0.973	0.0063				
				O[j]	0.362	0.0095				
6		0.0183	20	N	0.935	0.0037				
				O	0.368	0.0079				
7		0.0194	30	N	0.850	0.0012				
1		0.00278	50	N	0.835	0.0035				
2		0.00284	99.9	O	0.373	0.012	0.476	0.178	0.298	0.37
3		0.0185	99.9		0.325	0.012	0.604	0.196	0.408	0.26
4		0.0999	99.9		0.288	0.0065	0.731	0.210	0.521	0.19
8	t-BuOH	0.00276	50	N	0.600	0.0073				
9		0.00276	99.9	O	0.183	0.017	0.846	0.155	0.691	0.02
10		0.0185	99.9		0.164	0.017	0.956	0.157	0.799	0.01
11		0.0940	99.9		0.175	0.0082	0.929	0.162	0.767	0.03
12	DMA[k]	0.00276	50	N	0.819	0.0033				
13		0.00278	99.9	O	0.385	0.012	0.426	0.164	0.262	0.42
14		0.0927	99.9		0.310	0.0075	0.655	0.203	0.452	0.24
15	none[l]		99.9	O	0.509		0.86	0.44	0.42	

[a] Recovered nitrone. [b] Initial concentration of the mixture, 1 + 1-d_4. [c] Based upon kinetic data. [d] Calculated from eq 1. [e] Fraction of nitrone converted to O-benzhydrylbenzophenone oxime product. [f] Fraction of nitrone converted to O-benzhydrylbenzophenone oxime by intramolecular processes, equal to product of total O-ether yield and α; average precision of ±0.010. [g] Fraction of nitrone converted to O-benzhydrylbenzophenone oxime by intermolecular processes, equal to difference between total O-ether yield and the intramolecular O-ether yield. [h] Fraction of nitrone converted to 1,1,2,2-tetraphenylethane based on 1 mol of tetraphenylethane from 2 mol of nitrone; estimated average error of ±0.01. [i] Diethylcarbitol. [j] N is recovered nitrone. O is O-benzhydryloxime. [k] *N,N*-Dimethylacetamide. [l] In melt at 173 °C.

obtaining such values from mass spectral intensities have been described by Biemann.[7] Mass spectra of the undeuterated nitrone and O-ether were used to correct mass spectral intensities of isotopically labeled samples for isotopic natural abundances. The value of α is the fraction of the O-benzhydryloxime product or the fraction of recovered nitrone which is not formed by a statistical recombination of benzhydryl and iminoxy radicals. In the case of reisolated nitrone, the magnitude of α is determined in part by the fact that a portion of the nitrone has not undergone homolysis.

The value of α can theoretically be calculated from eq 2 for any value of m in the range 363–367. However, $|X_m - D_m|$ and $|C_m - D_m|$ have their largest valus for $m = 365$.[8]

$$\alpha = (X_m - D_m)/(C_m - D_m) \qquad (2)$$

The distribution of ion species derived from products (nitrone or O-ether shown in Table I) are presented in the tables in the experimental section. The values for the degree of intramolecularity (α) for the nitrones and O-benzhydryl oximes isolated in the above-described decompositions are shown in Table II. From these values the intramolecularities vs. intermolecularities are calculated.

In diethylcarbitol and DMA, as the initial nitrone concentration is reduced, the yield of intermolecularly formed O-ether decreases. This is to be expected since the hydrogen atom abstraction reaction of iminoxy radicals with solvent should become increasingly competitive with the bimolecular recombination of iminoxy radicals with benzhydryl radicals as dilution increases. The intermolecular formation of O-benzhydryloxime in diethylcarbitol and in

