Transfer hydrogenation of the starting diketone (in the enol form) gives enough glycolaldehyde[10] to start a *$RuCl_2(PPh_3)_3$-catalyzed condensation* with **6**. The slow rate in this step is presumably the reason for an induction period recorded in the catalysis. Further molecules of the aldehyde are formed by transfer hydrogenation of the α,β-unsaturated ketone **9**. The bicyclic compound **1** results then via Ru(II)-catalyzed ether formation from **10b**.[11,12]

The very high ratio of **1**:**7** (including the transformation products of **7**) indicate that glycol aldehyde formation in step **9** → **10a** is considerable faster than in **6b** → **7**.

At the elevated temperature of the catalysis the proposed reaction intemediates could not be isolated. We found, however, that in the initial stages of the catalysis (with dimedone as starting ketone) an unstable keto alcohol of mass 184 is formed. This compound may be the 5,5-dimethyl analog of **10**.

Finally it should be recalled that in the presence of *piperidine*, glycol aldehyde reacts with *two* molecules of dimedone to give 3,5,6,7-tetrahydro-3-(2-hydroxy-4,4-dimethyl-6-oxo-1-cyclohexen-1-yl)-6,6-dimethyl-4(2*H*)-benzofuranone,[14] which is not formed in our catalytic process.

Experimental Section

6,6-Dimethyl-3,5,6,7-tetrahydro-4(2*H*)-benzofuranone (2). In a 150-ml flask equipped with an *efficient* condensor, a mixture of 4.2 g of dimedone, 70 mg of $RuCl_2(PPh_3)_3$,[15] and 60 ml of ethylene glycol was refluxed for 4 hr. The clear solution was cooled to room temperature and the products were extracted (four times) with 100 ml of benzene. The benzene extract was washed with water, dried ($MgSO_4$), and concentrated and the residue (4.6 g) was analyzed by the aid of a 2-m GLC column packed with 10% SE-30 on Chromosorb W, operated at 130°. (Dimedone methyl enol ether served as internal standard.) The mixture was found to consist of 3.5% **3,3-dimethylcyclohexanone**, 15% **3,3-dimethylcyclohexanol**, 24% **3,3-dimethylcyclohexanone ethylene ketal**, and 42% of the bicyclic compound **2**. The first two compounds were identified by comparison with authentic samples.[16,17] The ethylene ketal: NMR ($CDCl_3$) δ 0.98 (s, 6), 1.3–2.0 (m, 8), 3.86 (s, 4); mass spectrum (70 eV) *m/e* (rel intensity) 170 (3), 155 (3), 152 (10), 127 (100), 101 (27), 99 (94), 96 (27), 81 (25), 78 (25). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.6; H, 10.6. Found: 70.3; H, 10.6. The **dimethyltetrahydrobenzofuranone 2**: uv max (EtOH) 274 mμ (ϵ 12,800); ir 1630 cm^{-1}; NMR[6] ($CDCl_3$) δ 1.10 (s, 6), 2.24 (s, 2), 2.30 (t, 2, J = 1.5 Hz), 2.83 (t, 2, J = 9 Hz), 4.55 (t, 2, J = 9 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 166 (21), 151 (4), 123 (4), 111 (11), 110 (100), 80 (9). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.3, H, 8.4. Found: C, 72.1; H, 8.4. The 2,4-dinitrophenylhydrazone derivative of **2** melted at 168–169° (lit.[6] mp 167–169).

The reaction mixture was distilled at 0.9 mm. The fraction of bp 89–90° was further purified by preparative GLC to give 2.0 g (40%) of analytically pure **2**.

6-*tert*-Butyl-3,5,6,7-tetrahydro-4(2*H*)-benzofuranone (3). By the same method 5.04 g of 5-*tert*-butylcyclohexane-1,3-dione[8] was converted into 1.57 g (27%) of **3**. The GLC analysis was accomplished by a 2-m long column packed with 10% FAAB on Chromosorb W at 160°: uv max (EtOH) 269 mμ (ϵ 11,000); ir 1635 cm^{-1}; NMR ($CDCl_3$) δ 0.85 (s, 9), 1.3–2.3 (m, 4), 2.68 (t, 2, J = 9 Hz), 3.80 (m, 1), 4.50 (t, 2, J = 9 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 194 (16), 179 (6), 155 (8), 138 (20), 137 (51), 110 (100), 57 (25). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.2; H, 9.3. Found: C, 73.9; H, 9.0.

