Kinetic and Product Study of the Thermolyses of Several Nitrones and *O*-Alkyloximes

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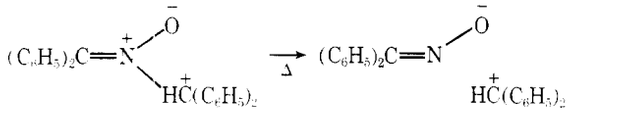
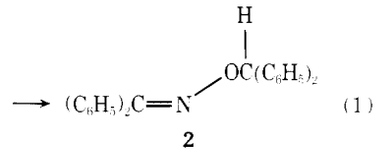
The products from the thermal decompositions of *N*-benzhydryl-α,α-diphenylnitrone (**1a**) in diethylcarbitol, in *tert*-butyl alcohol, and in *N,N*-dimethylacetamide have been determined. The products from the thermolyses of *N*-(*p*-methylbenzhydryl)-α,α-diphenylnitrone (**1b**), *N*-benzhydryl-α,α-bis(*p*-chlorophenyl)nitrone (**1c**), and *N*-benzhydryl-α,α-bis(*p*-methylphenyl)nitrone (**1d**) in diethylcarbitol have also been isolated and identified. Rates and activation parameters for thermal decompositions have been measured. The alkylation of (*Z*)-benzaldoxime anion with chlorotriphenylmethane has been repeated. The structure of the product is shown to be (*Z*)-*O*-triphenylmethylbenzaldoxime [(*Z*)-**6**] and not a nitrone as previously reported. The geometrically isomeric *p*-methylbenzophenone *O*-triphenylmethyloximes [(*E*)-**9** and (*Z*)-**9**] have been prepared and characterized. Thermal geometric equilibrations of (*Z*)-**6** and its isomer (*E*)-**6** as well as of (*Z*)-**9** and (*E*)-**9** are described. The mechanisms of these thermal processes are discussed in light of these experiments.

In several recent publications[2-4] we presented evidence bearing on specific stereochemical and kinetic properties of intermediates which are formed during the thermal decompositions of *N*-benzhydryl-α,α-diarylnitrones. In the present report we summarize kinetic and product data which support the mechanistic course of these reactions which was proposed earlier.[5] Some observations regarding the thermal behavior of *O*-alkyloximes are also presented.

The stereochemical course[2,4] of the nitrone to *O*-alkyloxime rearrangements as well as crossover studies[3] rule out a concerted process[6] as a major mechanistic path. At the inception of the present study it was hoped that a detailed kinetic and product study would provide a basis for distinguishing between two[7] alternate likely mechanistic routes (eq 1 and 2).



1a



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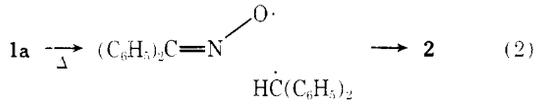

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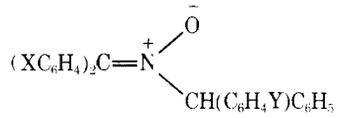
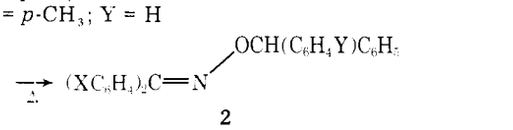


1a, X = Y = H
b, X = H; Y = *p*-CH_3
c, X = *p*-Cl; Y = H
d, X = *p*-CH_3; Y = H



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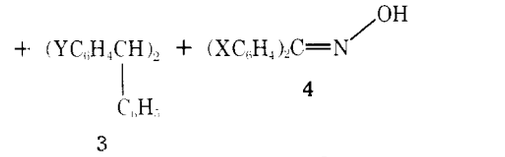
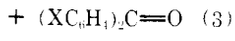


3 **4**



(3)

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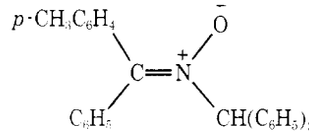
The kinetic investigation provides moderate support for the homolytic pathway and the results of the product analyses clearly require radical intermediates in these decompositions.

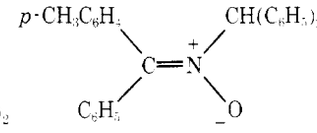
Results

Products from Nitrone Decompositions. The thermal decompositions of four nitrones gave some or all of the products[8] shown in eq 3. Complete (99%) decomposition typically required a minimum of 40 h at 144 °C. The results are shown in Table I.

