mines as 100/0, and that "neither heat nor acid or dimsyl sodium produced detectable amounts of the Z isomer": G. J. Karabatsos and S. Lande, *Tetrahedron*, **24**, 3907 (1968).
(24) Interestingly, Olah claims to have prepared a mixture of the *Z* and *E* isomers of *N*-(benzylidene)methylamine. In liquid SO_2, he assigned the upfield NCH_3 signal as that due to the *Z* isomer. The isomers were reportedly stable to distillation (in vacuo, temperature unspecified). G. A. Olah and P. Kreienbuhl, *J. Am. Chem. Soc.*, **89**, 4756 (1967).
(25) (a) M. S. Newman, N. Gill, and D. W. Thompson, *J. Am. Chem. Soc.*, **89**, 2059 (1967); (b) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).
(26) R. G. Pews, *J. Org. Chem.*, **32**, 1628 (1967).
(27) W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5739 (1957).
(28) B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 1670 (1956).
(29) J. P. Freeman, *J. Org. Chem.*, **28**, 2508 (1963).
(30) Gowenlock and Trotman report mp 84° and λ_{max} (H_2O) 266 for (*Z*)-nitrosoethane dimer which isomerized to the *E* isomer in various solvents. They were unable to isolate a crystalline *E* isomer but report a decrease in melting point of 10–40° upon cis to trans isomerization of two other nitrosoalkane dimers (nitrosomethane excepted). The present data[16] support a nitrosoethane dimer structure and we feel that it is the *E* diastereomer.
(31) B. W. Langley, B. Lythgoe, and L. S. Rayner, *J. Chem. Soc.*, 4191 (1952).
(32) Available from Ash Stevens Inc., Detroit, Mich.
(33) G. W. Smith and H. D. Williams, *J. Org. Chem.*, **26**, 2207 (1961).
(34) In ring compounds **2** the *E* and *Z* designations, which are traditionally used to show steric relations around one or more double bonds, are used nonsystematically here for the sake of consistency within the paper.

Aliphatic Azoxy Compounds. IV. Reaction of Nitrosoalkanes with Hydroxylamines. Synthesis of Unsymmetrical Primary and Secondary Azoxyalkanes by N–N Bond Formation[1]

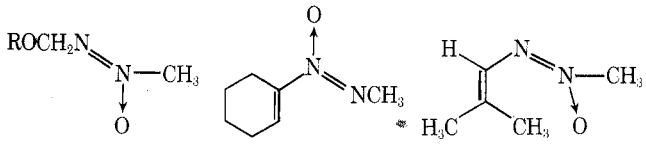
K. Grant Taylor,* S. Ramdas Isaac, and Melvin S. Clark, Jr.

Department of Chemistry, University of Louisville, Louisville, Kentucky 40208

Received August 12, 1975

The condensation of *N*-alkylhydroxylamines with photolytically monomerized nitrosoalkanes yields mixtures of O-position isomers of *Z* azoxyalkanes **5a–g** and **6c–g** in ~30–95% yields. The major isomer is that one with the less bulky N substituent syn to the oxygen atom of the azoxy group. This isomer predominates regardless of whether the less bulky group is on the hydroxylamine or nitrosoalkane reactant. Use of *N*-alkyl-*O*-methylhydroxylamines in the condensation gives a single azoxyalkane product, that isomer wherein the azoxy oxygen atom is derived from the nitrosoalkane; however, the yields are low in these reactions. Aspects of the uv and NMR spectra of the azoxyalkanes are discussed.

Aliphatic[2] and aromatic[3] azoxy compounds exist in nature and, without exception, are unsymmetrically substituted compounds with potent physiological activity. An example of recent interest is cycasin (**1a**), known to be carcinogenic in experimental animals.[2d] The aglycone of cycasin, **1b**, the synthetic acetate, **1c**, and synthetic low molecular weight azoxyalkanes are among the most potent of chemical carcinogens.[2d,4] There has been a sustained interest in the chemistry of azoxyalkanes, but, as Moss[5] has pointed out, until 1972 there existed no general, directed method for the synthesis of unsymmetrically substituted azoxyalkanes. The major approach to the synthesis of such compounds has been the oxidation of unsymmetrical azoalkanes,[6] and, to date, no clear mechanistic picture has emerged to permit a prediction of which NO-position isomer can be expected as the major product of oxidation. For example, **2** and **3** are the azoxy compounds isolated from oxidations of the respective azoalkenes.[7] In the aromatic series, all nonortho substituents on monosubstituted diaryldiazenes seem to mildly direct the oxidation toward the more remote N atom of the azo linkage.[8] Moss and co-workers' alkylation of alkane diazotates[5] of structure R′–N=N–O⁻ by alkyl iodides, RI, gives *Z* azoxyalkanes **4** in 32–64% yields. The reaction, a C–N bond synthesis via SN2 displacement,[5b] is best suited for the preparation of **4** when R is a primary alkyl group and R′ is either a primary or secondary alkyl group. When R is a secondary alkyl group the yield of azoxyalkane is decreased (competing E2?), as it also is when R′ is a tertiary alkyl group of an alkane diazotate (competing O-alkylation?).[5] Kovacic and co-workers[9] have also developed a directed synthesis of azoxyalkanes. Based on N–N bond formation between nitroso compounds and *N,N*-dichloroamines, the approach is applicable to the synthesis of unsymmetrical tertiary dialkyldiazene monoxides.



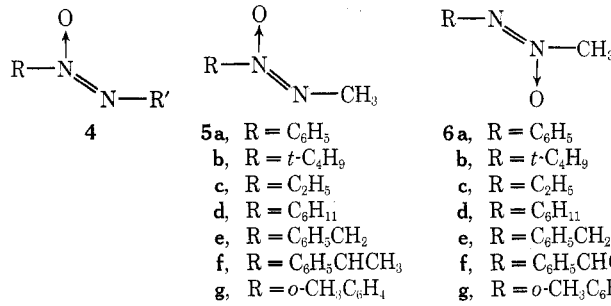
1a, R = D-glucosyl
b, R = H
c, R = $COCH_3$

2

3

Our attention was drawn to the N–N bond formation approach by the work of Freeman,[10] who, in extending Aston's[11] work, reported the formation of (for practical purposes) only **5a** and **5b** from the condensation of *N*-methylhydroxylamine with nitrosobenzene and 2-methyl-2-nitrosopropane, respectively. These results stood in sharp contrast to the results of such condensations in the aromatic series. For example, the condensation of *p*-chloronitrosobenzene with phenylhydroxylamine gives azoxybenzene and 4,4′-dichloroazoxybenzene in addition to an unsymmetrical azoxyarene.[12] Work by Russell and Geels[13] substantiated an oxidation–reduction pathway (eq 1) for the for-

$$ArNO + ArNHOH \longrightarrow [ArNHO\cdot] \longrightarrow ArN(O){=}NAr \quad (1)$$