The **3-*tert*-butylcyclohexanone**[18] and **3-*tert*-butylcyclohexanol**[19] were compared with authentic samples. **3-*tert*-Butylcyclohexanone ethylene ketal:** NMR ($CDCl_3$) δ 0.89 (s, 9), 1.0–1.8 (m, 9), 3.87 (s, 4); mass spectrum (70 eV) *m/e* (rel intensity) 1.98 (1), 155 (15), 141 (98), 137 (18), 99 (100), 57 (38). Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.6; H, 11.1. Found: C, 72.5; H, 11.0.

3,5,6,7-Tetrahydro-4(2*H*)-benzofuranone (1) was prepared similarly from cyclohexane-1,3-dione in 46% yield. The unsubstituted bicyclic compound **1** is less stable than **2** and **3**, and therefore had to be freshly distilled [bp 100° (4 mm)] or gas chromatographed (on 15% QF-1 on Chromosorb W at 120°) prior to each spectroscopic recording and the elementary analysis: uv max (EtOH) 272 mμ (ϵ 15,600); ir 1630 cm^{-1};[7] NMR[7] ($CDCl_3$) δ 1.88–2.58 (m, 6), 2.81 (t, 2, J = 9.5 Hz), 4.55 (t, 2, J = 9.5 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 138 (32), 124, (19), 111 (11), 110 (100), 80 (27), 67 (31). Anal. Calcd for $C_8H_{10}O_2$: C, 69.6; H, 7.2. Found: C, 69.2; H, 7.6.

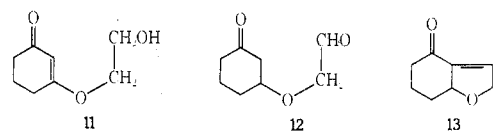
The **cyclohexanone ethylene ketal:** NMR ($CDCl_3$) δ 1.50 (s, 10), 3.80 (s, 4); mass spectrum (70 eV) *m/e* (rel intensity) 142 (22), 113 (62), 99 (100), 86 (60). Anal. Calcd for $C_8H_{14}O_2$: C, 67.5; H, 9.9. Found: C, 67.5; H, 10.0.

Acknowledgment. We are grateful to the Central Fund of the Hebrew University for financial support.

Registry No.—**1**, 42858-96-8; **2**, 19225-65-1; **3**, 55401-07-5; **6a**, 504-02-9; $RuCl_2(PPh_3)_3$, 15529-49-4; ethylene glycol, 107-21-1; dimedone, 126-81-8; 3,3-dimethylcyclohexanone ethylene ketal, 49673-67-8; 5-*tert*-butylcyclohexane-1,3-dione, 49673-64-5; 3-*tert*-butylcyclohexanone ethylene ketal, 49673-70-3; cyclohexanone ethylene ketal, 177-10-6.

References and Notes

(1) Y. Sasson, J. Blum, and E. Dunkelblum, *Tetrahedron Lett.*, 3199 (1973).
(2) Y. Tamura, Y. Kita, M. Shimagaki, and M. Terashima, *Chem. Pharm. Bull.*, **19**, 571 (1971).
(3) J. Nickl, *Chem. Ber.*, **91**, 553 (1958).
(4) F. Korte, D. Scharf, and K. H. Büchel, *Justus Liebigs Ann. Chem.*, **664**, 97 (1963).
(5) S. Uemura, T. Nakano, and K. Ichikawa, *Nippon Kagaku Zasshi*, **89**, 203 (1968).
(6) K. Ichikawa, O. Itoh, and T. Kawamura, *Bull. Chem. Soc. Jpn.*, **41**, 1240 (1960).
(7) J. M. McIntosh and P. M. Beaumier, *Can. J. Chem.*, **51**, 843 (1973).
(8) E. Dunkelblum, R. Levene, and J. Klein, *Tetrahedron*, **28**, 1009 (1972).
(9) Ichikawa et al. (ref 6) reported the preparation of an inseparable mixture of **4** and **5**. The NMR spectrum of our mixture and the reported one proved to have exactly the same peaks.
(10) Y. Sasson, M. Cohen, and J. Blum, *Synthesis*, 359 (1973).
(11) Y. Sasson and J. Blum, *J. Chem. Soc., Chem. Commun.*, 309 (1974).
(12) With the available evidence we cannot be certain that ether formation takes place at this stage. Thus in an alternative mechanism, e.g., **6b** may react with ethylene glycol to give ether **11**. Intramolecular hydrogen transfer from the OH function to the double bond (to give **12**) followed by internal cyclization may lead to **13**. The product **1** is then formed by Ru(II)-catalyzed migration of the C_3–C_{3a} double bond.[13]



