An Investigation of the Inter- vs. Intramolecularity of the Thermal Rearrangement of *N*-Benzhydryl-α,α-diphenylnitrone to Benzophenone *O*-Benzhydryloxime

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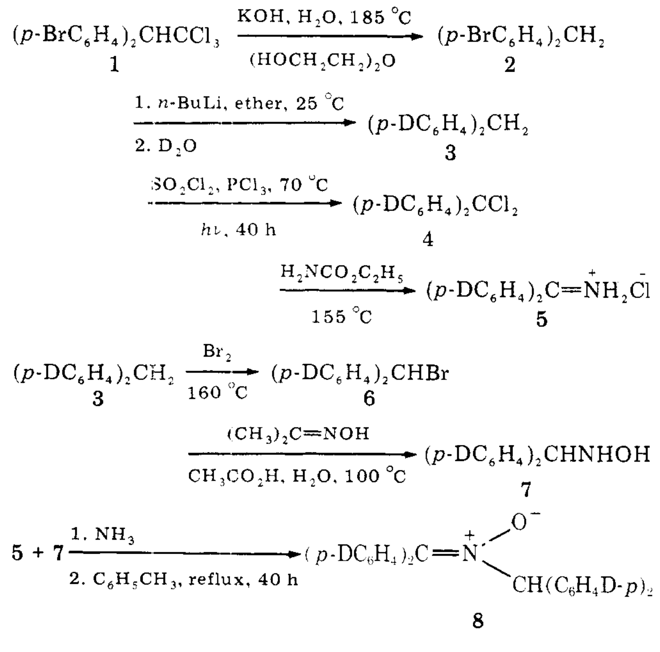
The synthesis of *N*-(benzhydryl-*p,p′*-d_2)-α,α-diphenyl-*p,p′*-d_2-nitrone (8) is described. Thermal decompositions of mixtures of 8 and the undeuterated analogue 9 have been conducted in diethylcarbitol, in *tert*-butyl alcohol, and in dimethylacetamide. On the basis of mass spectral analyses of the product (benzophenone *O*-benzhydryloxime), the extent of intermolecularity in the N to O rearrangement has been determined. Solvent effects on the partitioning of the radical intermediates is discussed. Evidence is also presented for iminoxy benzhydryl radical recombination at nitrogen to regenerate nitrone.

The currently available data[2] bearing on the thermal rearrangement of *N*-benzhydryl-α,α-diarylnitrones to the corresponding *O*-benzhydryloximes indicate that the principal mechanistic route involves the formation of iminoxy and benzhydryl radicals. In this report we describe the preparation of para-tetradeuterated *N*-benzhydryl-α,α-diphenylnitrone (8). Thermal decompositions of mixtures of 8 and the undeuterated analogue 9 are also described. The results allow an assessment of the inter- vs. intramolecular partitioning of this rearrangement.

Results

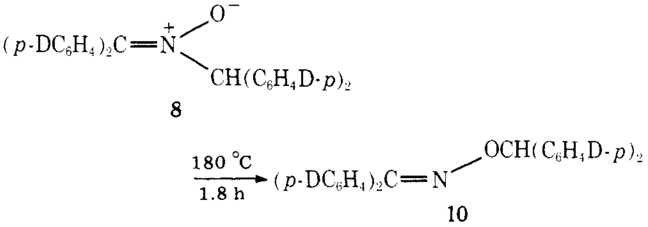
Syntheses. The synthesis of *N*-(benzhydryl-*p,p′*-d_2)-α,α-diphenyl-*p,p′*-d_2-nitrone (8) is illustrated in Scheme I. The starting trichloride was easily prepared by the acid-catalyzed alkylation of bromobenzene by chloral hydrate,[3] but in low (9%) yield. Conversion of the trichloride 1 to 4,4′-dibromodiphenylmethane (2) proceeded in high (85%) yield as previously described by Galun, Kaluszyner, and Bergmann.[4] This dibromide was treated with butyllithium in hexane, the concentration of which was determined by a double titration technique.[5] Adventitious contamination by water during the deuterolysis step led to less than complete dideuteration. Nonetheless, approximately 93% of theoretical maximum deuterium content was introduced into the two para positions. The chlorination of 3 proceeded in 74% yield. Conversion of 4 to the imine hydrochloride 5 was accomplished in 40% yield using ethyl carbamate.[6] Bromination of 3 provided 6 in 86% yield. The alkylation of acetone oxime by 6 and in situ hydrolysis afforded the deuterated *N*-benzhydrylhydroxylamine (7) in 43% yield. Finally, condensation in toluene of 7 and the imine liberated from 5 by ammonia provided the desired labeled nitrone 8 in 30% yield.