Kinetics of Nitrone Decompositions. Kinetic data are summarized in Table II. The rate plots for disappearance of nitrones **1a–d** show excellent linearity in accord with the first-order rate law. Included in the table are rate constants for the thermal decompositions (in diethylcarbitol) of the geometrically isomeric nitrones **1e** and **1f**.[9]

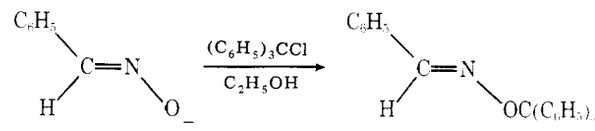


1e

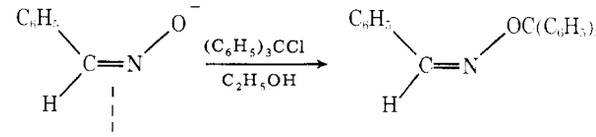


1f

Preparation and Thermolyses of *O*-Alkyloximes. The geometrically isomeric *O*-tritylbenzaldoximes [(*E*)-**6** and (*Z*)-**6**] were prepared as described previously by Buehler.[10] Alkylation of the two oxime anions with chlorotriphenylmethane afforded the geometrically pure *O*-trityloximes. The



(*E*)-**6**



(*Z*)-**6**

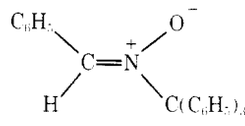


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Table I. Products from the Thermolyses of Various Nitrones at 144 °C

Nitrone	Solvent	Concn[a]	% yield 2	% yield 3[b]	% yield 4	% yield 5	Product balance[c]	% reaction
1a	DEC[d]	0.0037	43.9	34.8	22.0		72.2	99.2
1a	*t*-BuOH	0.0036	99.4				99.4	99.99
1a	DMA[e]	0.0083	50.0	38.7	26.9		82.8[f]	78.8
1b	DEC	0.0028	39.1	34.6	58.0		85.5	99.0
1c	DEC	0.0046	29.5	27.4	40.3	13.7	70.2	98.8
1d	DEC	0.0038	27.3	32.9	24.1	22.8	67.2	98.8

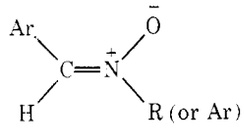
[a] Initial nitrone concentration. [b] Based on 1 mol of 3 from 2 mol of 1. [c] Percent of moles of unrecovered 1 accounted for in the products. [d] Diethyl carbitol. [d] *N,N*-Dimethylacetamide. [f] 21.4% of the starting nitrone was reisolated from this reaction.

Table II. Rate Constants[a] and Activation Parameters[b] for the Decomposition of Various Nitrones

Compd	Registry no.	Solvent	Temp, °C	10^3[1], M[c]	% reaction	10^5k, s^{-1}	E_a, kcal/mol	$\Delta S^{\ddagger}$, eu
1a	5076-57-3	DEC	130	3.20	61.5	0.579		
				2.52	79.7	0.594		
			144	2.15	64.4	2.86	38.8 ± 0.3	11.0 ± 0.8
				2.44	75.1	2.88		
				2.13	75.1	2.89		
				2.26	61.5	2.93		
				0.434	71.9	3.01		
				0.437	71.2	3.01		
			160	2.11	37.0	15.3		
				2.00	70.0	16.7		
				2.37	46.0	17.0		
		t-BuOH	130	3.44	62.4	0.250		
				0.733	59.7	0.232		
				0.745	60.5	0.236		
			144	2.41	69.9	1.26	40.9 ± 0.4	14.5 ± 0.8
				3.50	61.0	1.28		
				2.58	88.0	1.32		
				0.906	75.4	1.30		
				0.664	72.2	1.34		
				0.596	72.2	1.35		
			160	3.07	77.0	7.66		
				2.84	77.8	7.97		
				0.930	82.7	8.13		
				0.650	74.9	8.22		
		DMA	130	3.43	76.0	0.357		
				3.30	76.0	0.360		
			144	3.22	68.3	1.78	39.1 ± 0.3	10.7 ± 0.7
				3.64	69.9	1.80		
				0.926	68.3	1.84		
				0.902	69.9	1.90		
			160	3.10	78.1	10.5		
				3.34	78.1	10.6		
1b	5076-55-1	DEC	130	2.69	85.8	0.694		
				2.66	86.2	0.715		
			144	3.23	72.6	3.09	37.9 ± 0.2	9.2 ± 0.6
				3.21	72.8	3.10		
				2.39	64.2	3.22		
				2.45	66.0	3.32		
			160	3.03	46.5	17.4		
				2.27	69.3	17.9		
				2.76	74.4	18.9		
1c	5076-58-4	DEC	144	1.94	77.5	2.60		
				1.71	79.0	2.71		
				0.528	77.5	2.60		
				0.529	71.8	2.61		
1d	5120-68-3	DEC	144	2.36	60.9	1.66		
				2.29	62.4	1.71		
				0.630	62.7	1.73		
				0.793	63.8	1.78		
1e	42270-99-5	DEC	144	3.3	75.0	2.98[d] (2.60)[e]		
1f	42271-00-1	DEC	144	3.3	75.0	1.76[d] (2.65)[e]		

