Pyrex jacket on the immersion well limited the light entering the photolysis cell to wave lengths greater than 300 mμ.

Analytical Method.—The Cary model 14 ultraviolet recording spectrophotometer was used for the quantitative determination of the nitroso dimer[14]

The Perkin–Elmer model 154C vapor fractometer unit using a didecyl phthalate column was used for the quantitative analysis of 1-octanol, 1-octanal, heptane, 1-heptene and tetradecane.

The isomeric oximinoheptanes were separated at 90° on a 200 μ glass bead column containing 0.5% of Carbowax 400 as substrate. Methanal was determined quantitatively by the method of MacFayden.[28]

The Perkin–Elmer model 21 recording infrared spectrophotometer was used to determine 1-octyl nitrate quantitatively.

Paper chromatograms were run on the nitroso dimers in heptane–methyl Cellosolve in a descending manner, using Whatman No. 1 paper. The R_f values found for *y*-nitrosoheptane, *y*-nitrosoheptane 4-nitroso-1-octanol and 4-nitroso-1-octanol dimers were 1.00, 0.63 and 0.00, respectively. The amounts present were determined quantitatively by eluting the bands (which had been cut out) with methanol and determining the ultraviolet absorbance of the resulting solution at 294 mμ.

Photolysis Procedure.—Octyl nitrite (5 ml.) was photolyzed for about 2 hours at 18° in 200 ml. of solvent previously deaerated and continuously agitated during the photolysis by gently passing a stream of nitrogen through the solution, except when volatile products were to be analyzed. The course of the reaction was followed spectrophotometrically using the characteristic nitrite peaks in the 320–380 mμ region. At the end of the photolysis the absorbance of the solution at a wave length maximum near 294 mμ was determined.

4-Nitroso-1-octanol Dimer.—Octyl nitrite (22.5 g.) was photolyzed in 1800 ml. of heptane using an appropriate photolysis cell. The 4-nitroso-1-octanol dimer crystallized directly out of the reaction solution and was isolated by filtration; yield 7.0 g. (25.9% by ultraviolet analysis), m.p. 50–60°, λ_{max}^{MeOH} 294 mμ (ε 7,900). The analytical sample was recrystallized from heptane; m.p. 95–96°, λ_{max}^{MeOH} 294 mμ (ε 9,500). The product exhibits infrared absorption (in Nujol) at 3.1 μ (CO–H) and 8.5 μ (*trans*-nitroso dimer).

Anal. Calcd. for $C_{16}H_{34}N_2O_4$: C, 60.34; H, 10.76; N, 8.80. Found: C, 60.23; H, 10.68; N, 9.07.

4-Oximino-1-octanol.—The 4-nitroso-1-octanol dimer was quantitatively converted to 4-oximino-1-octanol by heating it at 60° for 48 hours in a closed vessel. The analytical sample was an oil, n^{25}D 1.4678; $\lambda_{end\ abs.}^{MeOH}$ 210 mμ (ε 850). The product exhibits infrared absorption (as a film) at 3.0 μ (CO–H and NO–H) and 6.0 μ (C═N of oxime).

Anal. Calcd. for $C_8N_{17}NO_2$: C, 60.34; H, 10.76; N, 8.80; neut. equiv., 159. Found: C, 60.46; H, 10.88; N, 9.07; neut. equiv., 153.[29]

***y*-Nitrosoheptane Dimer.**—The filtrate from the heptane photolysis was concentrated *in vacuo* to give 15.5 g. of oil. A 10.0-g. aliquot was chromatographed on a Florisil column. The first fraction eluted with heptane weighed 0.96 g. (6.6%). An analytical sample was obtained by rechromatographing; n^{25}D 1.4600, λ_{max}^{MeOH} 292 mμ (ε 8,500). The product exhibits infrared absorption (as a film) at 8.45 μ (*trans*-nitroso dimer); no hydroxyl bands were evident.

Anal. Calcd. for $C_{14}H_{30}N_2O_2$: C, 65.07; H, 11.70; N, 10.84. Found: C, 65.42; H, 11.79; N, 10.64.

***y*-Nitrosoheptane·4-Nitroso-1-octanol Mixed Dimer.**—From the continued chromatography of the heptane photolysis solution using diethyl ether as eluent was obtained a liquid fraction, 2.47 g. (17%), having the characteristic ultraviolet absorption for nitroso dimers but of intermediate polarity between the *y*-nitrosoheptane dimer and the 4-nitroso-1-octanol dimer. Quantitative infrared hydroxyl determination[30] indicated that it had one hydroxyl group per nitroso dimer moiety. It was not further characterized.

Quantum Yield.—Octyl nitrite in heptane was irradiated in the photolysis vessel with a 200 watt Hanovia 654A-36 ultraviolet lamp using a tubular black light filter (Corning #5874) which limited the radiation to the 334 and 366 mμ mercury lines (Fig. 1). The decrease in octyl nitrite concentration was followed spectrophotometrically. A uranyl sulfate–oxalic acid actinometer[31] gave a quantum yield of 0.76.