4

5a, R = C_6H_5
b, R = t-C_4H_9
c, R = C_2H_5
d, R = C_6H_{11}
e, R = $C_6H_5CH_2$
f, R = $C_6H_5CHCH_3$
g, R = o-$CH_3C_6H_4$

6a, R = C_6H_5
b, R = t-C_4H_9
c, R = C_2H_5
d, R = C_6H_{11}
e, R = $C_6H_5CH_2$
f, R = $C_6H_5CHCH_3$
g, R = o-$CH_3C_6H_4$

Table I. Yields of Unsymmetrical Azoxy Compounds from the Condensation of $(RNO)_2$ with R'NHOH at pH 6–7

Entry	R[i]	R'[j]	Conditions: Solvent,[a] λ[b] (temp, °C)	Yields[c]: % 5	% 6	Total	Ratio 5/6
1	C_6H_5	CH_3	A, dark (0)	69	Trace	69	25–30
2	t-C_4H_9	CH_3	A, dark (38)	52	1	53	25–30
3	CH_3	t-C_4H_9	B, 300 (45)	7[d]		7[d]	25–30
4	C_2H_5	CH_3	B, dark (25)			Low	2[e]
5	C_6H_{11}	CH_3	B, 350 (10)			83	11
6	C_6H_{11}	CH_3	B, dark (65)			84[f]	5[f]
7	C_6H_{11}	CH_3	C, dark (65)	63	16	95[g]	2.7[d]
8	CH_3	C_6H_{11}	B, 300 (45)	38.5[f]	5.9[f]	44.4[f]	6.5
9	$C_6H_5CH_2$	CH_3	D, 300 (45)	39.3[f]	16[d]	55	2.5[d]
10	$C_6H_5CHCH_3$	CH_3	D, 350 (10)	63.7[f]	16[d]	80	3.9[d]
11	$C_6H_5CHCH_3$	CH_3	D, dark (65)	41[f]	18[d]	59	2.3[d]
12	o-$C_6H_4CH_3$	CH_3	E, dark (0)	60[d]	7[d,h]	67[d]	8.5

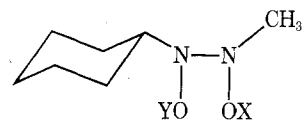
[a] Solvent A: THF–H_2O, 2:1 by volume; B: methanol; C: THF–methanol, 9:1 by volume; D: methanol–H_2O, 9:1 by volume; E: THF–H_2O, 9:1 by volume. [b] λ is the principal emission wavelength (nm) of the Rayonet RPR 100 photochemical reactor lamp used. [c] Yields are of isolated, pure products unless noted otherwise. [d] Determined by NMR analysis of the reaction mixture using an internal standard. [e] Yield was not determined; ratio was estimated by VPC analysis. [f] Determined by VPC analysis using an internal standard. [g] Yield includes a distillation fraction of a mixture of **5** and **6**. [h] Compound **6g** was isolated in small amount by preparative VPC. [i] Registry no. for respective compounds are 586-96-9, 6841-96-9, 14523-95-6, 57497-47-9, 13000-13-0, 26779-46-4, 30285-71-3, 611-23-4. [j] Registry no. for respective compounds are 4229-44-1, 57497-39-9, 25100-12-3.

mation of the symmetrical azoxybenzenes in such reactions. Thus, on the surface, the results of Freeman,[10] wherein the azoxy compound's oxygen atom was derived from the nitroso compound, gave indication that the condensation of nitrosoalkanes with *N*-alkyl hydroxylamines might provide a directed synthesis of unsymmetrical azoxyalkanes. We, accordingly, investigated this possibility and the results are outlined below.

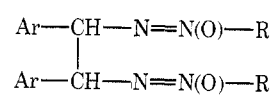
Results

The reaction conditions (basic, refluxing ethanol) employed by Freeman[10] for the preparation of **5a** and **5b** appeared to be too strong for general applicability, because of the sensitivity of nontertiary nitrosoalkanes toward base-catalyzed rearrangement to the corresponding oxime isomers.[14] Also, in our hands, repetition of Freeman's synthesis of **5a** produced azoxybenzene as the major product (70%), a synthesis more easily accomplished by mixing only nitrosobenzene with alcoholic sodium hydroxide.[15] We found that the reaction of nitrosobenzene with *N*-methylhydroxylamine at 0° in THF–H_2O, buffered with *N*-methylhydroxylamine hydrochloride at the start[16] to pH 6.8, gave consistent yields of **5a** near 69% with the yield of azoxybenzene reduced to 10–15% (see Table I, entry 1). The same conditions were applied successfully to the preparation of, first, the *o*-tolyl homologue, **5g** (Table I, entry 12), and secondly, by using a convenient temperature for the dissociation of 2-methyl-2-nitrosopropane dimer, to a somewhat improved preparation of **5b** (Table I, entry 2). In the syntheses of **5a** and **5b**, NMR spectral absorptions and VPC peaks attributable to the isomeric compounds **6a** and **6b** indicated that 3% or less of these isomers were formed in the reactions. In contrast, the reaction leading to **5g** gave a **5g/6g** ratio of 8.5, enough **6g** to permit isolation and characterization.

However, nitrosobenzene is monomeric and tertiary nitrosoalkane dimers are readily dissociated to monomers without the possibility of isomerization to the oxime. In contrast, merely permitting nitrosoethane dimer to dissociate at room temperature in the presence of *N*-methylhydroxylamine (pH 7–8) gave azoxyalkanes **5c** and **6c**, but the reaction time was too long (3 days) and the yields unsatisfactorily low with several by-products formed (Table I, entry 4).[17] In a similar vein, little or no reaction occurs between nitrosocyclohexane dimer and *N*-methylhydroxylamine at or below room temperature. However, as DeBoer demonstrated,[18] it is possible to dissociate nitrosoalkane dimers by photolysis without incurring dissociation of the resulting monomer into R· and NO. Accordingly, the reaction of nitrosocyclohexane dimer with *N*-methylhydroxylamine in buffered methanol at 10° gives an 83% isolated yield of a mixture of **5d** and **6d** if the reaction is irradiated with a medium- or high-pressure uv light source (Table I, entry 5). Although a mixture was obtained, the favorable ratio of **5d/6d** of 11 prompted us to test the alternate condensation of nitrosomethane dimer with *N*-cyclohexylhydroxylamine. As entry 8 of Table I records, however, **5d** was again the major azoxy isomer produced in a rather favorable ratio but in lower yield. In a like manner, *tert*-butylhydroxylamine reacted with nitrosomethane dimer to produce only **5b** in very low yield (Table I, entry 3). Close examination of the reactions described as entries 2, 3, 5, and 8 (particularly 5, 8, and others of the "cyclohexylmethyl" series, 6 and 7) revealed that the symmetrical azoxyalkanes were not formed in these reactions, a result which, in our thinking, ruled out an oxidation–reduction pathway (eq 1) as being responsible for the formation of the mixture of azoxyalkane isomers. Rather, we speculated that the formation of the **5d–6d** mixture resulted from the partitioning of an *N,N'*-diol intermediate, such as **7a** or