Scheme I



Combustion analysis of 8 showed it to have 17.63 atom % excess of deuterium (average of two analyses). Since the theoretical for fully tetradeuterated nitrone is 19.05 atom %, this represents 92.5% of complete para deuteration. This is in excellent agreement with the value obtained for 3. Thus no deuterium was lost in the intervening synthetic steps. The mass spectra of 8 (using mass spectra of the undeuterated analogue 9 to correct for naturally occurring isotope contributions) indicated that 8 was composed of 81.33% tetra-, 17.56% tri, and 1.11% dideuterated species.

A sample of the *O*-benzhydryl isomer of 8 was prepared by heating 8 in the melt at 180 °C, followed by chromatography and crystallization.



Crossover Experiments. Mixtures of the deuterated and undeuterated nitrones 8 and 9 were decomposed in degassed solutions prepared from diethylcarbitol, *tert*-butyl alcohol, and *N,N*-dimethylacetamide. The products were separated chromatographically and the isotopic composition of either the *O*-benzhydryloxime or recovered nitrone was then determined mass spectroscopically.[7] The product analyses for these decompositions are summarized in Table I.

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 by

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

where X_{365} is the mole fraction of dideuterated 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 8 and 9. The general methods and discussion of ap-

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Table I. Product Analyses from Decompositions of Mixtures of 8 and 9 at 144 °C in Several Solvents

Run no.	Weights of 8 and 9, mg	Solvent	Vol, mL	% reaction[a]	*O*-Ether,[b] mg	Nitrone,[c] mg	Tetraphenylethane, mg
I	10.2, 10.4	DEC[d]	20	99.9	9.8		3.5
II	10.2, 9.9	*t*-BuOH	20	99.9	17.0		0.2
III	10.0, 10.1	DMA[e]	20	99.9	8.6		3.9
IV	9.9, 10.1	*t*-BuOH	20	50		9.8	

[a] Based upon kinetic data. [b] Weight of *O*-benzhydryloxime. [c] Weight of recovered nitrone. [d] Diethylcarbitol. [e] *N,N*-Dimethylacetamide.

Table II. Distribution of Ion Species from *O*-Benzhydryloximes and Nitrone Isolated from the Decomposition of Mixtures of 8 and 9

Run no.[a]	Product analyzed	Fraction of ions with *m/e* 363	364	365	366	367	
I	*O*-Ether[b]	0.3397	0.0331	0.2862	0.0626	0.2784	*X*[c]
		0.4977	0.0	0.0058	0.0882	0.4085	*C*[c]
		0.2477	0.0494	0.4530	0.0450	0.2048	*D*[c]
II	*O*-Ether	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*
III	*O*-Ether	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*
IV	Nitrone	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*

[a] Corresponds to experiments summarized in Table I. [b] *O*-Benzhydryloxime. [c] Values in successive rows opposite *X*, *C*, and *D* correspond to fractional distributions calculated for previously defined X_m, C_m, and D_m.