[a] Average precision (probable error) of k was ±1%. [b] The errors listed for E_a and $\Delta S^{\ddagger}$ are standard errors. [c] Initial nitrone concentration. [d] Rate constants determined from slopes of plots corresponding to 0–10% reaction. [e] Rate constants determined from slopes of plots corresponding to 35–65% reaction.

product of the second alkylation shown was originally assigned a nitrone structure.[10] That this assignment was incorrect can be shown by the following observations. The ultraviolet spectrum reported for **7** [λ_{max} 252 nm (log ϵ 4.23)] is inconsistent with that expected for this compound. Nitrones having the general structure **8** are known to have intense π–π^* transitions with maxima in the region of about 290–340 nm.[11,12] Also the NMR spectrum of a nitrone of general structure **8** is expected to show two low-field protons (separated from and lower than the remaining aromatic protons).[13–15] This is not observed for the alkylation product from the (*Z*)-oxime anion. That the correct structure is (*Z*)-**6** is confirmed by the dipole moment comparisons shown in Table III. It is clear that the nitrone **7** would be expected to have a dipole moment several times larger than that exhibited by (*Z*)-**6**. The geometric assignments for **6** rest on firm ground since stereospecific O-alkylations[5] and arylations[15] of isomeric oxime anions have been previously observed.



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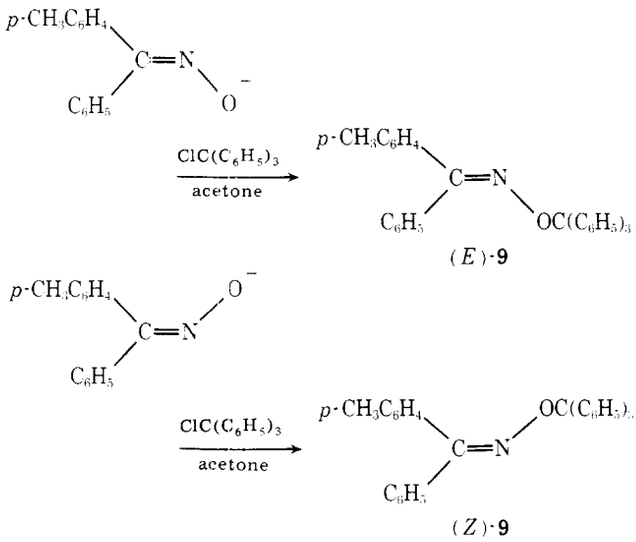
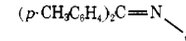
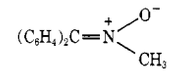
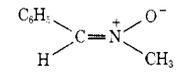
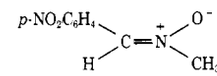
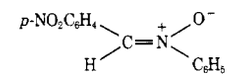
The isomeric *p*-methylbenzophenone *O*-trityloximes [(*E*)-**9** and (*Z*)-**9**] were similarly prepared by alkylation of the corresponding oxime anions with chlorotriphenylmethane.



Samples of (*Z*)-**6** and separately (*E*)-**6** were sealed in glass tubes under vacuum and heated. The products were chromatographically separated on alumina-packed columns eluting with benzene–hexane mixtures.[16] Starting with either isomer, an equilibrium mixture (*E*)-**6**/(*Z*)-**6** of 9.8 ± 0.1 was obtained at 200 °C.[17] No other product was observed in these melts. Geometric equilibration was complete within 30 min at 200 °C. The equilibration data at this temperature led to a free-energy difference between (*E*)-**6** and (*Z*)-**6** of approximately 2 kcal/mol.

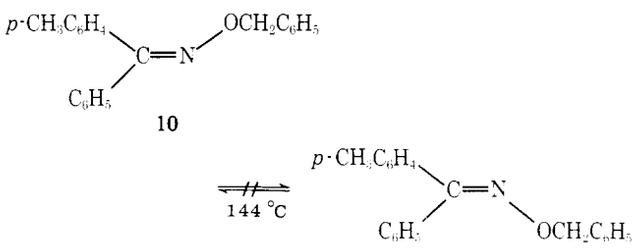
The thermal $E \rightleftharpoons Z$ equilibration of (*E*)-**9** and (*Z*)-**9** were observed in melts after about 6 h at 180 °C and after 96 h in *tert*-butyl alcohol at 144 °C.[18] The NMR and IR spectra of the recovered samples were identical with those of a 50:50 mixture of pure isomers. The EPR spectrum determined during the thermal isomerization of (*Z*)-**9** in the melt (180 °C) consisted of three lines of equal intensity. The nitrogen hyperfine coupling constant was 31.4 ± 0.6 G. No additional coupling to hydrogen was observable.