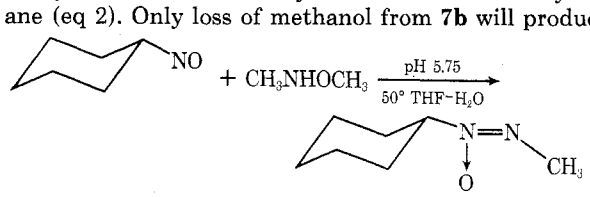


7a, X = Y = H
b, X = CH_3; Y = H
c, X = H; Y = CH_3



8

some reactive equivalent, in a final dehydration step which yields the azoxyalkanes.[19] Accordingly, we "synthesized" intermediate **7b** by the condensation of *N,O*-dimethylhydroxylamine with thermally monomerized nitrosocyclohexane (eq 2). Only loss of methanol from **7b** will produce an



(2)

5d

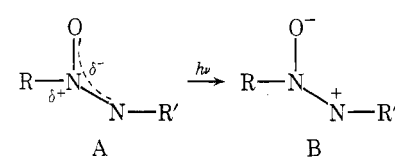
azoxyalkane, and only azoxyalkane **5d** was produced in this reaction (55%). Also, we "synthesized" intermediate **7c** by the condensation of *N*-cyclohexyl-*O*-methylhydroxylamine with photolytically monomerized nitrosomethane, and this time only **6d** was formed (16%). Thus, reaction 2 and its counterpart just mentioned represent directed syntheses of unsymmetrical azoxyalkanes. It should be pointed out, however, that the yield of reaction 2 is an optimized yield. *N,O*-Dimethylhydroxylamine (pK'_a = 4.75) is more sluggish than *N*-methylhydroxylamine (pK'_a = 5.97) in its reaction with nitrosobenzene (little **5a** after 14 h at 0°), and the similar lowering of reactivity toward nitrosocyclohexane requires a prolonged irradiation of the photolytically aided condensation which leads in turn to an increase in photochemical side reactions. Also, the low yield of **6d** from the *N,O*-dialkylhydroxylamine route was not a promising sign.

Thus, while that condensation which uses *N*-alkylhydroxylamines gives azoxyalkane mixtures, the yields can be quite high and the azoxyalkane isomers are separable by standard techniques. As entries **6** and **7** of Table I illustrate, thermal dissociation of nitrosoalkane dimers in this synthesis is also feasible. The nitrosoalkane monomer, though it condenses with the alkylhydroxylamine, does tautomerize to the corresponding (unreactive) oxime during these condensations. Thus, cyclohexanone oxime was detected (5–10% by VPC) in the reaction mixtures of entries 5–7 of Table I as was benzaldehyde oxime (entry 9) and acetophenone oxime (entries 10 and 11). The benzylic-type nitrosoalkane dimers of entries 9–11 of Table I were chosen, in part, to provide a test of the method with easily tautomerized and photolytically cleaved nitrosoalkane monomers. The method gives satisfactory yields of azoxyalkanes, and entries 10 and 11 allow a comparison of the thermal and photolytic methods for the monomerization of easily tautomerized nitrosoalkanes. It should be noted that azoxyalkane **6e** was not completely characterized but could be reproducibly detected by NMR analysis of freshly extracted reaction mixture [δ 4.05 (broadened, singlet, CH_3NO), 4.57 (narrow quartet, $-CH_2N=$)]. The compound was somewhat unstable, presumably owing to a facile oxidative dimerization which has been known to yield compounds of type **8** in similar structural situations.[20]

In every case recorded in Table I, isomer **5** is the major product. Were electronic factors dominant such that the dehydrative partitioning of **7a** placed the more electron-releasing R group on the formally (+) charged oxidized nitrogen atom (e.g., $\sigma^*_{t\text{-}C_4H_9}$ −0.30, $\sigma^*_{CH_3}$ 0.00), then for the **5e–6e** and **5f–6f** isomer pairs, one would predict that the **6** isomers should predominate, since the benzyl group (σ^* +0.215) and the α-phenylethyl group (σ^* ~+0.10) are electron withdrawing relative to CH_3. Thus, steric factors dominate in the partitioning of **7a** such that the major final product has the less bulky CH_3 group (in general, that group with the higher Taft E_s value[21]) located syn to the oxygen atom.

In summary of the above, the condensation of *N*-alkylhydroxylamines and nitrosoalkanes would appear to be useful for the good-yield preparation of unsymmetrical azoxyalkanes **4,** wherein R is a secondary or tertiary alkyl group and R′ is methyl or a primary or secondary alkyl group. While our interests led us to prepare examples of azoxyalkanes all of which contained an *N*-methyl group, there are isolated examples of symmetrical secondary[6,22] and tertiary[6,23] azoxyalkanes having been synthesized by N–N bond formation such that we feel the above general statement of utility is justified.

Uv Spectra. The uv spectra of azoxyalkanes **5b, 6b,** and **5d** and **6d** had uv maxima in the expected range for *Z* azoxyalkanes [λ_{max} 215–224 nm (ϵ ~7000), infl at 270–280 nm (ϵ ~500)]. The work of Jaffé and co-workers has indicated that upon electronic excitation, the azoxy function of azoxybenzenes shows a substantial increase in basicity[24a] [e.g., for $C_6H_5N(O)=NC_6H_5$, ground-state pK_a = −6.57, excited state pK'_1 = 3.23]. Since the initial site of protonation of ground-state azoxybenzene is the azoxy oxygen atom,[24b] it would seem that in the excited state that atom experiences a substantial increase in electron density, and, later work by Jaffé lends strong support to this supposition.[24c] In azoxybenzenes, the increase in electron density at oxygen can come at the expense of the aromatic π system and its substituents. In azoxyalkanes, such an increase in electron density at the O terminus must be compensated for by a loss of electron density principally from the N terminus and, to what extent is possible, from the N-terminus substituent. (See structures A and B.) As the data of Table II show (with but single exception), it is R′ which influences the position of the principal λ_{max} of azoxyalkanes, with the better electron-donating substituents (those with a lower Taft σ^* or σ_I) moving the λ_{max} toward longer wavelength. Thus, when R′ is CH_3 or primary alkyl, λ_{max} = 216 ± 2 nm; when R′ is secondary or tertiary alkyl, λ_{max} = 222 ± 2 nm.