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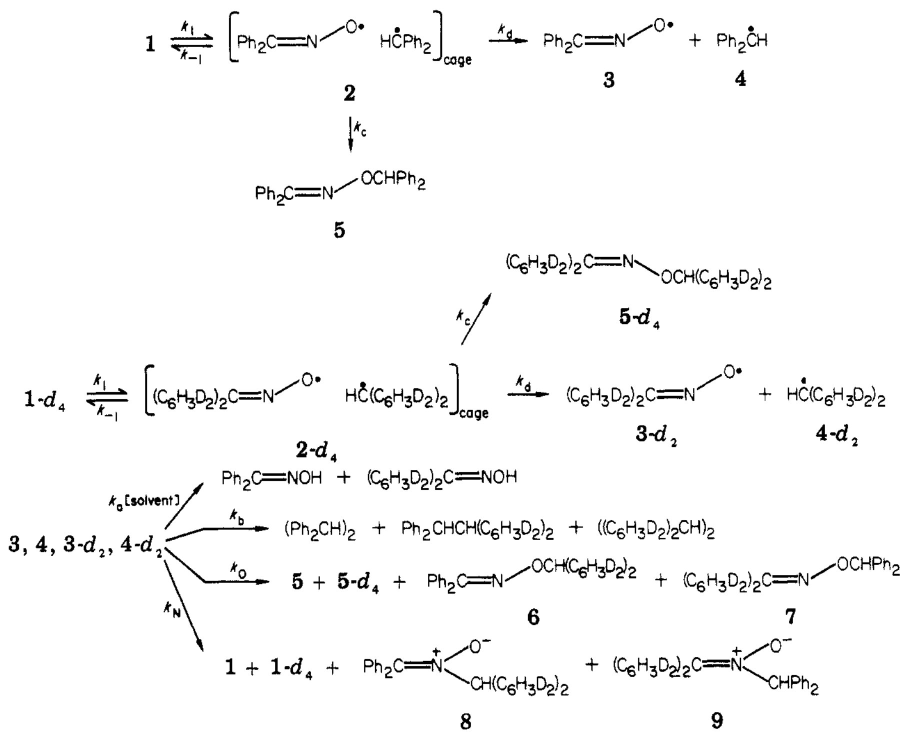
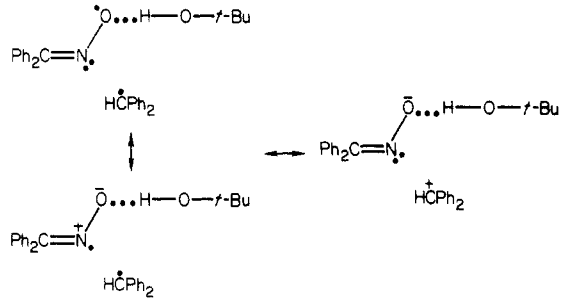
[7] Biemann, K. "Mass Spectrometry: Organic Chemical Applications", McGraw-Hill: New York, 1962; pp 59–69, 212–227.

[8] A propagation of error treatment shows that the standard error of α calculated from $m = 363$ or 367 data is four times larger on the average than for $m = 365$.

Scheme I



N,N-dimethylacetamide clearly occurs at the expense of tetraphenylethane (Table II), the yield of this dimer falling by a factor of nearly two for a 33-fold increase in the initial nitrone concentration. A remarkable inability of benzhydryl–benzhydryl (and apparently iminoxy–iminoxy) dimerization processes to compete with benzhydryliminoxy free-radical recombinations is observed in *tert*-butyl alcohol (cf. Table II). Even though 69–80% of the nitrone is converted to O-benzhydryloxime via an intermolecular path, only trace amounts of tetraphenylethane were formed. No completely adequate explanation for this observation is readily apparent. One possibility is that in the protic solvent, the radical pair possesses partial ionic character[9a] and diffuses with little dissociation until collision with a second pair leads to products.[9b] In the alcohol solvent, the initially formed intermediates might be formulated as shown below. Conceivably the hydrogen bonding could increase the contribution of the ion pair resonance form. The partial charge on the benzhydryl moiety might then account for the suppression of benzhydryl–benzhydryl dimerization. If this hypothesis is correct, a predictable variation of benzhydryl substituent effects on decomposition rates with solvent change should be observable. A more direct probe would be an ESR study of solvent effects upon the nitrogen hyperfine coupling constant in the iminoxy radicals generated from this nitrone. Unfortunately in our system the steady-state concentration of the iminoxy radical has been large enough to observe directly in decomposing melts of the nitrone, but not in solution.