Table III. Dipole Moments of Several Nitrones and *O*-Alkyloximes

Compd	Registry no.	μ, D	Solvent	Ref
(*E*)-**6**		0.84 (0.86)	Benzene	*a*
	65311-13-9	1.16	Benzene	*a*
	7500-79-0	4.31	Benzene	*a*
(*Z*)-**6**		1.23 (1.34)	Benzene	*a*
		3.49	Benzene	11
		6.20	Dioxane	11
		6.32	Dioxane	11

[a] These values were determined in the course of this work. Dielectric constants of solutions were measured using a Dipolmeter Type DM 01 (Wissenshaftlich-Technische Werkstätten GmbH, Weilheim, Germany). The Guggenheim method [E. A. Guggenheim, *Trans. Faraday Soc.*, **74**, 2193 (1952)] was employed for obtaining dipole moments.

The thermal configurational stability of *p*-methylbenzophenone (*Z*)-*O*-benzyloxime (**10**)[19] was also tested. The *O*-benzyloxime was heated in *tert*-butyl alcohol at 144 °C for 116 h under sealed tube conditions. After removal of the solvent, spectroscopic analysis showed that no detectable isomerization or decomposition had occurred.



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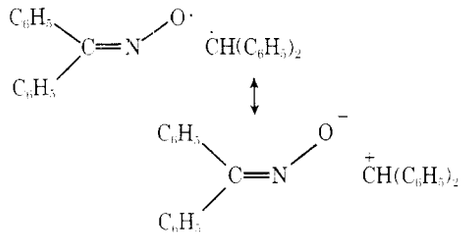
Discussion

The products of the thermal decompositions of **1a** and its methyl- and chloro-substituted analogues are more diverse than originally reported by Cope.[6] Only in *tert*-butyl alcohol is the N to O rearrangement essentially free of side products. The production of a substantial quantity of *sym*-tetraarylethane (**2**) from each of the nitrones studied provides evidence for the intermediacy of benzhydryl radicals. Also, the formation of diarylketoximes[20] (**4**) is most easily explained on the basis of hydrogen atom abstraction by iminoxy radicals. An alternative source of the oximes, namely, proton transfer to an oxime anion (eq 1), is inconsistent with the absence of this product only in *tert*-butyl alcohol. Rather, since *tert*-butyl alcohol is a notoriously poor hydrogen atom donating solvent, recombination of iminoxy radicals with benzhydryl radicals appears to become the dominant reaction course. The almost quantitative formation of *O*-benzhydryloxime in *tert*-butyl alcohol cannot be attributed to an unusually efficient cage effect, since the fraction of the total *O*-ether product generated which is formed via an intermolecular process is actually greater for *tert*-butyl alcohol than for the other two solvents (see accompanying paper). It should be noted that traces of tetraphenylethane were isolated under similar conditions during crossover studies in *tert*-butyl alcohol (ac-

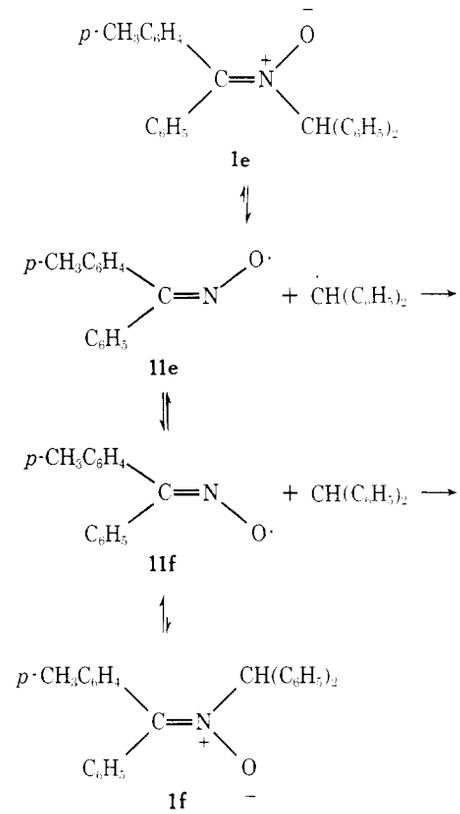
companying paper). It would be reasonable to assume that the use of efficient radical scavengers during decompositions in *tert*-butyl alcohol would trap the free radicals in competition with recombination to give *O*-benzhydryloximes. Such experiments have not yet been performed with this system. The undecomposed nitrone might have been expected to behave as a reasonably good spin trap. In fact, nitroxide radicals attributed to reactions between **1a** and benzhydryl radicals have been observed for decompositions of **1a** either in the melt or in diethylcarbitol.[5b] If such processes are taking place in *tert*-butyl alcohol, only very small quantities of nitroxide must be forming or the process is rapidly reversible. Perhaps more interesting is the basis for the inability of iminoxy–iminoxy and benzhydryl–benzhydryl dimerization processes to compete with benzhydryl–iminoxy radical combinations. Although radical–radical terminations are believed to have very low activation energies, a benzhydryl–iminoxy recombination may be more nearly a diffusion-controlled process because of resonance stabilization of the transition state as shown. This possibility is being subjected to experimental tests.