11 12 13

(13) Cf., e.g., Y. Pickholtz, Y. Sasson, and J. Blum, *Tetrahedron Lett.*, 1263 (1974).
(14) D. C. C. Smith, *J. Chem. Soc.*, 1244 (1956).
(15) T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 945 (1966).
(16) O. H. Wheeler and J. Zabicky, *Can. J. Chem.*, **36**, 656 (1958).
(17) E. L. Eliel and C. A. Lukach, *J. Am. Chem. Soc.*, **79**, 5986 (1957).
(18) C. Djerassi, E. J. Warawa, R. E. Wolff, and E. J. Eisenbraun, *J. Org. Chem.*, **25**, 917 (1960).
(19) W. Hückel and K. Thiele, *Chem. Ber.*, **94**, 2027 (1961).

Intramolecular and Intermolecular 1,3-Dipolar Cycloadditions of Nitrile Oxides Bearing an Alkenyl Substituent

Luisa Garanti,* Alberto Sala, and Gaetano Zecchi

Istituto di Chimica industriale dell'Universita', Centro del C.N.R. per la Sintesi e stereochimica di speciali sistemi organici, 20133 Milano, Italy

Received March 21, 1975

Oxidation of 2-allyloxybenzaldoxime by nitrogen dioxide has been recently reported[1] to give the fused ring compound **2a**, the product of an intramolecular cycloaddition of the intermediate nitrile oxide **1a**. The stereochemistry of the latter molecule reasonably accounts for the intramolecular process as well as for the unusual orientation, leading to 5-unsubstituted 2-isoxazoline.[2]

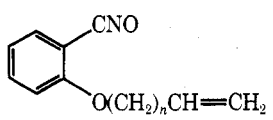
This result led us to examine whether the intramolecular reaction proceeds as the chain length between the dipole

Table I
Yields, Physical Data, and Spectral Properties of Aldehydes 3 and Oximes 4[a]

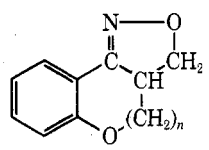
Compd	Yield, %	Bp, °C (mm) (mp, °C)	Ir spectrum (film), cm^{-1}	NMR spectrum ($CDCl_3$), δ (J, Hz)
3a	41	90–92 (0.3)	1690 (C=O)	2.4–2.8 (2 H, m, CH_2CH=), 4.12 (2 H, t, J = 6 Hz, CH_2O), 4.95–5.35 (2 H, m, CH_2=), 5.6–6.2 (1 H, m, CH=), 6.8–7.9 (4 H, m, aromatics), 10.50 (1 H, s, CHO)
3b	43	119–121 (0.7)	1690 (C=O)	1.6–2.6 [4 H, m, $(CH_2)_2CH$=], 4.08 (2 H, t, J = 6 Hz, CH_2O), 4.85–5.25 (2 H, m, CH_2=), 5.5–6.1 (1 H, m, CH=), 6.8–7.9 (4 H, m, aromatics), 10.53 (1 H, s, CHO)
3c	60	111–113 (0.1)	1690 (C=O)	1.5–2.4 [6 H, m, $(CH_2)_3CH$=], 4.09 (2 H, t, J = 6 Hz, CH_2O), 4.8–5.2 (2 H, m, CH_2=), 5.6–6.2 (1 H, m, CH=), 6.8–8.0 (4 H, m, aromatics), 10.52 (1 H, s, CHO)
4a	85	145–150 (0.1) (40–41)	3280 (OH) 1650 (C=N)	2.3–2.7 (2 H, m, CH_2CH=), 4.00 (2 H, t, J = 6 Hz, CH_2O), 4.9–5.3 (2 H, m, CH_2=), 5.5–6.2 (1 H, m, CH=), 6.7–7.9 (4 H, m, aromatics), 8.55 (1 H, s, CH=N), 9.3 (1 H, broad s, OH)
4b	75	170–175 (0.5) (49–50)	3270 (OH) 1650 (C=N)	1.6–2.4 [4 H, m, $(CH_2)_2CH$=], 3.96 (2 H, t, J = 6 Hz, CH_2O), 4.8–5.2 (2 H, m, CH_2=), 5.5–6.1 (1 H, m, CH=), 6.7–7.8 (4 H, m, aromatics), 8.57 (1 H, s, CH=N), 9.0 (1 H, broad s, OH)
4c	82	155–160 (0.4)	3270 (OH) 1640 (C=N)	1.5–2.3 [6 H, m, $(CH_2)_3CH$=], 4.02 (2 H, t, J = 6 Hz, CH_2O), 4.8–5.2 (2 H, m, CH_2=), 5.5–6.2 (1 H, m, CH=), 6.8–8.0 (4 H, m, aromatics), 8.60 (1 H, s, CH=N), 9.2 (1 H, broad s, OH)