Table III. Summary of Crossover Experiments[a] Corresponding to Total Decompositions of Mixtures of 8 and 9 at 144 °C

Solvent	Nitrone concn, M[b]	Total *O*-ether yield[c]	α[d]	Yield of intramol *O*-ether[e]	Yield of intermol *O*-ether[f]	Yield of coupling product[g]
DEC[h]	0.00284	0.476	0.373	0.178	0.298	0.37
t-BuOH	0.00276	0.846	0.183	0.155	0.691	0.02
DMA[i]	0.00278	0.426	0.385	0.164	0.262	0.42

[a] Based upon data in Tables I and II. [b] Initial concentration of the mixture. [c] Fraction of nitrone converted to benzophenone *O*-benzhydryloxime. [d] Degree of intramolecularity in N to O rearrangement. [e] Fraction of nitrone converted to *O*-ether by an intramolecular process; equal to product of total *O*-ether yield and α. [f] Difference between total *O*-ether yield and the intramolecular *O*-ether yield. [g] Fraction of nitrone converted to 1,1,2,2-tetraphenylethane based upon 1 mol of tetraphenylethane from 2 mol of nitrone. [h] Diethylcarbitol. [i] *N,N*-Dimethylacetamide.

proximations for obtaining such values from mass spectral intensities have been described by Biemann.[8] Mass spectra of 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 the reisolation of unrearranged nitrone, the magnitude of α is influenced by the fact that a portion of the nitrone never undergoes homolysis.

The value of α can theoretically be calculated from the equation

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

for any value of *m* in the range of 363–367. However, $|X_m - D_m|$ and $|C_m - D_m|$ have the largest values for $m = 365$.[9]

The distribution of ion species derived from products (nitrone or *O*-ether) shown in Table I are presented in Table II. Necessary control experiments (employing mass spectral analyses) with nitrones and *O*-ethers of known isotopic composition demonstrated that neither isotopic scrambling nor structural isomerization occur during the isolation and separations following partial or total decompositions of nitrone mixtures.

The intra- vs. intermolecularity of the N to O rearrangements under conditions effecting total decompositions of nitrones is given in Table III.

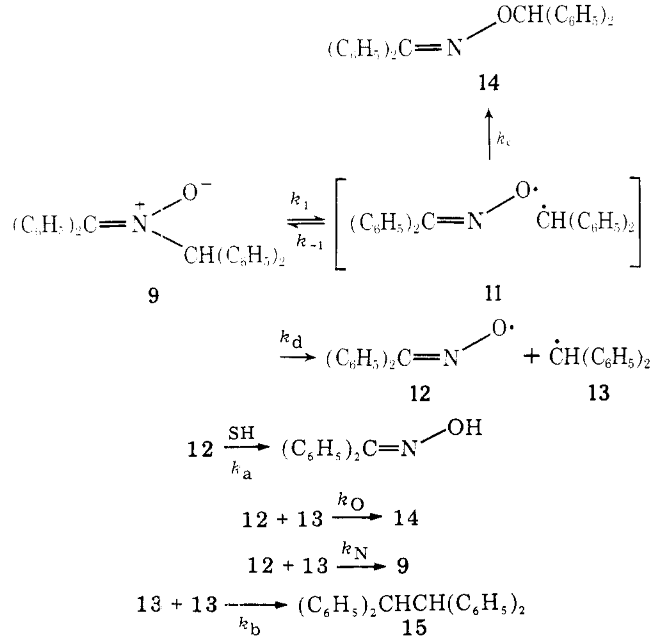
Discussion

The data and data summary in Tables I–III demonstrate that in all solvents employed, the major portion of benzophenone *O*-benzhydryloxime from rearrangement of nitrone is formed via an intermolecular process. Thus, in diethylcarbitol 62.5% of the *O*-ether isolated is produced intermolecularly; in dimethylacetamide the corresponding value is 68.1%, and in *tert*-butyl alcohol it is 81.7%.

The substantial intermolecularity of the N to O rearrangement together with the isolation of tetraphenylethane in each case provide evidence for the initial formation of benzhydryl and iminoxy radicals from homolysis of the nitrone C–N bond.