The first-order rate constants (Table II) for the decomposition of the nitrones in diethylcarbitol at 144 °C differ by less than a factor of 2. In addition, the rate constants for the decomposition of **1a** in each of the three solvents vary over a range of only 2.2 at 144 °C. The small variation in rate with changing substituents and solvents is more compatible with a radical or concerted process than an ionic route such as eq 1.

The net effects expected for an ionic process with the substituent changes made in **1c** and **1d** are difficult to assess. The substituents in **1c** and **1d** are both probably capable of stabilizing the ground state via resonance. But if oxime anion formation were nearly complete in a transition state, the *p*-chloro substituents would presumably stabilize and the *p*-methyl substituents destabilize the activated complex. The net effect anticipated from the substitution of H by methyl in the benzhydryl portion of the nitrone is less ambiguous. This substitution would be expected to lead to a considerable rate enhancement if a benzhydryl cation were substantially formed in the transition state. In diethylcarbitol at 144 °C the rate ratio for **1b**/**1a** is only 1.1. This value is comparable to *p*-methyl substitution effects in the radical decompositions of *tert*-butyl arylperacetates ($k_{p\text{-}CH_3}/k_H \sim 2$)[22] and in the homolyses of azocumenes ($k_{p,p'\text{-}CH_3}/k_H \sim 1.7$).[23]

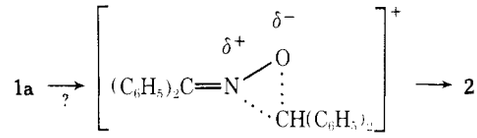
Only the rate plots for the decompositions of nitrones **1e** and **1f** show curvature. The final "slopes" (35–65% reaction) are essentially identical and reflect the fact that at this stage of the reaction, geometric equilibration[24] of the starting nitrones is largely complete. These nitrones have been shown spectroscopically (NMR analysis of reisolated nitrone) to equilibrate during the decompositions, finally reaching a 50:50 ± 2% composition. If one concludes (from the data from the present study and from the others referred to herein) that the initial step in the decomposition of **1e** and **1f** is the formation of iminoxy radicals and benzhydryl radicals, then the free-energy difference between the two iminoxy radicals, **11e** and **11f**, in diethylcarbitol can be estimated. If the usual assumption is made that the activation energy is negligible for the recombination of radicals (in this case to reform **1e** and



1f), then the difference between the "initial" rate constants (obtained during the first 10% of the decomposition) can be ascribed to differences in the free energies of the two iminoxy radicals. This value at 144 °C is 437 cal, corresponding to an equilibrium constant of 1.70. A similar observation has been made for the iminoxy radicals formed in *tert*-butyl alcohol, where k was found to be 1.4.[4]

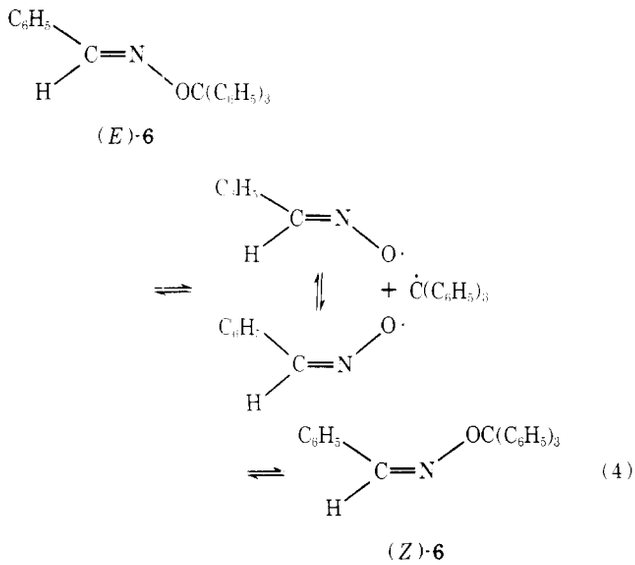
The rates and activation parameters for decomposition–rearrangement of **1a** were determined in three solvents varying substantially in hydrogen-bonding capability and polarity.[25] The essential invariance in rates and activation parameters is most easily accommodated by a homolytic dissociation.