[a] All the compounds listed gave correct elemental analyses.

and dipolarophile functions is increased, and, if so, which of the two possible orientations the product acquires. In this context, an exploratory investigation on the behavior of the structurally related nitrile oxides **1b–d** was undertaken. By analogy with **1a**, compounds **1b–d** were generated in situ from the corresponding aldoximes by NO_2 oxidation.

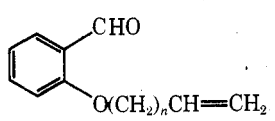


1a, $n = 1$
b, $n = 2$
c, $n = 3$
d, $n = 4$

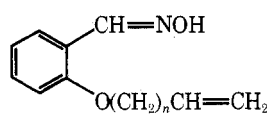


2a, $n = 1$
b, $n = 2$

The hitherto unknown aldehydes **3a–c** were synthesized by allowing equimolar amounts of salicylaldehyde, sodium hydroxide, and the proper ω-bromo-1-alkene to react in aqueous ethanol. From them, oximes **4a–c** were easily ob-



3a, $n = 2$
b, $n = 3$
c, $n = 4$

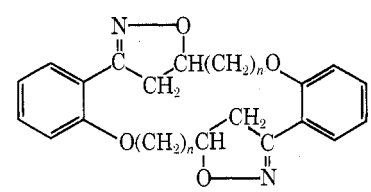


4a, $n = 2$
b, $n = 3$
c, $n = 4$

tained by the standard procedure. Yields, physical data, and spectral properties are collected in Table I.

The treatment of the above aldoximes with nitrogen dioxide was carried out in 0.05 *M* ethereal solutions. In all cases, the crude reaction product was a very complex mixture; however, somewhat different results were obtained for the different substrates, as is illustrated below.

When starting from **4a**, the column chromatography of the product mixture afforded, besides some **3a** and **4a**, 3,3a,4,5-tetrahydro[1]benzoxepino[5,4-*c*]isoxazole (**2b**, 17% yield) and 3,17-dioxa-13,14,27,28-tetrahydrobis([3]orthocyclo[0](3,5)isoxazolo)phane (**5a**) (2% yield). A sizable quantity of uncharacterized resinous material was also obtained.



5a, $n = 2$
b, $n = 3$
c, $n = 4$

In the case of **4b** and **4c**, the reaction led predominantly to resinous material, as found for **4a**; however, in addition to trivial compounds such as the starting aldoximes and the corresponding aldehydes, the macrocyclic compounds **5b** and **5c** were isolated in 13 and 19% yield, respectively.[3]

The structures **2b** and **5a–c** were assigned on the basis of elemental analysis, molecular weights measured by mass spectrometry, and ir and NMR spectra (see Table II). In particular, the unsubstituted positions of the isoxazoline rings in these compounds were established on the basis of the following evidence.