Referring to Scheme I, the kinetic fate of the caged radical pair 2 is defined by the values of k_{-1}/k_c and k_d/k_c. In order to determine k_{-1}/k_c, the ratio r, millimoles of intermolecularly formed nitrone/millimole of intermolecularly formed O-ether, was evaluated. These data were obtained from decompositions interrupted after a short reaction time. The value of r will approach k_{-1}/k_c as the percent decomposition of nitrone approaches zero. This can be seen as follows by using k's for processes in the initial cage and k_N, k_O, and k_{other} for subsequent processes. At early stages of nitrone decomposition

rate of formation of intermolecularly formed nitrone

$$= k_1[\text{nitrone}]\left(\frac{k_d}{k_{-1} + k_c + k_d}\right)\left(\frac{k_N}{k_N + k_O + k_{\text{other}}}\right)$$

rate of formation of intermolecularly formed O-ether

$$= k_1[\text{nitrone}]\left(\frac{k_d}{k_{-1} + k_c + k_d}\right)\left(\frac{k_O}{k_N + k_O + k_{\text{other}}}\right)$$

and if we assume that free radical pairs which come together behave like initial caged radical pairs, i.e., $k_N/k_O = k_{-1}/k_C$, then

$$r = \frac{\text{yield of intermolecularly formed nitrone}}{\text{yield of intermolecularly formed } O\text{-ether}} = \frac{k_{-1}}{k_c}$$

Thus 0.182 mmol of an equimolar mixture of 1 and 1-d_4 (0.0183 M in DEC) was allowed to undergo 10% decomposition at 144 °C. After this period (61 min), 0.164 mmol of nitrone was recovered. Mass spectral analysis showed this to contain 0.0044 mmol of nitrone formed via intermolecular recombination of free radicals. The intermo-

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[9] (a) For a recent discussion of reactions on the borderline between radical and ionic chemistry, see: Martin, J. C. *ACS Symp. Ser.* **1978**, *69*, Chapter 5. (b) A referee has suggested an alternative explanation involving iminoxy radicals attacking caged radical pairs in what could be considered a chain-like process producing O-benzhydryloxime and a new iminoxy radical.

Table III. Partial Decomposition of Mixtures of 1 and 1-d_4 in DEC at 144 °C

% reaction	t, min	initial mixture 1 + 1-d_4, mmol	total nitrone remaining, mmol	nitrone remaining with isotopic composition 1 + 1-d_4, mmol[a]	f, fraction of original 1 + 1-d_4 remaining
10	61	0.1823	0.164	0.160	0.878
20	129	0.0908	0.0727	0.0680	0.749
30	204	0.0577	0.0404	0.0344	0.596
50	391	0.0548	0.0274	0.0229	0.418

[a] These values correspond to α × millimoles of total nitrone remaining.

Table IV. Summary of Relative Rate Constants (k_{-1}, k_c, and k_d) and Homolytic Rate Constants, k_1, for Primary Processes in Scheme I

	relative rate constants			
solvent	k_{-1}	k_c	k_d	$10^5 k_1$, s^{-1}
DEC	0.11	0.17	0.71	4.0
t-BuOH	0.14	0.13	0.73	2.6

lecularly formed *O*-ether isolated amounted to 0.0077 mmol. The ratio, r, is then 0.57[10] and approximates k_{-1}/k_c. The ratio k_d/k_c is equal to (100% − yield of intramolecularly formed *O*-ether)/(yield of intramolecularly formed *O*-ether) determined from runs involving total decomposition of nitrone. From the decomposition of an equimolar mixture of 1 and 1-d_4 (0.0185 M in DEC) the yield of intramolecularly formed *O*-ether was 19.6% (cf. Table II). Thus k_d/k_c under these conditions is 4.10.[11] Consequently, of the caged radical pairs formed in step k_1, approximately 11% recombine at nitrogen (k_{-1}) regenerating nitrone, 17% collapse to *O*-benzhydryloxime (k_c), and 71% diffuse to free radicals, eventually leading to the observed mixture of products.

The homolysis rate constant, k_1, can be derived from the data in Table III. The first-order rate constant, k', for the disappearance of nitrone of original composition 1 + 1-d_4 can be derived from the reaction steps in Scheme I, making the steady-state approximation for the caged radical pairs 2 and 2-d_4, and is given in eq 3. The integrated first-order rate law is shown in eq 4. The ratio [1

$$k' = k_1(k_c + k_d)/(k_c + k_d + k_{-1}) \tag{3}$$

$$\ln\left(\frac{[1 + 1\text{-}d_4]_0}{[1\ + 1\text{-}d_4]_t}\right) = k't \tag{4}$$

+ 1-d_4]$_t$/[1 + 1-d_4]$_0$ is equal to f in Table III. A plot of log f vs. t shows excellent linearity (correlation coefficient 0.997), passing through the origin which is the theoretical point for $t = 0$, $f = 1$. The slope of this plot yields a value for k' of 3.64×10^{-5} s^{-1}.