On the basis of product studies, only for the decomposition of **1a** in *tert*-butyl alcohol is a cyclic concerted rearrangement



to **2** a viable mechanistic option. However, the nearly identical activation parameters for the decomposition of **1a** in the three solvents renders this possibility highly unlikely. Also, the high degree of intermolecularity for the rearrangement in *tert*-butyl alcohol (see accompanying paper) relegates a concerted process to a minor competing role if at all existent.

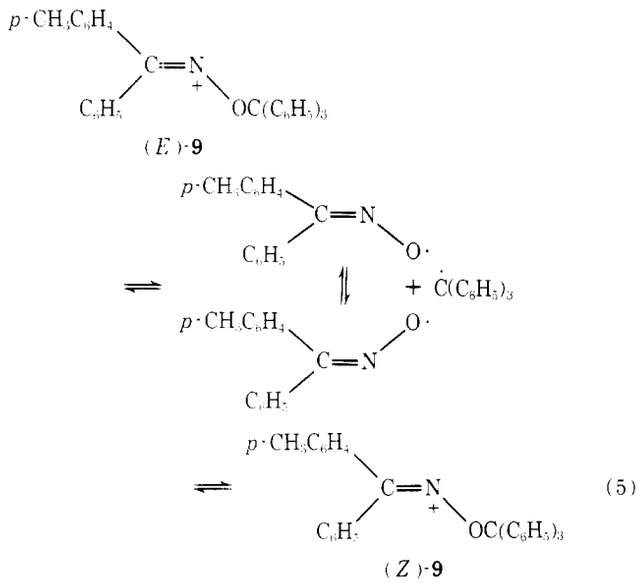
The *O*-trityloximes (*E*)-**6**, (*Z*)-**6**, (*E*)-**9**,[27] and (*Z*)-**9** were shown to undergo geometric equilibration in the melt or/and in solution at temperatures ranging from 144 to 200 °C. The most likely course of these isomerizations is again a homolysis of the N–O bond, followed by rapid geometric isomerization of the iminoxy radicals[4] and recombination as shown in eq 4 and 5. Were a nondissociative (rotational or lateral shift) mechanism operative, the *O*-benzhydryl analogues of **9** would be expected to undergo a similar geometric isomerization. But the *O*-benzhydryl derivatives have been shown to be completely configurationally stable under the above conditions.[4] Similarly, the (*Z*)-benzyl derivative, **10**, was shown to be



(E)-6

(4)

(Z)-6



(E)-9

(5)

(Z)-9

configurationally stable. The remarkable configurational stability of benzophenone *O*-methyloxime derivatives has been previously reported.[28] Thus, in contrast with *O*-methyl, benzyl, and benzhydryl derivatives, the stability of the developing trityl radical appears to be responsible for lowering the activation energy and promoting the homolysis. It is possible that trityloxyphenyl nonbonded interactions in **9** raise ground-state free energies and thereby accelerate the homolysis. But the facile isomerization of (*E*)-**6** (possessing only a trityloxy–hydrogen interaction) suggests that this factor is of relatively minor importance. The observation of the iminoxy radicals in isomerizing melts at 180 °C by electron-spin resonance supports the above mechanistic proposal.

Conclusions

The available evidence now indicates that the nitrone decompositions and the *O*-trityloxime isomerizations are initiated by a homolysis of C–N or a C–O bond producing reasonance-stabilized iminoxy and alkyl radicals. Conceivably the formation of these radicals could be formed in a reversible electron-transfer step following a heterolysis as in eq 1. Bilevitch and co-workers[29] have reported ESR evidence for such an electron transfer between trityl cations and *tert*-butoxy anions with resultant formation of the ether. The absence of appreciable substituent or solvent effects in the nitrone decompositions diminishes the likelihood that such a multistep process is operative in these reactions.

$$(C_6H_5)_3C^+ + (CH_3)_3CO^- \rightarrow (C_6H_5)_3C\cdot + \cdot OC(CH_3)_3 \rightarrow (C_6H_5)_3COC(CH_3)_3$$

Experimental Section[30]