The NMR spectrum of **2b** shows a double doublet centered at δ 4.60 (1 H, J = 8 and 10 Hz) which may well be regarded as half of the signal of the isoxazoline methylene group; the other half of this signal appears to be overwhelmed by the signal due to the OCH_2 grouping of the seven-membered ring (δ 4.1–4.3). The multiplet centered at δ 3.7 should then be attributed to the isoxazoline methynic group. This interpretation is supported by the literature data on 3,4-disubstituted 2-isoxazolines, whose ring protons gave ABC systems with δ values for 5-H_2 in the range 4.5–4.8 ($J_{gem} \simeq 8.5$, $J_{4,5cis} \simeq 11$, and $J_{4,5trans}$ = 5.92–8.45 Hz).[4]

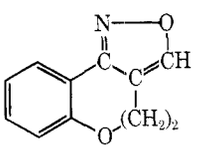
Table II
Physical and Spectral Properties of Heterocyclic Compounds 2b, 5a–c, 6, and 7b,c[a]

Compd	Mp, °C (recrystn solvent)	Mass spectrum, M^+ m/e	NMR spectrum, δ (J, Hz)
2b	57 (*n*-pentane)	189	$CDCl_3$: 1.6–2.7 (2 H, m, CH_2CH_2O), 3.4–4.8 (5 H, m, CH_2O and $CHCH_2O$),[b] 6.8–7.5 and 7.6–7.9 (3 H and 1 H, m, aromatics)
5a	293–295 (pyridine)	378	C_5D_5N: 2.0–2.4 (4 H, m, CH_2CH_2O), 3.3–3.7 (4 H, m, $CH_2C{=}$), 4.0–4.4 (4 H, m, CH_2O), 4.7–5.2 (2 H, m, CH), 6.8–7.55 and 7.65–8.0 (6 H and 2 H, m, aromatics)
5b	218–219 (acetone)	406	C_5D_5N: 1.6–2.1 [8 H, m, $(CH_2)_2CH_2O$], 3.2–3.6 (4 H, m, $CH_2C{=}$), 3.8–4.1 (4 H, m, CH_2O), 4.4–4.9 (2 H, m, CH), 6.8–7.4 and 7.6–8.0 (6 H and 2 H, m, aromatics)
5c	233–234 (chloroform)	434	$CDCl_3$: 1.5–2.1 [12 H, m, $(CH_2)_3CH_2O$], 3.1–3.5 (4 H, m, $CH_2C{=}$), 3.9–4.2 (4 H, m, CH_2O), 4.4–4.9 (2 H, m, CH), 6.8–7.6 and 7.8–8.0 (6 H and 2 H, m, aromatics)
6	(bp 128–130, 0.2 mm)	187	$CDCl_3$: 3.02 (2 H, dt, J = 5 and 1 Hz, CH_2CH_2O), 4.25 (2 H, t, J = 5 Hz, CH_2O), 6.9–7.4 and 8.15–8.4 (3 H and 1 H, m, aromatics), 8.24 (1 H, t, J = 1 Hz, CH)
7b	236–237 (pyridine)	402	C_5D_5N: 1.8–2.4 (4 H, m, CH_2CH_2O), 2.8–3.2 (4 H, m, $CH_2C{=}$), 3.8–4.1 (4 H, m, CH_2O), 6.85 (2 H, s, CH), 6.9–7.5 and 8.1–8.4 (6 H and 2 H, m, aromatics)
7c	168 (toluene)	430	$CDCl_3$: 1.6–2.0 [8 H, m, $(CH_2)_2CH_2O$], 2.5–2.9 (4 H, m, $CH_2C{=}$), 3.8–4.1 (4 H, m, CH_2O), 6.44 (2 H, s, CH), 6.7–7.5 and 7.6–7.9 (6 H and 2 H, m, aromatics)

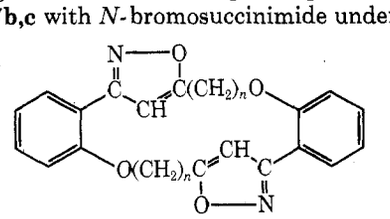
[a] All the compounds listed gave correct elemental analyses and showed, in the ir spectrum, a band of moderate intensity at ca. 1600 cm^{-1} ($\nu_{C=N}$). [b] At 100 MHz: 3.5–3.9 (1 H, m), 4.1–4.3 (3 H, m), 4.60 (1 H, dd, J = 8 and 10 Hz) (see text).