A B

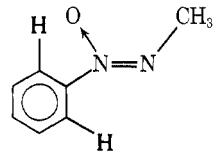
Table II. Uv Absorption Maxima of Representative Azoxyalkanes, RN(O)=N–R′

Structure		
R	R′	λ_{max}, nm
CH_3	CH_3	217[a]
n-C_3H_7	n-C_3H_7	217[a]
n-C_4H_9	n-C_4H_9	218[b]
i-C_3H_7	i-C_3H_7	220.5[a]
Cyclohexyl[f]	Cyclohexyl	224[c]
t-C_4H_9	t-C_4H_9	221[b]
t-C_8H_{17}	t-C_8H_{17}	223[a]
C_2H_5	n-C_8H_{17}	217.5[d]
C_2H_5	sec-C_8H_{17}	221.5[d]
CH_3	Cyclohexyl	222[c]
C_2H_5	t-C_8H_{17}	224[d]
Cyclohexyl	CH_3	214[c]
sec-C_4H_9	n-C_8H_{17}	222.5[d,e]
t-C_4H_9	CH_3	215[c]

[a] Reference 25. [b] Reference 26. [c] This work. [d] Reference 5. [e] The exception to the rule; see text. [f] Registry no., 57497-40-2.

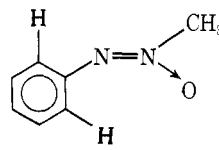
With the benzyl-type compounds **5e, 5f,** and **6f,** the azoxy group absorption was masked by the intense benzene-ring "end absorption"[28] (ϵ ~10^4 at 220 nm).

Chart I. Principal Uv Maxima (nm) and Ortho Proton Chemical Shifts of Aryl–Alkyl Azoxy Compounds



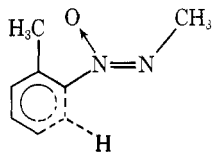
δ 8.17

5a, λ_{max} 245



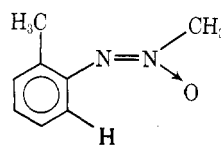
δ 7.87

6b, λ_{max} 228, 288



δ 7.50

5g, λ_{max} 223



δ 7.60

6g, λ_{max} 228, 294

NMR Spectra. The NMR chemical shifts of the α H's of azoxyalkanes are, by and large, unpredictable. Recent theoretical efforts by Snyder[29] have given some rationale to the observed nuances but problems remain.[1b] Table III records

Table III. Proton NMR Chemical Shifts (δ) of Azoxyalkanes in $CDCl_3$ Solvent

Compd	Proximal H_α[a]	Distal H_α[a]	H_β (other)
5b		3.12 s[b]	1.50 s proximal
6b	3.96 s		1.25 s distal
5c	3.98 q[c]	2.94 s	1.39 t[c] proximal
6c	3.99 t[d]	3.37 q[c]	1.23 t[c] distal
5d	4.14 m	3.10 s	
6d	4.02 s	3.98 m	
5e	5.25 s	3.15 s	7.33 bs (C_6H_5)
6e[e]	4.05 bs	4.57 q[d]	7.36 bs (C_6H_5)
5f	5.50 q[c]	3.20 s	1.83 d[c] proximal
6f	4.05 s	5.15 q[c]	1.47 d[c] distal
5g		3.40 s	2.34 (o-$C_6H_4CH_3$)
6g	4.23 s		2.22 (o-$C_6H_4CH_3$)

[a] Defined as follows: proximal-HC_β–HC_α–N(O)=N–C_αH–C_βH-distal. [b] s = singlet; bs = broadened singlet; m = multiplet; t = triplet; d = doublet; q = quartet. [c] $J \simeq 7$ Hz. [d] $J = 1$–1.5 Hz. [e] Signals observed in a mixture of **5e**, **6e**, and benzaldehyde oxime, and also in a small sample of **6e** separated by chromatography.

the chemical shifts of the proximal and distal[30] α H's of the azoxy compounds prepared in this work. Features of the NMR spectra (see Chart I) of aryl compounds **5a**,[27] **6a**,[27] **5g**, and **6g** are consistent with a noncoplanar aryl ring and azoxy group in **5g** as was deduced earlier from the uv data. Thus, the ortho aryl proton of **5g** is shielded by almost 0.7 ppm relative to the ortho protons of **5a** (see Chart I). By contrast, the ortho proton of **6g** has a more "normal" chemical shift (compare **6a**). Similar shielding of ortho protons was observed for the *E* diastereomers of **5a** and **6a**.[27] Tilting of the aryl ring out of copolanarity with the azoxy function apparently moves the ortho proton to a location of relative long-range shielding above the plane of the azoxy group.[31] The ortho CH_3 group might be expected to experience this same effect, but at present no unequivocal model for comparison is available.

Experimental Section

General. NMR spectra were obtained with a Varian A-60A spectrometer using tetramethylsilane as internal standard. Infrared spectra were obtained on Perkin-Elmer 337 or Beckman IR-12 spectrophotometers. Uv spectra were obtained on a Cary 14 spectrophotometer in 95% ethanol solutions. Midwest Microlab, Inc., Indianapolis, Ind., performed the elemental analyses. VPC analyses were conducted on Hewlett-Packard 5750 (flame detector) and 700 (thermal conductivity detector) instruments.

For VPC analyses the following columns were used: A, 5% Carbowax 20M on Anakrom or Chromosorb W (AW and DMCS); B, 5% UCW-98 on Diatoport S; C, 10–20% Carbowax 20M on Chromosorb W (AW and DMCS); D, 20% SE-30 on Anakrom.

Photochemical reactions were performed in a nitrogen atmosphere using either a medium-pressure 450-W Hanovia type L lamp (lamp H) or, more often, with a Rayonet photochemical reactor, Model RPR-100 (lamp R) equipped with a 16-tube, variable light source with 350 or 300 nm as the principal emission wavelength choices.