***p*-Methylbenzophenone (*Z*)-*O*-Trityloxime [(*Z*)-9].** *p*-Methylbenzophenone (*Z*)-oxime[2,4] (0.917 g, 4.34 mmol) in 20 mL of absolute ether was converted to its sodium salt with metallic sodium. The ether was removed using dry nitrogen and 15 mL of acetone was distilled into the reaction flask. An equivalent of chlorotriphenylmethane was added and the mixture was stirred under nitrogen for 24 h at room temperature. The reaction mixture was concentrated under reduced pressure, dissolved in boiling CCl_4, and filtered. The filtrate was again concentrated to an oil and then crystallized from 9:1 dioxane–water and again from petroleum ether (bp 60–80 °C), affording 0.576 g (29%) of (*Z*)-9, mp 171.5–173 °C. The important spectral features are as follows: NMR ($CHCl_3$) δ 7.60–6.90 (m, 24 H, aromatic), 2.42 (s, 3 H, *p*-CH_3); UV (C_2H_5OH) λ_{max} 263.5 nm (log ε 4.16).

Anal. Calcd for $C_{33}H_{27}NO$: C, 87.38; H, 6.00; N, 3.09. Found: C, 87.46; H, 6.32; N, 3.33.

***p*-Methylbenzophenone (*E*)-*O*-Trityloxime [(*E*)-9].** The *E* isomer was prepared from the (*E*)-oxime[2,4] as described for (*Z*)-**9**. It was obtained in 25% yield following crystallizations (of the CCl_4-extracted oil) from hexane and then from absolute ethanol, mp 124–134 °C. The important spectral features are as follows: NMR ($CHCl_3$) δ 6.83–7.50 (m, 24 H, aromatic), 2.26 (s, 3 H, *p*-CH_3); UV (C_2H_5OH) λ_{max} 266.5 nm (log ε 4.20).

Anal. Calcd for $C_{33}H_{27}NO$: C, 87.38; H, 6.00; N, 3.09. Found: C, 87.17; H, 6.06; N, 3.29.

(*Z*)-*O*-Tritylbenzaldoxime [(*Z*)-6] (previously assigned structure 7) was prepared as described by Buehler[31] in 52% yield: mp 144–145.5 °C (lit.[31] mp 143–144 °C); UV (C_2H_5OH) λ_{max} 251 nm (log ε 4.24) [lit.[31] λ_{max} 252 nm (log ε 4.23)].

(*E*)-*O*-Tritylbenzaldoxime [(*E*)-6] was prepared as previously described[31] in 63% yield: mp 120.5–121.5 °C (lit.[31] mp 118 °C); UV (C_2H_5OH) λ_{max} 260 nm (log ε 4.26) [lit.[31] λ_{max} 260 nm (log ε 4.27)].

4,4′-Dimethylbenzophenone *O*-Methyloxime. To a mixture of 5.06 g (22.4 mmol) of 4,4′-dimethylbenzophenone oxime and 39.7 g (0.280 mol) of iodomethane was slowly added 7.28 g (31.4 mmol) of silver oxide. The mixture was heated under reflux for 1 h and filtered. The residue was washed with 50 mL of ether. The combined filtrate was concentrated, whereupon the product crystallized. The *O*-methyloxime was then recrystallized four times from absolute ether, affording 2.04 g (38%) of colorless crystals, mp 99–100 °C. The NMR spectrum (CCl_4) shows the following: δ 6.58–7.40 (m, 8 H, aromatic), 3.87 (s, 3 H, OCH_3), 2.32 and 2.37 (2 s, 3 H, 3 H, *p*-CH_3).

Anal. Calcd for $C_{16}H_{17}NO$: C, 80.40; H, 7.16; N, 5.86. Found: C, 80.26; H, 7.30; N, 5.62.

***N*-Methyl-α,α-diphenylnitrone.** Samples of 1.47 g (17.6 mmol) of *N*-methylhydroxylamine hydrochloride and 3.81 g (17.6 mmol) of benzophenone imine hydrochloride were mixed in 35 mL of 90–100 °C petroleum ether under nitrogen. Ammonia was bubbled through the stirred mixture for 45 min. The mixture was then boiled under reflux for 12 h. The mixture was filtered. Concentration and cooling of the filtrate afforded 1.56 g (42%) of the nitrone, mp 98–100 °C (lit.[32] mp 102–103 °C). The NMR spectrum (CCl_4) shows the following: δ 7.90 (m, 2 H, ortho protons on α-phenyl cis to oxygen), 7.38 (m, 8 H, aromatic), and 3.56 (s, 3 H, NCH_3).