Rearrangement of eq 3 gives eq 5 in which the true

$$k_1 = k'(1 + k_d/k_c + k_{-1}/k_c)/(1 + k_d/k_c) \tag{5}$$

homolysis rate constant k_1 is expressed as a function of k', just determined, and the ratios k_d/k_c and k_{-1}/k_c previously evaluated. By use of the value 0.57 for k_{-1}/k_c and 4.10 for k_d/k_c (vide supra), a value for k_1 of 4.0×10^{-5} s^{-1} is obtained. The spectroscopically (UV) determined observed first-order rate constant for disappearance of 1 in DEC at 144 °C is 2.93×10^{-5} s^{-1}.[3a]

Similar kinetic information can be estimated for nitrone decompositions in *tert*-butyl alcohol although only one crossover experiment was conducted in this solvent under conditions of partial decomposition. In this experiment, the reaction was interrupted after 50% decomposition had occurred (cf. Tables I and II). The value of k' (previously defined) can be calculated by using eq 4. After one half-life at 144 °C (t = 882 min) in *tert*-butyl alcohol the fraction of the original nitrone mixture remaining is (0.49)(0.60)/1.00 or 0.29. The value of k' is then 2.3×10^{-5} s^{-1}. The value of k, the spectrophotometrically determined rate constant for the decomposition of the nitrone under these conditions, is 1.31×10^{-5} s^{-1}.[3a] These two rate constants can be combined to obtain k_{-1}/k_c and k_1, the homolysis rate constant. From Scheme I, the rate constant k (experimentally determined spectrophotometrically) for the decomposition of nitrone 1 can be derived in terms of k_1, k_{-1}, k_c, k_d, k_O, and k_N. This is shown in eq 6. For this

$$k = [k_1/(k_c + k_d + k_{-1})][k_c + k_d k_O/(k_N + k_O)] \tag{6}$$

derivation, the reaction steps corresponding to k_a and k_b in Scheme I were omitted from consideration because of the relative insignificance of these reactions in *tert*-butyl alcohol. The steady-state approximation was made for both the caged radical pair 2 and for the free radicals 3 and 4. When eq 3 is divided by eq 6, k_1 is eliminated, giving eq 7. Equation 7 can then be rearranged whereby

$$\frac{k'}{k} = [k_c + k_d]/[k_c + k_d k_O/(k_N + k_O)] \tag{7}$$

k'/k is obtained in terms of k_d/k_c and k_N/k_O as shown in eq 8. The ratio k'/k is $2.3 \times 10^{-5}/1.3 \times 10^{-5}$ or 1.76. The

$$\frac{k'}{k} = [1 + k_d/k_c]/[1 + (k_d/k_c)/(1 + k_N/k_O)] \tag{8}$$

ratio k_d/k_c is (1 − 0.155)/0.155 or 5.45 (cf. Table II). By use of these values in eq 8, k_N/k_O is calculated to be 1.05. Again on the assumption that k_{-1}/k_c is approximately the same as k_N/k_O, the relative magnitudes of k_{-1}, k_d, and k_c in *tert*-butyl alcohol at 144 °C are 1.05, 5.45, and 1.00, respectively. Thus, of the caged radical pairs generated by the homolysis in *tert*-butyl alcohol, 14% recombine to form nitrone, 13% collapse to *O*-benzhydryloxime, and 73% diffuse from the cage to become free radicals. And finally from eq 5 the homolysis rate constant, k_1, in *tert*-butyl alcohol is found to be 2.6×10^{-5} s^{-1}. Table IV lists the relative rate constants (for competitive processes within