(*Z*)-Phenylmethyldiazene 1-Oxide (5a). To a solution of 4.42 g (0.094 mol) of *N*-methylhydroxylamine in 200 ml of water and 100 ml of THF, buffered at pH 6.85 with 400 mg of *N*-methylhydroxylamine hydrochloride, at 0° was added (dropwise) a solution of 10.0 g (0.093 mol) of nitrosobenzene in 30 ml of THF. After the 3-h addition, the solution was stirred for an additional 3 h at 0°, at which time the pH was 4.8. The reaction mixture was diluted with 100 ml of water and extracted with 3 × 150 ml of pentane. The pentane extracts were washed with 2 × 150 ml of 1 N HCl, washed with 2 × 150 ml of water, and then dried (Na_2SO_4). Fractionation, in vacuo, of the yellow-green organic concentrate gave 8.55 g (68%) of **5a**, bp 49° (0.1 mm), and the pot residue contained 1.74 g (19%) of diphenyldiazene oxide (azoxybenzene), mp 34–36°. The spectral data for **5a** have been reported previously.[27]

(*Z*)-*tert*-Butylmethyldiazene 1-Oxide (5b). Methylhydroxylamine hydrochloride (4.34 g, 52 mmol) was added, under nitrogen, to a solution of KOH (3.09 g, 55 mmol) in 100 ml of absolute ethanol. After stirring briefly the ethanolic suspension was treated with 4.35 g (25 mmol) of 2-methyl-2-nitrosopropane dimer. The mixture was stirred for 2 h at room temperature and for 16 h at 38°, after which dilution with 100 ml of 1 N HCl, extraction with pentane (10 × 10 ml), drying (Na_2SO_4), and distillation (1 atm) gave a colorless concentrate. Distillation of the concentrate gave 3.03 g (52%) of 99% pure **5b**: bp 84–88° (104 mm); uv λ_{max} 215 nm (ε 6300) with inflection at 270 nm (ε ~1000); NMR see Table III. The spectral data for **5b** agreed with previously published data.[10,26] A second preparation gave 96% pure **5b** in 73% yield.

In a second approach, 0.14 g (11 mmol) of *N*-*tert*-butylhydroxylamine hydrochloride, neutralized and buffered at pH 6.1 in 15 ml of methanol, was condensed with 0.045 g (5.5 mmol) of nitrosomethane dimer, under irradiation (lamp R, 300 nm) for 4 h. Dilution with water, extraction with ether, and distillation (1 atm) of the solvent gave a concentrate to which was added a weighed amount of CH_2Cl_2. Integration of the NMR spectrum showed that 79 mg (6.8%) of **5b** had been formed, but no detectable amount of **6b** was present. VPC analysis confirmed the low yield of **5b** (column C).

(*Z*)-Methyl-*tert*-butyldiazene 1-Oxide (6b). Small samples of what is likely **6b** could be obtained, contaminated by **5b**, by preparative VPC of the following "photothermal" rearrangement experiments on **5b**. Solutions of **5b** (1% weight to volume) in pentane were irradiated as follows: (1) for 5 h in quartz by lamp R (254 nm) to give six compounds (VPC, columns A or C) including **5b** (73%) and **6b** (4%); (2) for 3 h in quartz by lamp R (300 nm) to give five compounds (VPC) including **5b** (90%) and **6b** (4%). (The percentages are relative VPC peak areas). NMR spectra of the mixtures of **5b** and **6b** obtained by preparative VPC gave the signals for **6b** recorded in Table III. The data for **6b** seem to agree with that obtained by previous authors,[10,26] who suggest the same structure.

(*Z*)-Ethylmethyldiazene 1-Oxide (5c). A solution of 0.55 g (0.024 mol) of sodium in 10 ml of methanol was added to a methanol solution of 2.0 g (0.024 mol) of *N*-methylhydroxylamine hydrochloride. The resulting white precipitate was removed by filtration and the filtrate was added, dropwise, to 1.18 g (0.01 mol) of nitrosoethane dimer[1b] which had been dissolved in 3 ml of methanol. The mixture was stirred for 3 days under a nitrogen atmosphere, diluted with 30 ml of dilute HCl, and extracted with 4 × 20 ml of ether. The residue from concentration at atmospheric pressure was subjected to preparative VPC (column C) to yield **5c** (retention time 0.7 relative to **6c**): ir (neat) 1518 and 1323 cm^{-1}; NMR, see Table III.

Anal. Calcd for $C_3H_8N_2O$: C, 40.89; H, 9.15; N, 31.80. Found: C, 40.95; H, 9.39; N, 31.70.

(*Z*)-Methylethyldiazene 1-Oxide (6c). This azoxyalkane was isolated by preparative VPC from the preceding experiment, **5c**/**6c** ratio ~2: ir (neat) 1504 and 1325 cm^{-1}; NMR, see Table III.

Anal. Calcd for $C_3H_8N_2O$: C, 40.89; H, 9.15; N, 31.80. Found: C, 40.60; H, 9.34; N, 31.98.

(*Z*)-Cyclohexylmethyldiazene 1-Oxide (5d). A solution of 4.6 g (0.055 mol) of *N*-methylhydroxylamine hydrochloride in 95 ml of methanol was neutralized (pH 10.2) by the dropwise addition of a saturated potassium hydroxide–methanol solution. The resulting solution was buffered at pH 6.97 by the further addition of 1.8 g of *N*-methylhydroxylamine hydrochloride and was cooled to 0° in a Pyrex photochemical immersion well. To this cooled solution, by dropwise addition over 0.75 h, was added 5.65 g (0.025 mol) of nitrosocyclohexane dimer[32] in 160 ml of methanol. At the same time, the reaction was irradiated with a uv lamp (lamp R, 350 nm) with aliquots being periodically removed for VPC analysis (column A). After 10.5 h (complete reaction) the mixture was diluted with 150 ml of water and extracted thoroughly with pentane (total volume 375 ml). The pentane extracts were dried (Na_2SO_4), concentrated (1 atm), and distilled in vacuo to give 5.88 g (83%) of a mixture of **5d** and **6d**, bp 65° (3.0 mm), **5d/6d** ratio 11. Preparative VPC (column C) gave pure **5d**: uv λ_{max} 214 nm (ϵ 6000) with an inflection at 280 nm (ϵ ~20) observable at higher concentrations; NMR, see Table III.

Anal. Calcd for $C_7H_{14}N_2O$: C, 59.13; H, 9.92; N, 19.70. Found: C, 59.27; H, 9.91; N, 19.92.

(*Z*)-Methylcyclohexyldiazene 1-Oxide (6d). This azoxyalkane was isolated from the preceding experiment by preparative VPC: uv λ_{max} 222 nm (ϵ 7600); NMR, see Table III.

Anal. Calcd for $C_7H_{14}N_2O$: C, 59.13; H, 9.92; N, 19.70. Found: C, 59.18; H, 9.63; N, 19.95.

Thermally Induced Condensations Yielding 5d and 6d. A. A solution of 0.231 g (0.0275 mol) of *N*-methylhydroxylamine hydrochloride was neutralized (pH 10.4) with saturated potassium hydroxide in methanol and was then buffered at pH 6.9 by the further addition of 0.10 g of the hydrochloride salt. After the addition of 0.280 g (0.0125 mol) of nitrosocyclohexane dimer in 25 ml of methanol the mixture was heated at reflux for 8 h. After dilution with water, extraction, and drying, the organic extract was analyzed by VPC (column A) using naphthalene as internal standard. The analysis indicated the formation of 0.24 g (70.3%) of **5d**, 0.050 g (14.1%) of **6d**, and 7% of cyclohexanone oxime.