The preparations of *N*-benzhydryl-α,α-diphenylnitrone (1a) and the substituted analogues 1b–d were previously described.[33]

Thermal Configurational Stability of *p*-Methylbenzophenone (*Z*)-*O*-Benzyloxime[19] (10). The *O*-benzyloxime (33.7 mg) was placed in a Pyrex tube (8 × 200 mm). Dry *tert*-butyl alcohol (2 mL) was added. The solution was degassed and the tube was sealed under vacuum and heated at 144 °C for 116 h. The tube was opened, the solvent was evaporated, and the NMR ($CDCl_3$) of the residue was determined.

The Thermal Isomerizations of *p*-Methylbenzophenone (*E*)- and (*Z*)-*O*-Trityloximes [(*E*)-9 and (*Z*)-9]. The pure *O*-trityloximes [degassed solutions (~0.03 M in *tert*-butyl alcohol)] were separately heated at 144 °C for 96 h. The resulting solutions were concentrated to remove solvent. The NMR and IR spectra of the residues were then determined.

The Thermal Isomerization (*E*)- and (*Z*)-*O*-Triphenylmethylbenzaldoxime [(*E*)-6 and (Z)-6]. Samples of (*E*)-**6** and separately (*Z*)-**6** were heated for various periods of time at temperatures of 200 °C of ~145 °C. The products were chromatographically separated on alumina-packed columns eluting with hexane–benzene mixtures.

General Procedures for Kinetic Experiments. Rate constants were measured for the disappearance of the nitrone by following the decrease in its maximum absorbance at about 310 nm. A solution (~10 mL) of the nitrone was prepared with freshly distilled solvent. About 1 mL of solution was pipetted into each of ten Pyrex tubes. The solutions in the tubes were degassed and then sealed under vacuum and placed simultaneously in a constant temperature (±0.1 °C) oil bath.

Tubes were removed from the oil bath at approximately equal time intervals and quenched in an ice–water mixture. The first (zero time) tube in a given run was generally quenched 15–30 min after the time of immersion of all the tubes. From five to ten tubes were used for each kinetic run. Infinity absorptions were obtained for each solvent and for each nitrone.

After all the quenched tubes had been opened and allowed to thermally equilibrate (~1 h) to room temperature in a desiccator, aliquots (~1 mL) were weighed by difference into volumetric flasks and then diluted with chloroform (ACS reagent grade) at room temperature. Absorbances were measured at 25.0 °C with a Beckman Model DU spectrophotometer.

The first-order rate constant, which is the slope of the plot of ln ($A - A_\infty$) vs. t (A is the absorbance at time t, and A_∞ is the absorbance at $t = \infty$), was calculated by method of least squares. The Arrhenius activation energy, E_a, was calculated from the least-squares slope of the plot of ln k vs. $1/T$.

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Registry No.—(*Z*)-**6**, 23057-28-5; (*E*)-**6**, 10229-67-1; (*Z*)-**9**, 65311-11-7; (*E*)-**9**, 65311-12-8; **10**, 42449-53-6; *p*-methylbenzophenone (*Z*)-oxime, 2998-92-7; chlorotriphenylonethane, 76-83-5; *p*-methylbenzophenone (*E*)-oxime, 2998-91-6; 4,4′-dimethylbenzophenone oxime, 1714-49-4; iodomethane, 74-88-4; *N*-methylhydroxylamine hydrochloride, 4229-44-1; benzophenone imine hydrochloride, 5319-67-5.

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(7) A less likely alternative to eq 1 with the charges reversed on the intermediates would also be amenable to kinetic probes.
(8) Product mixtures were chromatographed over alumina and/or Florisil columns. Separated components were compared with authentic samples by means of mixed melting points and infrared spectra.
(9) These nitrones were employed in a study of the stereochemical course of N to O rearrangements.[2,4] Complete quantitative product analyses were not performed for these decompositions, since only geometric compositions of the *O*-benzhydryloximes and recovered nitrones were of interest.
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(16) Pure samples of (*E*)-**6** and (*Z*)-**6** were shown to be stable under the chromatographic separation conditions.
(17) Total recovery of the *O*-trityloximes after heating and separating amounted to at least 96%.
(18) Quantitative rates of approach to equilibrium have not been determined.
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(20) The formation of diaryl ketones, **5** (Table I), was observed in only two instances. The origin is not known with certainty. Hydrolysis of oximes via adventitious contamination by water is one possible source. In fact, benzophenone oximes are known to be sensitive to exposure to ordinary atmospheric conditions and decompose fairly readily to the corresponding ketone and nitric acid.[21] The autocatalytic nature of these decompositions suggests the intervention of radical intermediates.
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