For compounds **5a–c**, the presence of only one hydrogen at the 5 position of each isoxazoline ring was inferred from the intensity (2 H) of the furthest downfield NMR signal. In fact, isoxazoline 5 hydrogens resonate downfield from those in the 4 position.[4–7]

The above structural assignments were confirmed for **2b** and **5b,c** by converting them into the corresponding isoxazole derivatives **6** and **7b,c** with *N*-bromosuccinimide under



6



7a, $n = 2$
b, $n = 3$
c, $n = 4$

free-radical conditions.[8] In addition to correct elemental analyses, molecular weights (from mass spectra), and ir absorptions, compounds **6** and **7b,c** gave NMR spectra (Table II) of unequivocal interpretation. In fact, the isoxazole proton of **6** resonates at δ 8.24 while those of **7b,c** give signals at δ 6.85 and 6.44, respectively. These data agree with the reported δ values of variously substituted isoxazoles, which are in the range of 8.0–9.8 for the 5 hydrogens[1,4,9–12] and 6–7.5 for the 4 hydrogens.[4,11–16]

Analogous oxidation of **5a** to **7a** was not performed because of the small amount of the available material.

The reported results show the effect of the chain length between the dipole and dipolarophile groups on the intramolecular cycloadditions. Thus, while nitrile oxide **1a** gave **2a** in 42% yield,[1] formation of **2b** from **1b** occurred to a minor extent (17%) and no compound of formula **2** was present, within the detection limits, among the products arising from **1c,d**. On the other hand, the formation of the large ring compounds **5a–c** involves an intermolecular cycloaddition to originate long-chain intermediates capable of undergoing an intramolecular ring closure to the final products.

The above results confirm that nitrile oxides add to terminal double bonds preferably giving 5-substituted rather than 4-substituted 2-isoxazolines, as amply shown in intermolecular reactions.[2] The existence of geometrical restraints to such orientation can force the reaction to occur in the opposite manner, as observed in the intramolecular cycloadditions of **1a,b**.

Experimental Section

All melting points and boiling points are uncorrected. Ir spectra were taken on a Perkin-Elmer Model 377 spectrophotometer. NMR spectra were recorded on a Varian A-60A instrument with Me_4Si as internal standard. Mass spectra were obtained on a Hitachi Model RMU-6L spectrometer.

Preparation of Aldehydes 3. General Procedure. A solution of salicylaldehyde (0.20 mol), ω-bromo-1-alkene (0.20 mol), and sodium hydroxide (0.20 mol) in 75% aqueous ethanol (300 ml) was heated at 70° during 30 hr. The mixture was then poured into ice–water and extracted several times with ether. The organic solution was dried over $MgSO_4$ and evaporated. Distillation in vacuo of the residue afforded aldehyde **3** (see Table I).

Preparation of Oximes 4. General Procedure. A solution of sodium carbonate (0.06 mol) in water (50 ml) was added dropwise to a stirred solution of aldehyde **3** (0.10 mol) and hydroxylamine hydrochloride (0.12 mol) in 50% aqueous ethanol (100 ml). The mixture was then heated at 70° for 1 hr. After removal of the solvent, water was added and the mixture was extracted several times with ether. The organic layer was dried over $MgSO_4$ and evaporated; the residue was distilled in vacuo to give oxime **4** (see Table I).

Treatment of Oximes 4 with Nitrogen Dioxide. Typical Procedure. A slow current of gaseous NO_2 (99.5%, J. T. Baker) was bubbled into a solution of oxime **4a** (5.75 g, 0.030 mol) in anhydrous ether (600 ml) under cooling at 0°, until all the starting material practically disappeared [TLC analysis with ether–*n*-hexane (3:2), 6 hr]. The resulting mixture was refluxed during 48 hr. The solvent was then removed under reduced pressure and the residue was chromatographed on a silica gel column (600 g) using benzene–ethyl acetate (9:1) as eluent. The following compounds were isolated in order of elution, the volume of eluent and yield being given in parentheses: aldehyde **3a** (200 ml, 0.45 g), oxime **4a**

(280 ml, 0.50 g), isoxazoline **2b** (550 ml, 0.97 g), bisisoxazoline **5a** (100 ml, 0.11 g), and a uncharacterized pale yellow solid (700 ml, 1.7 g).

Treatment of oximes **4b,c** with nitrogen dioxide was carried out under identical conditions.