B. A solution of 9.2 g (0.11 mol) of *N*-methylhydroxylamine hydrochloride in 30 ml of methanol was neutralized (pH 10.8) as before and then buffered at pH 6.98 by the further addition of 5 g of the hydrochloride salt. To this was added a solution of 11.3 g (0.050 mol) of nitrosocyclohexane dimer in 75 ml of THF and the resulting mixture was heated at reflux for 18 h. After dilution with 250 ml of water, the mixture was subjected to continuous extraction with 100 ml of pentane. After drying (Na_2SO_4) the pentane extract was concentrated and the concentrate was subjected to column chromatography on 200 g of silica gel. Fractions eluted with mixtures of pentane and methylene chloride were monitored by VPC analysis (column A); 20–40% CH_2Cl_2 in pentane gave pure **5d**, 9.0 g (63%) after short-path distillation, bp 61° (3.8 mm); 50–75% CH_2Cl_2 in pentane gave a mixture of **5d** and **6d**, 2.28 g (16%) after distillation in vacuo; and elution with 100% CH_2Cl_2 gave 98% pure **6d**, 2.26 g (16%) after distillation, bp 66° (3.8 mm). In the crude reaction mixture, VPC analysis indicated a **5d/6d** ratio of 2.7.

Preparation of 5d and 6d Using *N*-Cyclohexylhydroxylamine. A solution of 0.34 g (0.0030 mol) of *N*-cyclohexylhydroxylamine[33] in 10 ml of methanol was buffered at pH 6.89 by addition of a solution of the corresponding hydrochloride salt. To this was added 0.115 g (0.013 mol) of nitrosomethane dimer[1b] and the resulting mixture was irradiated (lamp R, 300 nm) for 8.5 h with cooling by an air circulating fan only. VPC analysis (column A) using an internal standard indicated the formation of 0.142 g (38.5%) of **5d**, 0.0217 g (5.9%) of **6d**, 10% of cyclohexanone oxime, plus unreacted *N*-cyclohexylhydroxylamine.

Directed Synthesis of 5d. A solution of 0.985 (0.010 mol) of *N,O*-dimethylhydroxylamine hydrochloride in 1 ml of H_2O was neutralized (pH 11.4) with saturated aqueous potassium hydroxide and was then buffered at pH 5.75 by the further addition of 60 mg of the hydrochloride salt. To this was added 0.057 g (0.025 mol) of nitrosocyclohexane dimer in 8 ml of THF after which the mixture was heated at 50° for 12 h. The usual work-up gave a concentrate which was analyzed by NMR spectroscopy using a weighed amount of CH_2Cl_2 as an internal standard. The only azoxyalkane was **5d**, 0.040 g (55.8%), and this was confirmed by VPC analysis (column A) which also showed the presence of cyclohexanol and cyclohexanone.

Directed Synthesis of 6d. A solution of 0.066 g (0.004 mol) of *N*-cyclohexyl-*O*-methylhydroxylamine hydrochloride in 2 ml of H_2O was neutralized with saturated aqueous potassium hydroxide. The resulting organic solid was extracted with 4 × 1.5 ml of THF and this extract was buffered at ~pH 4.6 by the further addition of the hydrochloride salt. To this was added 0.018 g (0.2 mmol) of nitrosomethane dimer[1b] and the resulting mixture was irradiated (lamp R, 300 nm) in a Pyrex vessel for 8 h. VPC analysis (column B) using tetradecane as an internal standard indicated the formation of 0.0090 g (16%) of **6d** as the only azoxyalkane. A substantial amount of unreacted starting hydroxylamine was detected.

***N*-Cyclohexyl-*O*-methylhydroxylamine Hydrochloride.** A solution of 0.46 g (0.029 mol) of ethyl *N*-methoxy-*N*-cyclohexylcarbamate and 0.40 g (0.072 mol) of potassium hydroxide in 3 ml of methanol and 0.5 ml of H_2O was refluxed for 24 h. After extraction with ether (5 × 5 ml) and drying (Na_2SO_4), the extract was concentrated to 5 ml volume and excess saturated 2-propanol–HCl was added. This solution was evaporated to dryness with the last traces of water being removed by azeotropic distillation with benzene. The resulting hydrochloride salt was recrystallized from methanol–ether to give 0.23 g (63%) of white crystals: mp 143–144.5°; NMR (D_2O) δ 3.45 (m, 1 H, cyclohexyl methine H), 3.9 (s, OCH_3).

Anal. Calcd for $C_7H_{15}ClNO$: C, 50.76; H, 9.57. Found: C, 50.88; H, 9.97.

Ethyl *N*-Methoxy-*N*-cyclohexylcarbamate. To a rapidly stirred solution of 0.94 g (0.050 mol) of ethyl *N*-hydroxy-*N*-cyclohexylcarbamate and 0.52 g (0.093 mol) of potassium hydroxide in 8 ml of methanol at 0° was added 0.6 ml (0.095 mol) of methyl iodide. The mixture was stirred for 1 h at 0° and then at reflux temperature for 8 h. The addition of 50 ml of pentane precipitated the potassium iodide, and, after drying and concentration the crude product, 0.56 g (46%), was chromatographed over 8 g of silica gel. Elution with 10% ether in pentane gave 0.5 g of a colorless liquid which was distilled at 62° (0.5 mm) to give the analytically pure product: NMR ($CDCl_3$) δ 4.21 (q, OCH_2), 3.70 (s, OCH_3), 1.31 (t, CH_3).

Anal. Calcd for $C_{10}H_{19}NO_3$: C, 59.68; H, 9.52. Found: C, 59.66; H, 9.58.

Ethyl *N*-Hydroxy-*N*-cyclohexylcarbamate. Ethyl chloroformate (1.73 ml, 0.018 mol) was added dropwise to a solution of 2.08 g (0.018 mol) of *N*-cyclohexylhydroxylamine[33] and 1.95 g (0.018 mol) of Na_2CO_3 in 15 ml of H_2O and 65 ml of THF at 0°. The mixture warmed to room temperature while being stirred for 3 h. The reaction was neutralized (litmus) by adding 6 N HCl and the product was isolated by extraction with ether (3 × 50 ml), drying (Na_2SO_4), and concentration in vacuo. Chromatography over 60 g of silica gel (eluent pentane, ether) gave 2.24 g (66%) of product which was further purified by molecular distillation at 65° (0.15 mm): ir ($CHCl_3$) 3300 and 1670 cm^{-1}; NMR ($CDCl_3$) δ 4.16 (q, OCH_2), 3.75 (m, cyclohexyl methine H), and 1.27 (t, CH_3).