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[10] A similar analysis of products from a run stopped after 20% reaction (at which point 93.5% of the recovered nitrone still possessed its original isotopic distribution) gave $r = 0.70$. The estimated error of r at 10% reaction is ±23%. The estimated error of r determined at 20% reaction is ±8%. The error is due principally but not exclusively to uncertainty in α_N at early stages of decomposition (cf. Table II). The total amount of *O*-ether formed at 10% reaction was 0.0121 mmol of which 0.0077 mmol was scrambled. At 20% reaction the corresponding quantities were 0.0106 and 0.0067 mmol. Starting nitrone concentrations, but not the weights of 1 + 1-d_4, were identical for these separate experiments. A rate constant, k', for the first-order disappearance of nitrone of original isotopic composition (namely that of pure 1 + 1-d_4) can be determined and is presented in the discussion section. By use of this k', the values of r can be corrected, giving values of 0.56 and 0.61. The average of these two values is 0.58, virtually the same as the uncorrected value of r obtained directly from the 10% decomposition experiment.

[11] The ratio k_d/k_c is somewhat dependent upon initial nitrone concentration as seen from the data in Table II. For example in diethylcarbitol at a molarity of 0.00284, k_d/k_c is 4.6; at 0.0999 M it is 3.8.

Table V. Distributions of Deuterated Species in *O*-Benzhydryloximes Obtained from Total^a Decomposition of Mixtures of 1 and 1-d_4 at 144 °C

run^b	solvent	nitrone concn, M^c	fraction of ions with m/e					
			363	364	365	366	367	
2	DEC^d	0.00284	0.3397	0.0331	0.2862	0.0626	0.2784	X^e
			0.4977	0.0	0.0058	0.0882	0.4085	C^e
			0.2477	0.0494	0.4530	0.0450	0.2048	D^e
3	DEC	0.0185	0.3175	0.0465	0.3069	0.0664	0.2627	X
			0.5181	0.0	0.0054	0.0846	0.3919	C
			0.2684	0.0494	0.4522	0.0414	0.1885	D
4	DEC	0.0999	0.3252	0.0306	0.3240	0.0548	0.2654	X
			0.5038	0.0	0.0055	0.0871	0.4036	C
			0.2538	0.0451	0.4530	0.0439	0.2000	D
9	*t*-BuOH	0.00276	0.3023	0.0387	0.3710	0.0534	0.2346	X
			0.5101	0.0	0.0054	0.0860	0.3985	C
			0.2602	0.0494	0.4528	0.0428	0.1949	D
10	*t*-BuOH	0.0185	0.2957	0.0358	0.3796	0.0511	0.2378	X
			0.4976	0.0	0.0056	0.0882	0.4086	C
			0.2476	0.0494	0.4530	0.0450	0.2049	D
11	*t*-BuOH	0.0940	0.2973	0.0338	0.3748	0.0477	0.2464	X
			0.5014	0.0	0.0055	0.0875	0.4055	C
			0.2514	0.0494	0.4530	0.0443	0.2018	D
13	DMA^f	0.00278	0.3343	0.0331	0.2806	0.0652	0.2869	X
			0.5084	0.0	0.0055	0.0863	0.3998	C
			0.2585	0.0494	0.4528	0.0431	0.1962	D
14	DMA	0.0927	0.3254	0.0333	0.3143	0.0617	0.2654	X
			0.5026	0.0	0.0055	0.0873	0.4046	C
			0.2526	0.0494	0.4530	0.0441	0.2009	D
15	none^g		0.3765	0.0207	0.2252	0.0657	0.3119	X
			0.5025	0.0	0.0055	0.0873	0.4046	C
			0.2525	0.0494	0.4530	0.0441	0.2010	D

[a] Runs in Table V correspond to 99.9% reaction. [b] Run numbers correspond to experiments summarized in Table I. [c] Initial concentrations of the mixtures 1 plus 1-d_4. [d] Diethyl carbitol. [e] Values in successive rows opposite X, C, and D correspond to fractional distributions calculated for previously defined X_m, C_m, and D_m. Note that X and C values are mass spectrometrically determined; D values are calculated from the limiting model of complete statistical recombination of radicals. [f] *N,N*-Dimethylacetamide. [g] Decomposition in the melt at 173 °C.