Oxidation of 5b,c to 7b,c. A mixture of compound **5b** or **5c** (1 mmol), *N*-bromosuccinimide (2 mmol), and a trace of 2,2′-azobis(2-methylpropionitrile) in carbon tetrachloride (50 ml) was refluxed for 12 hr. The solvent was removed and the residue was taken up by dry triethylamine (15 ml). After 12 hr of refluxing, the mixture was poured into water and extracted several times with carbon tetrachloride (200 ml). The organic solution was dried over $MgSO_4$ and evaporated. The residue was chromatographed on a silica gel column (40 g) using benzene–ethyl acetate (9:1) as eluent to give compound **7b** or **7c** (see Table II), yield ca. 30%.

Oxidation of 2b to 6. Treatment of compound **2b** (1 mmol) with *N*-bromosuccinimide (1 mmol) according to the above procedure afforded compound **6** (see Table II) in 62% yield.

Acknowledgment. We wish to thank Mr. Giorgio Tuan (Lepetit SpA) for determining the mass spectra.

Registry No.—**2b,** 55400-93-6; **3a,** 55400-94-7; **3b,** 55400-95-8; **3c,** 55400-96-9; **4a,** 55400-97-0; **4b,** 55400-98-1; **4c,** 55400-99-2; **5a,** 55401-00-8; **5b,** 55401-01-9; **5c,** 55401-02-0; **6,** 55401-03-1; **7b,** 55401-04-2; **7c,** 55401-05-3; salicylaldehyde, 90-01-7; sodium hydroxide, 1310-73-2; ω-bromo-1-butene, 5162-44-7; ω-bromo-1-pentene, 1119-51-3; ω-bromo-1-hexene, 2695-47-8; hydroxylamine hydrochloride, 5470-11-1; nitrogen dioxide, 10102-44-0; *N*-bromosuccinimide, 128-08-5.

References and Notes

(1) R. Fusco, L. Garanti, and G. Zecchi, *Chim. Ind. (Milan)*, **57**, 16 (1975).
(2) For the orientation in the 1,3-dipolar cycloadditions of nitrile oxides to ethylenic bonds, see C. Grundmann and P. Grünanger, "The Nitrile Oxides", Springer-Verlag, West Berlin, 1971; A. Dondoni and G. Barbaro, *J. Chem. Soc., Perkin Trans. 2*, 1769 (1973); K. Bast, M. Christl, R. Huisgen, W. Mack, and R. Sustmann, *Chem. Ber.*, **106**, 3258 (1973).
(3) When higher concentrations of aldoximes **4b** and **4c** were used, cycloaddition products could not be isolated.
(4) M. Christl and R. Huisgen, *Chem. Ber.*, **106**, 3345 (1973).
(5) G. Bianchi, P. Grünanger, and A. Perotti, *Tetrahedron Lett.*, 2157 (1964).
(6) M. C. Aversa, G. Cum, and M. Crisafulli, *Gazz. Chim. Ital.*, **96**, 1046 (1966).
(7) R. Sustmann, R. Huisgen, and H. Huber, *Chem. Ber.*, **100**, 1802 (1967).
(8) G. Bianchi and P. Grünanger, *Tetrahedron*, **21**, 817 (1965).
(9) W. L. Meyer, R. W. Huffman, and P. G. Schroeder, *Tetrahedron*, **24**, 5959 (1968).
(10) R. Jacquier, C. Petrus, F. Petrus, and M. Valentin, *Bull. Soc. Chim. Fr.*, 2678 (1970).
(11) R. G. Micetich, *Can. J. Chem.*, **48**, 467, 3753 (1970).
(12) P. Battioni, L. Vo-Quang, J. Raymond, and J. Vo-Quang, *C. R. Acad. Sci.*, **271**, 1468 (1970).
(13) Higher δ values were found in DMSO-d_6 for 3-(3-nitrophenyl)- and 3-(4-nitrophenyl)-5-carbomethoxy-2-isoxazoline (8.17 and 8.32 respectively).[4]
(14) H. Laurent and G. Schulz, *Chem. Ber.*, **102**, 3324 (1969).
(15) W. W. Paudler and A. G. Zeiler, *J. Org. Chem.*, **34**, 999 (1969).
(16) A. Battaglia, A. Dondoni, and F. Taddei, *J. Heterocycl. Chem.*, **7**, 721 (1970).