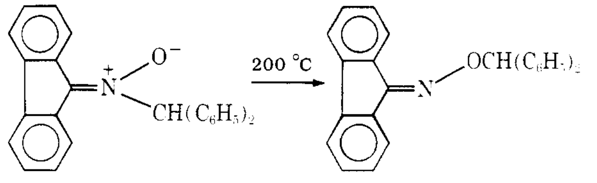
The fraction of nitrone converted to *O*-benzhydryloxime by an intermolecular process is clearly solvent dependent.[10] By contrast, the fraction of nitrone converted to *O*-benzhydryloxime via an intramolecular route is nearly independent

Scheme II



of the nature of the solvent (at least at this elevated temperature of 144 °C), the value being 16.5 ± 1%. These results can be explained in terms of the behavior of the radical pair initially formed in these solvents. The options available to the radical pair are outlined (using undeuterated structures for simplicity) in Scheme II. The radical pair, **11**, is initially formed via C–N homolysis within a solvent cage. This caged pair of radicals can collapse to *O*-benzhydryloxime (giving intramolecularly formed **14**) before they diffuse (k_d) and become free radicals or they can recombine at nitrogen, regenerating nitrone. The fraction of radical pairs that eventually collapse to the cage product, **14**, prior to diffusion, is nearly identical in the three solvents at this elevated temperature.[11] The bulk of the remaining radical pairs, **11**, are converted to free radicals. The free benzhydryl and iminoxy radicals thus formed by the diffusion process can recombine at oxygen to form "intermolecular *O*-ether" or at nitrogen. That the latter as well as the former occurs can be deduced from the data in Table II, wherein reisolated nitrone was analyzed mass spectrometrically after 50% decomposition. Using eq 1, α is found to be 0.60. The coupling of benzhydryl radicals to form tetraphenylethane and the abstraction of hydrogen atoms from the solvent[13] (primarily by iminoxy radicals to form benzophenone oxime) are, however, processes which compete with the bimolecular recombination of these two free radicals. The hydrogen atom donating abilities of the three solvents are reflected in the yield of benzophenone oxime. Under conditions comparable to those employed for the crossover studies, the yields of benzophenone oxime in diethylcarbitol and in DMA were 22 and 27%, respectively; in *tert*-butyl alcohol, the yield was virtually zero.[14] Thus the diminished yields of intermolecularly formed *O*-benzhydryloxime in diethylcarbitol and in DMA is a result of extensive destruction of free iminoxy radicals via hydrogen-atom transfer from the solvents.

The crossover experiments discussed above show that free benzhydryl and iminoxy radicals are generated to a major extent during the decomposition of *N*-benzhydryl-α,α-diphenylnitrone. The intramolecularly formed rearrangement product presumably originates from cage recombination of the radical pair at oxygen, an irreversible process at the operating temperature.[2a,c] The possibility that a small amount of this product is formed by way of a fully concerted mechanism[15] cannot be excluded. In this regard it is interesting to note the following. Nitrone **16** has been decomposed in a solution of hexachlorobutadiene at 200 °C.[2d] During the decomposition, CIDNP (emission) was observed for the benzhydryl proton of the rearrangement product **17**, formed in 52% yield. Thus, caged radical recombination is implicated during the thermolysis of this nitrone, which is closely related to the substrate in the present study.



16 **17**

A full report describing the kinetic partitioning of processes available to the benzhydryl–iminoxy radical pair, **11**, will be published at a later time.