Anal. Calcd for $C_9H_{17}NO_3$: C, 57.75; H, 9.15; N, 7.48. Found: C, 58.01; H, 9.22; N, 7.31.

(*Z*)-Benzylmethyldiazene 1-Oxide (5e). A solution of 0.095 g (0.0011 mol) of *N*-methylhydroxylamine hydrochloride in 1 ml of H_2O was neutralized and buffered (pH 6.2) as previously mentioned. To this was added 0.12 g (0.5 mmol) of α-nitrosotoluene dimer[32] in 10 ml of methanol and the resulting solution was irradiated (lamp R, 300 nm) through Pyrex for 4 h with cooling by air circulation only. An aliquot of the reaction was extracted with ether, and after drying (Na_2SO_4) and concentration, was analyzed by NMR spectroscopy. The **5e/6e** ratio thus obtained was 2.46 (integration of CH_3 and CH_2 signals) and the ratio was seen to increase with time. This aliquot was then analyzed by VPC, using nitrobenzene as internal standard (column C), the results of which indicated the formation of 0.059 g (39.3%) of **5e**; thus the yield of **6e** was 16% and the total yield 53%. Pure **5e** could be separated from benzaldehyde oxime by chromatography over 15 g of alumina (neutral or basic), eluting with pentane, followed by molecular distillation: ir ($CDCl_3$) 1506 and 1280 cm^{-1}; uv λ_{max} 273 nm (ϵ 350) and 278 (225); both are peaks on strong end absorption with $\epsilon \sim 10^4$ at 210 nm; NMR, see Table III.

Anal. Calcd for $C_8H_{10}N_2O$: C, 63.98; H, 6.71; N, 18.65. Found: C, 63.70; H, 6.94; N, 18.75.

(*Z*)-Methylbenzyldiazene 1-Oxide (6e). A small sample of this azoxyalkane could be obtained by silica gel chromatography of the preceding experiment, a technique which failed to separate **5e** from benzaldehyde oxime. Elution with ether gave **6e**, the most polar compound of the three: ir ($CDCl_3$) 1500 and 1260 cm^{-1}; NMR, see Table III.

(*Z*)-1-(1-Phenylethyl)methyldiazene 1-Oxide (5f). A solution of 0.095 g (1.2 mmol) of *N*-methylhydroxylamine hydrochloride in 1 ml of H_2O was neutralized and buffered (pH 6.2) as previously described. To this was added 0.135 g (0.5 mmol) of 1-nitroso-1-phenylethane dimer[34] in 10 ml of methanol, and the resulting solu-

tion was irradiated (lamp R, 350 nm) at 10° (water circulation) for 3 h. VPC analysis of the reaction using sulfolane as internal standard indicated the formation of 0.104 g (64%) of **5f**, 0.027 g (16%) of **6f**, and 0.017 g (13%) of acetophenone oxime. From an experiment using the same quantities of reactants, but which was heated at reflux for 14 h, VPC analysis showed the formation of 0.067 g (41%) of **5f**, 0.055 g (41%) of acetophenone oxime, and, by NMR analysis, 0.26 g (18%) of **6f**. From an experiment increased in scale by a factor of 10, and heated at reflux for 14 h, pure **5f** (0.5 g, 30%) could be isolated by chromatography over 20 g of silica gel (eluting with 10% ether in pentane) followed by molecular distillation at 68° (1 mm): ir ($CHCl_3$) 1510 cm^{-1}; uv λ_{max} 257, 263, and 268 nm (ϵ ~300) as peaks on strong end absorption (ϵ ~10^4 at 210 nm) plus an inflection at 280 nm (~150); NMR, see Table III.

Anal. Calcd for $C_9H_{12}N_2O$: C, 65.83; H, 7.37; N, 17.06. Found: C, 65.85; H, 7.49; N, 16.82.

(*Z*)-Methyl-2-(1-phenylethyl)diazene 1-Oxide (6f). This azoxyalkane could be isolated from the preceding preparative experiment by preparative VPC (column D): uv λ_{max} no resolved maxima on a strong end absorption ϵ ~10^4 at 220 nm; NMR, see Table III.

Anal. Calcd for $C_9H_{12}N_2O$: C, 65.83; H, 7.37, N, 17.06. Found: C, 65.76; H, 7.08; N, 16.86.

(*Z*)-*o*-Tolylmethyldiazene 1-Oxide (5g). A solution of 2.78 g (0.033 mol) of *N*-methylhydroxylamine hydrochloride in 50 ml of H_2O was neutralized and buffered (pH 6.7) as in previous experiments and then cooled to 0°. To this was added 3.03 g (0.030 mol) of *o*-nitrosotoluene in 200 ml of THF and the resulting solution was stirred for 14 h. The mixture was diluted with 300 ml of H_2O and extracted with 3 × 100 ml of benzene. The benzene extract was washed with 1 N HCl, with H_2O, dried (Na_2SO_4), and concentrated to give 3.4 g of liquid. NMR analysis using a weighed amount of CH_2Cl_2 as internal standard indicated the formation of 2.7 g (60%) of **5g**, 0.3 g (7%) of **6g**, and about 0.4 g (18%) of di-*o*-tolyldiazene oxide [by integration of the *N*-methyl signals of **5g** and **6g** and the *C*-methyl signals (~δ 2.5) of the diarylazoxy compound]. Analytically pure **5g** was isolated by fractional distillation of the reaction mixture: 1.34 g (30%), bp 67° (1.2 mm); ir ($CHCl_3$) 1490, 1375, and 1320 cm^{-1}; uv λ_{max} 223 nm (ϵ 7700) and 264 (1500); NMR, see Chart I and Table III.

Anal. Calcd for $C_8H_{10}N_2O$: C, 63.98; H, 6.71. Found: C, 63.79; H, 6.72.

(*Z*)-Methyl-*o*-tolyldiazene 1-Oxide (6g). This azoxyalkane could be isolated from the preceding experiment by preparative VPC (column C) of higher boiling distillation fractions: ir ($CHCl_3$) 1500, 1420, and 1340 cm^{-1}; uv λ_{max} 228 nm (ϵ 9800) and 294 (5600); NMR, see Chart I and Table III; mol wt, calcd, 150.0793; found, 150.0784.

Acknowledgment. The authors wish to thank Mr. Tilford Riehl for the preparations of compounds **5b** and **6b**. The mass spectrum of **6g** was obtained through the courtesy of Professor M. E. Munk, Arizona State University.