Comparison of Photochemical Reactions of $(C_6H_5)_2CHXCH(C_6H_5)_2$ (X = NH, CH_2, O, S) Systems

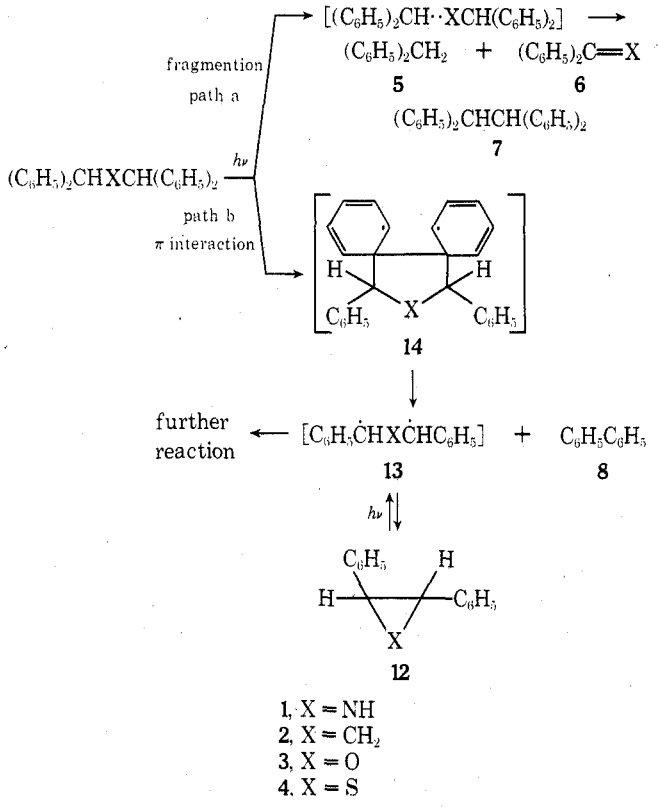
Roger W. Binkley,* Shen-Chu Chen, and David G. Hehemann

Department of Chemistry, Cleveland State University, Cleveland, Ohio 44115

Received February 25, 1975

Several years ago it was reported that photochemical reaction of 1,1,1′,1′-tetraphenyldimethylamine (**1**) resulted in formation of diphenylmethane (**5**), benzophenone imine (**6**), and a small amount of 1,1,2,2-tetraphenylethane (**7**).[1]

Scheme I
Proposed Reaction Pathways



1, X = NH
2, X = CH_2
3, X = O
4, X = S

Mechanistic studies led to the proposed reaction sequence shown in Scheme I (path a). More recent investigation has uncovered a quite different reaction (Scheme I, path b) for a structurally similar compound, 1,1,3,3-tetraphenylpropane (**2**).[2] An understanding of this difference in reactivity is now possible as a result of further investigation of the photochemistry of **1** as well as study of two related systems, bis(diphenylmethyl) ether[3] (**3**) and bis(diphenylmethyl) sulfide (**4**).[4]

Results

Corex-filtered irradiations of compounds **1–3** were conducted in ethyl ether (1 mmol/350 ml) for both preparative runs and quantum yield determinations.[5] Reaction mixture separations were achieved by adsorption chromatography on Florisil followed by preparative GLC of fractions containing photoproduct mixtures. Product analysis from irradiation of **1** agreed with that reported earlier[1] except for the isolation of biphenyl (**8**) as an additional photoproduct. This new product is quite significant, however, since it suggests that the initially observed nitrogen–carbon bond fragmentation process (path a) is accompanied by a π-interaction reaction[6] (path b). The primary reaction process previously described for 1,1,3,3-tetraphenylpropane (**2**) was unaffected by the change in reaction solvent.[2] The reactivity of bis(diphenylmethyl) ether (**3**) was similar to that of **2** in that products characteristic of π interaction were the only ones observed. Irradiation of **3** gave biphenyl (**8**, 40%) and, although no stilbene oxide (**12**) was isolated, 2-ethoxy-1-phenylpropane (**9**, 35%), benzaldehyde (**10**, 31%), and 2-ethoxy-1-phenyl-1-propanol (**11**, 12%)[7] were produced. The intermediacy of stilbene oxide (**12**) or its precursor **13** (X = O) in the formation of **9**, **10**, and **11** is clearly suggested by the fact that compounds **9–11** arise from irradiation of **12**[8] in the same relative amounts as from **3**. Also, photolysis of benzaldehyde (**10**) in ether produced **11**, indicating **10** to be an intermediate in the formation of **11**.