Experimental Section[16]

1,1-Bis(4-bromophenyl)-2,2,2-trichloroethane (**1**)[3] was converted to **4,4′-dibromodiphenylmethane** (**2**) by a previously described method.[4]

Diphenylmethane-*4,4′-d*$_2$ (3) was prepared from 4,4′-dibromodiphenylmethane via a metal–halogen exchange (using butyllithium) followed by deuterolysis. A 96.0-g (0.295 mol) sample of the dibromide in 1500 mL of anhydrous ether was treated with 320 mL of a 1.68 M solution (0.538 mol) of butyllithium in hexane over a period of 30 min. The reaction was carried out under an atmosphere of nitrogen while stirring the mixture continuously. Following an additional 25-min period of stirring, an excess of 99.5 mol % pure deuterium oxide was added dropwise with cooling and stirring. The reaction mixture was filtered and concentrated to about 100 mL. The concentrate was then distilled affording 36.4 g (79.6%) of **3**, bp 146–157 °C (27–30 mm). This product was combined with 5.8 g of **3** similarly obtained and redistilled to give 36.1 g of **3** as a colorless liquid, bp 105–108 °C (3.3 mm). Diphenylmethane reportedly distills at 149 °C (29 mm).[17] The NMR spectrum (CCl_4) is as follows: δ 3.90 (s, 2 H, CH_2) and 7.12 (m, ~8 H, aromatic). Duplicate combustion analyses of the product indicated 15.45 and 15.55 atom % excess D (theoretical for fully dideuterated diphenylmethane is 16.67%).

Dichlorodiphenylmethane-*4,4′-d*$_2$ (4). A mixture of 18.2 g (0.107 mol) of dideuteriodiphenylmethane, 35 mL (0.433 mol) of freshly distilled sulfuryl chloride, and 1.4 mL (0.016 mol) of phosphorus trichloride was placed in a 250-mL quartz flask equipped with a condenser and acidic gas trap. The mixture was placed in a Rayonet photochemical reactor fitted with 253.7-nm lamps. The solution was stirred and irradiated for 40 h at about 70 °C. The reaction mixture was distilled affording 18.8 g (74%) of a light-yellow liquid, bp 138–145 °C (2.4 mm). Dichlorodiphenylmethane reportedly distills at 164–167 °C (12 mm).[18] The IR spectrum (neat) showed the C–D stretches at 2260 and 2280 cm^{-1}. The NMR spectrum (CCl_4) showed only a symmetrical multiplet at δ 7.40.

Benzophenone Imine-4,4′-*d*$_2$ hydrochloride (5) was prepared from **4** using a method previously described for the undeuterated analogue.[19] The crude hydrochloride was purified by sublimation [185 °C (1 mm)]. The white crystalline product was obtained in 40% yield and used directly as described below.

Bromodiphenylmethane-*4,4′-d*$_2$ (6) was prepared by brominating **3** as described for the undeuterated analogue.[20] The product (obtained in 86% yield) distilled as a yellow liquid, bp 135–145 °C (0.9 mm). Bromodiphenylmethane distills at 183 °C (23 mm).[7] The infrared spectrum (neat) showed C–D stretches at 2260 and 2280 cm^{-1}. The NMR spectrum (CCl_4) was as follows: δ 6.17 (s, 1 H, CBrH) and 7.42 (m, ~8 H, aromatic).

***N*-Benzhydrylhydroxylamine-*4,4′-d*$_2$ (7)** was prepared from **6** as described for the undeuterated analogue.[21] The colorless product (obtained in 43% yield) crystallized from cyclohexane, mp 76.5–77.5 °C. The reported[21] melting point of the undeuterated compound is 75 °C.