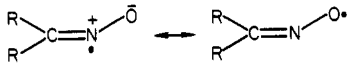
Table VI. Distributions of Deuterated Species in Nitrones^a and *O*-Benzhydryloximes Obtained from Partial Decomposition of Mixtures of 1 and 1-d_4 at 144 °C

run^b	solvent	nitrone concn, M^c	compd	% reacn^h	fraction of ions with m/e					
					363	364	365	366	367	
5	DEC^d	0.0183	N^a	10	0.5142	0.0	0.0176	0.0827	0.3855	X^f
					0.4996	0.0	0.0056	0.0879	0.4070	C^f
					0.2496	0.0495	0.4530	0.0446	0.2033	D^f
			O^g		0.3385	0.0428	0.2910	0.0602	0.2674	X
					0.4996	0.0	0.0056	0.0879	0.4070	C
					0.2496	0.0495	0.4530	0.0446	0.2033	D
6	DEC	0.0183	N^a	20	0.4708	0.0012	0.0350	0.0868	0.4062	X
					0.4816	0.0	0.0058	0.0910	0.4216	C
					0.2319	0.0494	0.4525	0.0479	0.2182	D
			O^g		0.3271	0.0259	0.2883	0.0615	0.2972	X
					0.4816	0.0	0.0058	0.0910	0.4216	C
					0.2319	0.0494	0.4525	0.0479	0.2182	D
7	DEC	0.0194	N^a	30	0.4691	0.0125	0.0727	0.0789	0.3667	X
					0.5049	0.0	0.0055	0.0869	0.4027	C
					0.2549	0.0494	0.4529	0.0437	0.1991	D
1	DEC	0.00278	N^a	50	0.4589	0.0033	0.0794	0.0784	0.3800	X
					0.5084	0.0	0.0055	0.0863	0.3998	C
					0.2585	0.0494	0.4528	0.0431	0.1962	D
8	*t*-BuOH	0.00276	N^a	50	0.3969	0.0162	0.1846	0.0727	0.3297	X
					0.4976	0.0	0.0056	0.0882	0.4086	C
					0.2476	0.0494	0.4530	0.0450	0.2049	D
12	DMA^e	0.00276	N^a	50	0.4540	0.0048	0.0868	0.0813	0.3732	X
					0.4976	0.0	0.0056	0.0882	0.4086	C
					0.2476	0.0494	0.4530	0.0450	0.2049	D

[a] Recovered nitrone. [b] Run numbers correspond to experiments summarized in Table I. [c] Initial concentrations of the mixtures 1 plus 1-d_4. [d] Diethylcarbitol. [e] *N,N*-Dimethylacetamide. [f] Values in successive rows opposite X, C, and D correspond to fractional distributions calculated for previously defined X_m, C_m, and D_m. Note that X and C values are mass spectrometrically determined; D values are calculated from the limiting model of complete statistical recombination of radicals. [g] *O*-Benzhydryloxime. [h] Based upon kinetic data.

a given solvent), k_{-1}, k_c, and k_d as well as the values for the homolysis rate constants, k_1. Estimated errors in these rate constants are ±5–10%.

Clearly the fraction of caged radical pairs being destroyed through diffusion is about the same in diethylcarbitol and in *tert*-butyl alcohol. This is not surprising considering the small and apparently similar viscosities of these solvents at our relatively high (144 °C) working temperature.[12] Although the data used to obtain the kinetic parameters in *tert*-butyl alcohol are admittedly limited, there is an indication that the ratio of rates of collapse of the caged radicals at nitrogen compared with oxygen (k_{-1}/k_c) is significantly greater in *tert*-butyl alcohol than in diethylcarbitol. Alcohols are known to hydrogen bond to nitrones.[14] And iminoxy radicals possess nearly equal spin density at nitrogen and oxygen.[15] Thus hydrogen bonding which may persist with the iminoxy radical following initial homolysis (vide supra) may alter recombination rate ratios, k_{-1}/k_c, when compared with these competitive processes in aprotic solvents. Qualitatively this would be expected to increase k_{-1}/k_c in *tert*-butyl alcohol.