Registry No.—**5a**, 35150-71-1; **5b**, 57497-28-6; **5c**, 57497-29-7; **5d**, 35214-91-6; **5e**, 57497-30-0; **5f**, 57497-31-1; **5g**, 57497-32-2; **6b**, 57497-33-3; **6c**, 57497-34-4; **6d**, 57497-35-5; **6e**, 57497-36-6; **6f**, 57497-37-7; **6g**, 57497-38-8; azoxybenzene, 495-48-7; *N,O*-dimethylhydroxylamine HCl, 6638-79-5; *N*-cyclohexyl-*O*-methylhydroxylamine HCl, 57497-41-3; ethyl *N*-methoxy-*N*-cyclohexylcarbamate, 57497-42-4; ethyl *N*-hydroxy-*N*-cyclohexylcarbamate, 57497-43-5; methyl iodide, 74-88-4; ethyl chloroformate, 541-41-3; *N*-cyclohexylhydroxylamine, 16649-50-6.

References and Notes

(1) (a) Partial support for this work by the National Institutes of Health, Grant NS07119 is acknowledged with thanks. (b) Part III: K. G. Taylor, M. S. Chi, and M. S. Clark, Jr., *J. Org. Chem.*, preceding paper in this issue. (c) Portions of this work were previously reported: K. G. Taylor, M. S. Clark, Jr., and S. R. Isaac, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973, No. MEDI-55.
(2) (a) C. L. Stevens, B. T. Gillis, and T. H. Haskell, *J. Am. Chem. Soc.*, **81**, 1435 (1959); (b) W. J. McGahren and M. P. Kunstman, *ibid.*, **92**, 1587 (1970); (c) B. W. Langley, B. Lythgoe, and L. S. Rayner, *J. Chem. Soc.*, 2309 (1951); (d) M. Spatz, *Ann. N.Y. Acad. Sci.*, **163**, 697 (1969).
(3) A. Gasco, A. Serafino, V. Mortarini, E. Menziant, M. A. Bianco, and J. C. Scurti, *Tetrahedron Lett.*, 3431 (1974).
(4) J. H. Weisburger, *Cancer*, **28**, 60 (1971), and references cited therein.
(5) (a) R. A. Moss, M. J. Landon, K. M. Luchter, and A. Mamantov, *J. Am. Chem. Soc.*, **94**, 4392 (1972); (b) R. A. Moss and G. M. Love, *ibid.*, **95**, 3070 (1973).
(6) S. R. Sandler and W. Karo, "Organic Functional Group Preparations", Vol. 12-II, Academic Press, New York, N.Y., 1971, Chapters 14 and 15.
(7) B. T. Gillis and J. D. Hagarty, *J. Org. Chem.*, **32**, 95 (1967).
(8) M. A. Berwick and R. E. Rondeau, *J. Org. Chem.*, **37**, 2409 (1972).
(9) F. R. Sullivan, E. Luck, and P. Kovacic, *J. Org. Chem.*, **39**, 2967 (1974).
(10) J. P. Freeman, *J. Org. Chem.*, **28**, 2508 (1963).
(11) J. G. Aston and D. M. Jenkins, *Nature (London)*, **167**, 863 (1951).
(12) Y. Ogata, M. Tsuchida, and Y. Takagi, *J. Am. Chem. Soc.*, **79**, 3397 (1957).
(13) G. A. Russell and E. J. Geels, *J. Am. Chem. Soc.*, **87**, 122 (1965).
(14) A. DiGiacomo, *J. Org. Chem.*, **30**, 2614 (1965).
(15) "Nitrosobenzene in basic ethanol solutions produces a significant but low steady-state concentration of nitrosobenzene radical anion that persists for minutes . . . these solutions . . . in the absence of oxygen [produce] azoxybenzene". See footnote 4 of ref 13.
(16) As methylhydroxylamine is consumed during the course of the reaction, the pH decreases toward its final value between 4 and 5.
(17) This was an early experiment and the yields could probably be improved by application of later-learned techniques.
(18) A. Mackor, T. A. J. W. Wajer, and T. J. DeBoer, *Tetrahedron Lett.*, 2757 (1967).
(19) The azoxyalkanes are stable under the conditions of their formation; i.e., the ratio **5d/6d** in a given reaction is invariant over the course of the reaction.
(20) R. B. Woodward and C. Wintner, *Tetrahedron Lett.*, 2693 (1969).
(21) (a) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 3120 (1952). (b) A. J. Gordon and R. A. Ford, "The Chemist's Companion", Wiley, New York, N.Y., 1972, pp 144–154. (c) A plot of log k/k_0 vs. E_s using the **5/6** ratios of entries 2, 4, 8, and 9 (T = 25–45°) gave a surprisingly good straight line. However, entry 10 was far off. Thus, the relation of the **5/6** ratio to E_s must be considered as qualitative.
(22) H. Meister, *Justus Liebigs Ann. Chem.*, **679**, 83 (1964).
(23) J. G. Aston and D. E. Ailman, *J. Am. Chem. Soc.*, **60**, 1930 (1938).
(24) (a) H. H. Jaffé and H. L. Jones, *J. Org. Chem.*, **30**, 964 (1965); (b) C.-S. Hahn and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 949 (1962); (c) R. H. Eilerhorst, H. H. Jaffé, and A. L. Miller, *ibid.*, **88**, 5342 (1966), and references cited therein.
(25) B. W. Langley, B. Lythgoe, and L. S. Rayner, *J. Chem. Soc.*, 4191 (1952).
(26) F. D. Greene and S. S. Hecht, *J. Org. Chem.*, **35**, 2482 (1970).
(27) K. G. Taylor and T. Riehl, *J. Am. Chem. Soc.*, **94**, 250 (1972).
(28) We note here that while a distinct short-wavelength maximum is observable for the azoxy group of **5g** this is not the case for the benzyl compounds **5e**, **5f**, and **6f**. In all of these cases the phenyl ring is not conjugated with the azoxy group. Perhaps the phenyl K band experiences a bathochromic shift (due to alkyl substitution) of sufficient magnitude to mask the azoxy group absorption in the latter three cases.
(29) J. P. Snyder, V. T. Bandurco, F. Darack, and H. Olsen, *J. Am. Chem. Soc.*, **96**, 5158 (1974).
(30) Defined as follows: proximal HC_α–N(O)=N–C_αH-distal.
(31) In this respect the azoxy and nitrone groups are similar: K. Koyano and H. Suzuki, *Tetrahedron Lett.*, 1859 (1968).
(32) W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 6455 (1957).
(33) W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5739 (1957).
(34) Prepared by the method of Emmons[32] with melting point[35] and NMR spectrum in agreement with the structure.
(35) A. Mackor and T. J. DeBoer, *Recl. Trav. Chim. Pays-Bas*, **89**, 151 (1970).