***N*-(Benzhydryl-*p,p′-d*$_2$)-α,α-diphenyl-*p,p′-d*$_2$-nitrone (8)** was prepared by condensing 0.031 mol of **5** and 0.031 mol of **7** in 57 mL of toluene essentially as described for the undeuterated nitrone.[6a] The crude oily solid product mixture was dissolved in 85 mL of hot ethanol. The pale yellow crystalline product (6.8 g) was collected and dried, mp 157–165 °C. This material was further purified by chromatography on Florisil. In a typical purification, 2.21 g of crude product was chromatographed on a 3.4 × 19 cm column of Florisil (75 g). Hexane through benzene–hexane (1:4) eluted 0.220 g of deuterated benzophenone *N*-benzhydrylimine.[22] Benzene–hexane (3:2) eluted 0.460 g of nitrone contaminated with the *N*-benzhydrylimine and a yellow substance, and benzene–hexane (4:1) eluted 0.246 g of slightly discolored nitrone. Pure nitrone was eluted as a white solid (1.255 g) by benzene and benzene–ether (19:1). Colorless fractions of nitrone thus obtained were recrystallized twice from absolute ethanol, affording 3.44 g (30.4%) of **8**, mp 167–169 °C. The reported melting point of the undeuterated nitrone is 165–167 °C.[15] The important spectral features of **8** are as follows: IR (KBr) 2280 (C–D stretch) and 1220 cm^{-1} (N $\rightarrow$ O); NMR (CDCl$_3$) δ 6.45 (s, 1 H, benzhydryl C–H), 7.33 (m, ~14 H, aromatic), and 8.08 (d, 2 H, *o*-H of α-phenyl ring cis to oxygen).

Combustion analyses of **8** indicated 17.60 and 17.65 atom % excess D (theoretical for fully tetradeuterated nitrone is 19.05 atom %). The mass spectrum (19 eV) of **8** shows peaks at *m/e* 365, 366, 367, 368, and 369. No peaks were present between the parent ion region (*m/e* 363–367) and the region *m/e* 347–351 which corresponds to the loss of oxygen. Corrections for natural isotope contributions by comparison with an undeuterated sample (possessing peaks at *m/e* 363, 364, and 365) were made. The calculated distribution (average of three spectra) of deuterated species in **8** was thus found to be 1.11% di-, 17.56% tri-, and 81.33% tetradeuterated (all ±0.11%). The atom % excess D calculated from the mass spectral data is 18.11.

Benzophenone-*p,p′*-d_2 *O*-(Benzhydryl-*p,p′*-d_2)oxime (10). A 67-mg sample of the deuterated nitrone was heated in an evacuated tube at 180 °C for 1.8 h. The product mixture was chromatographed twice over columns (~1 × 7 cm) of alumina. Hexane–benzene (4:1) eluted a colorless oil which crystallized from absolute ethanol, affording 50 mg (75%) of **10** as a white solid, mp 101.5–103.5 °C. The reported melting point of the undeuterated analogue is 101.5–102 °C.[15] Hexane–benzene (49:1) and ether also eluted 4 and 6 mg, respectively, of deuterated tetraphenylethane and benzophenone oxime.

The important spectral features of **10** are as follows: IR (KBr) 2260 and 2290 cm^{-1} (C–D stretch); NMR (CDCl$_3$) δ 5.55 (s, 1 H, benzhydryl C–H), 7.32 (m, ~16 H, aromatic). The mass spectrum (17 eV) of **10** showed peaks at *m/e* 365, 366, 367, 368, and 369 in the parent ion region. The calculated distribution (average of three spectra) of deuterated species in **10** was 1.07% di-, 17.85% tri-, and 81.08% tetradeuterated (all ±0.10%).

Crossover Experiments. Approximately equimolar amounts of deuterated and undeuterated nitrones (typically about 10 mg of each) were weighed into Pyrex tubes. The appropriate solvent (freshly distilled) was added with a pipet. The solutions were then degassed and sealed under vacuum. The tubes were heated in a constant temperature bath at 144 ± 0.1 °C. After a time required for 99.9% reaction, the *O*-benzhydryloxime product was isolated quantitatively by chromatography on alumina. Hexane–benzene (4:1) eluted this product. Mass spectral analyses were then used to determine the extent of crossover. In the decomposition corresponding to 50% disappearance of nitrone, it was necessary to first chromatograph the decomposition mixture on Florisil in order to isolate the undecomposed nitrone which is unstable on alumina.

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Registry No.—**2**, 1941-86-2; **3**, 65311-45-7; **4**, 65311-46-8; **5**, 65311-47-9; **6**, 65311-48-0; **7**, 65311-49-1; **8**, 65311-50-4; **9**, 5076-57-3; **10**, 65311-51-5; benzophenone *O*-benzhydryloxime, 65311-52-6.