In recent years considerable interest has been expressed in effects of viscosity (and other solvent parameters[16]) on cage recombination processes. An examination of the range of yields of cage combinations to form *O*-benzhydryloxime in the three solvents (Table II) suggests only small variations in these solvent properties at our elevated working temperatures (144 °C). However, in one experiment, a mixture of 1 and 1-d_4 was decomposed at 173 °C in the absence of solvent. The melt, consisting primarily of nitrone and *O*-benzhydryloxime, is highly viscous at this temperature. The degree of intramolecularity (α = 0.51) for the *O*-oxime product was considerably higher than that obtained in any of the solution decompositions (cf. Table II). An 86% yield of *O*-ether was isolated from this decomposition. Thus the yield of *O*-benzhydryloxime formed via cage recombination was 44%. This compares with yields of 16–21% for solution decompositions at lower temperature. This suggests that diffusion of the geminate radical pair has been more severely limited in the melt.[17]

Experimental Section

Approximately equimolar amounts of deuterated and undeuterated nitrones (cf. Table I) were weighed into Pyrex tubes. The appropriate dry solvent (freshly distilled) was added with a pipet. The solutions were degassed and the tubes sealed under vacuum. The tubes were heated in a constant temperature bath at 144 ± 0.1 °C. In one experiment the decomposition was performed at 173 ± 0.1 °C. After a time required for 99.9% reaction, the *O*-benzhydryloxime and tetraphenylethane products were isolated quantitatively by chromatography on alumina. Hexane–benzene (49:1) eluted the tetraphenylethane. Hexane–benzene (4:1) eluted the *O*-oxime. After the decompositions corresponding to 10, 20, 30, and 50% reaction, it was necessary to first chromatograph the decomposition mixture on Florisil in order to isolate the undecomposed nitrone which was unstable on alumina. The fractions eluted prior to elution of nitrone were combined and chromatographed on alumina to isolate the *O*-benzhydryloxime.

The mass spectra of *O*-benzhydryloxime samples were obtained with scans under ionizing voltages of 12.5–20.5 eV at chamber temperatures of 60–95 °C. For the nitrones the corresponding conditions were 12.5–19 eV and 80–115 °C. Fragmentation due to loss of hydrogen was negligible under these conditions. Distributions of deuterated species obtained from the decompositions of mixtures of 1 and 1-d_4 are given in Tables V and VI.

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Registry No. 1, 5076-57-3; 1-d_4, 65311-50-4; *O*-benzhydrylbenzophenone oxime, 65311-52-6; 1,1,2,2-tetraphenylethane, 632-50-8.

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[12] The viscosities of these solvents are very low at 144 °C. The value for DMA at 144 °C is approximately 4.3 × 10^{-3} P.[13] Those for *tert*-butyl alcohol and diethylcarbitol, based upon extrapolations, appear to be somewhat smaller.

[13] Friend, J. N.; Hargreaves, W. D. *Philos. Mag.* **1946**, *37*, 201.

[14] Hamer, J.; Macaluso, A. *Chem. Rev.* **1964**, *64*, 473.

[15] Symons, M. C. R. *J. Chem. Soc.* **1963**, 1189.

[16] Nodelman, N.; Martin, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 6597 and references therein.

[17] It is possible that induced decomposition becomes important in the condensed phase. The nitrone does appear to trap free benzhydryl radicals to form nitroxides.[3c] And nitroxides are known to disproportionate to nitrones and hydroxylamines. Whether any induced decomposition leads to *O*-benzhydryloxime is not known.

Reaction of Allylic and Benzylic Methyl Ethers with Sodium and Trimethylchlorosilane. Evidence for the Intermediacy of Allylic Radicals and Anions

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Allyl methyl ether and benzyl methyl ether react with sodium and trimethylchlorosilane to yield, respectively, allyltrimethylsilane and benzyltrimethylsilane. α,α-Dimethylallyl methyl ether and γ,γ-dimethylallyl methyl ether react with sodium and trimethylchlorosilane to yield γ,γ-dimethylallyltrimethylsilane. α-Methylallyl methyl ether and *trans*-γ-methylallyl methyl ether react with trimethylchlorosilane and sodium to yield similar product mixtures of α-methylallyltrimethylsilane and *cis*- and *trans*-γ-methylallyltrimethylsilane. These results are discussed in terms of a mechanism involving electron transfer to yield allylic radicals and allylic anion intermediates.

We report herein a novel synthesis of allylic trimethylsilanes. Specifically, allylic methyl ethers react with trimethylchlorosilane and sodium metal in hydrocarbon solvents such as *n*-decane or toluene to yield the corresponding allylic trimethylsilane and methoxytrimethylsilane in good yields. There is considerable interest in allylic trimethylsilanes since they have been shown to be versatile intermediates in organic synthesis which react

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