References and Notes

(1) Abstracted in part from the Ph.D. Thesis of J. A. Villarreal, University of California, San Diego, and San Diego State University, 1973.

(2) See (a) E. J. Grubbs, J. A. Villarreal, J. D. McCullough, Jr., and J. S. Vincent, *J. Am. Chem. Soc.*, **89**, 2234 (1967); (b) J. S. Vincent and E. J. Grubbs, *ibid.*, **91**, 2022 (1969); (c) T. S. Dobashi, D. R. Parker, and E. J. Grubbs, *ibid.*, **99**, 5382 (1977); (d) D. G. Morris, *Chem. Commun.*, 221 (1971); and the accompanying paper in this issue.

(3) K. Brand and D. Krücke-Amelung, *Ber. Dtsch. Chem. Ges.*, **72**, 1029 (1939).

(4) A. B. Galun, A. Kaluszyner, and E. D. Bergmann, *J. Org. Chem.*, **27**, 1426 (1962).

(5) R. G. Jones and H. Gilman, *Org. React.*, **6**, 353 (1951).

(6) (a) E. J. Grubbs, J. D. McCullough, Jr., B. H. Weber, and J. R. Maley, *J. Org. Chem.*, **31**, 1098 (1966); (b) A. Hantzsch and F. Kraft, *Ber. Dtsch. Chem. Ges.* **24**, 3511 (1891).

(7) The isotopic compositions of isolated tetraphenylethane samples were not determined, and no attempt was made to isolate benzophenone oxime from these crossover mixtures.

(8) K. Biemann, "Mass Spectrometry: Organic Chemical Applications", McGraw-Hill, New York, N.Y., 1962, pp. 59–69, 212–227.

(9) A propagation of error treatment shows that the standard error of α calculated for $m = 363$ or 367 is four times larger on the average than for $m = 365$.

(10) The fraction of nitrone converted to *O*-benzhydryloxime by an intermolecular process also depends upon the initial concentration of nitrone mixture as will be described in a later publication.

(11) 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.[12] Those for *tert*-butyl alcohol and diethyl carbitol, based upon extrapolations, appear to be somewhat smaller.

(12) J. N. Friend and W. D. Hargreaves, *Philos. Mag.*, **37**, 201 (1946).

(13) Presumably some of the benzophenone oxime can also be formed via direct solvent hydrogen atom abstraction by the iminoxy radical in **11** prior to diffusion.

(14) See J. A. Villarreal, T. S. Dobashi, and E. J. Grubbs, *J. Org. Chem.*, proceeding paper in this issue.

(15) A. C. Cope and A. C. Haven, Jr., *J. Am. Chem. Soc.*, **72**, 4896 (1950).

(16) Melting points and boiling points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 621 recording spectrophotometer. NMR spectra were determined on a Varian Model A-60 spectrometer. Deuterium analyses were performed by J. Nemeth, University of Illinois. Mass spectra were obtained by Dr. G. Spiteller, University of Göttingen. Solvents were dried over sodium or calcium oxide (*tert*-butyl alcohol) and distilled under nitrogen.

(17) H. Adkins and R. Conner, *J. Am. Chem. Soc.*, **53**, 1091 (1931).

(18) M. G. Voronkov and E. P. Popova, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, 689 (1966); *Chem. Abstr.*, **67**, 81865u (1967).

(19) A. Hantzsch and F. Kraft, *Ber. Dtsch. Chem. Ges.*, **24**, 3511 (1891).

(20) J. F. Norris, R. Thomas, and B. M. Brown, *Ber. Dtsch. Chem. Ges.*, **43**, 2940 (1910).

(21) O. Exner, *Chem. Listy*, **50**, 779 (1956); *Chem. Abstr.*, **50**, 15477h (1956).

(22) The origin of this side product is under investigation.