4-Hydroxyoctanoic Acid Lactone.—*n*-Octyl nitrite (5.0 g.) was photolyzed in benzene (Φ = 0.25). The reaction mixture was concentrated to an oil and then heated in a closed vessel at 75° for 48 hours. The resulting mixture was dissolved in 250 ml. of acetone and oxidized at −10° by the addition over a 2-hour period of 20 ml. (0.15 equivalent) of CrO_3–H_2SO_4 reagent. After the inorganic salts were filtered off, the solvent was removed by flash evaporation and replaced by methylene chloride. The acidic components were separated by aqueous potassium carbonate extraction and isolated by appropriate manipulations. The acid fraction (3.24 g.) was reduced with 2.3 g. of sodium borohydride in 130 ml. of tetrahydrofuran. The usual work-up[16] yielded 0.93 g. (20.3% from the *n*-octyl nitrite) of a neutral fraction, n^{20}D 1.4439. The infrared spectrum of this compound was identical with that of the known 4-hydroxyoctanoic acid lactone.[16]

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(28) D. A. MacFayden, *J. Biol. Chem.*, **158**, 107 (1945).

(29) C. A. Streuli, *Anal. Chem.*, **31**, 1652 (1959).

(30) P. Kabasakalian, E. R. Townley and M. D. Yudis, *Anal. Chem.*, **31**, 375 (1959).

(31) G. S. Forbes and W. G. Leighton, *J. Am. Chem. Soc.*, **52**, 3139 (1930).

[Contribution from the Chemical Research and Development Division, Schering Corporation, Bloomfield, N. J.]

Photolysis of Nitrite Esters in Solution. II. Photochemistry of Aromatic Alkyl Nitrites

By Peter Kabasakalian, Edward R. Townley and Milton D. Yudis

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Photolysis of aromatic alkyl nitrites indicated that nitroso dimer formation *via* the Barton reaction only occurred when the alkyl chain contained four or more carbon atoms. It always involved the carbon atom in the alkyl chain which permitted the formation of a six-membered ring intermediate without regard for the ease of hydrogen abstraction. The formation of nitroso dimer during the photolysis of 2-phenyl-1-ethyl nitrite was not found to be an exception to the six-membered ring intermediate requirement of the Barton reaction (*alkoxy radical rearrangement mechanism*) since the nitroso dimer was formed by another mechanism, *i.e.*, *alkoxy radical decomposition*.

Introduction

In a previous publication[1] the photochemistry of *n*-octyl nitrite in heptane has been described. The principal product, 4-nitroso-1-octanol dimer, required the formation of a six-membered ring intermediate. To determine whether the formation of a six-membered ring intermediate was a necessary prerequisite for the Barton reaction[2] a series of

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(1) P. Kabasakalian and E. R. Townley, *J. Am. Chem. Soc.*, **84**, 2711 (1962).

(2) D. H. R. Barton, J. M. Beaton, L. E. Geller and M. M. Pechet, *ibid.*, **82**, 2640 (1960).

aromatic alkyl nitrites, whose alkyl chain varied from one to five carbon atoms, was studied photochemically.

Results

The study of the effect of solvents on the photolysis of 3-phenyl-1-propyl nitrite using a mercury arc light source with a filter which limited the radiation to wave lengths greater than 300 $m\mu$ indicated this order for increasing solvent products: benzene, Freon #113, acetonitrile, toluene and heptane.

The yields of nitroso dimers (as indicated by their molar absorptivity values at 294 $m\mu$) resulting from the photolysis of aromatic alkyl nitrites in benzene are shown in Table I.

Table II lists the 2-phenyl-1-ethyl nitrite photolysis product composition.

The unexpected dimeric ω-nitrosotoluene obtained from the photolysis of 2-phenyl-1-ethyl nitrite was characterized by conversion to ω-oximinotoluene.

Photolysis of 4-phenyl-1-butyl and 5-phenyl-1-pentyl nitrites afforded 4-nitroso-4-phenyl-1-butanol and 4-nitroso-5-phenyl-1-pentanol dimers, respectively. These were characterized by converting them[1] to the known 3-benzoylpropionic[3] and 5-phenyllevulinic[4] acids. In the latter case, ultraviolet spectrophotometry on the oxime intermediate failed to detect the presence of any 5-oximino-5-phenyl-1-butanol.

TABLE I

AROMATIC NITRITE PHOTOLYSIS NITROSO DIMER YIELD

Starting nitrite	Product[a] ϵ (294 $m\mu$)
1-Phenylmethyl	0
2-Phenyl-1-ethyl	4100
3-Phenyl-1-propyl	0
4-Phenyl-1-butyl	3500
5-Phenyl-1-pentyl	3500
(2-Methylphenyl)-methyl	1000

[a] For 100% yield $\epsilon \sim 9500$.

TABLE II

2-PHENYL-1-ETHYL NITRITE PHOTOLYSIS PRODUCT COMPOSITION (Photolysis run in benzene at 18°)

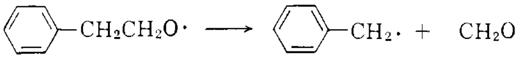
Product	Found, %
ω-Nitrosotoluene dimer	43
Methanal	29
2-Phenyl-1-ethanol	14
2-Phenyl-1-ethanal	14
ω-Oximinotoluene	0

Discussion

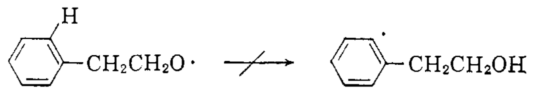
In the preceding paper[1] it was shown that the method of choosing the best solvent for nitroso dimer production *via* the Barton reaction[2] using the molar absorptivity of the strong ultraviolet absorption band near 294 $m\mu$ of the photolyzed solution[5] failed because of the formation of nitroso dimer products from the solvent. In the present paper the choice of the best solvent for the Barton reaction has been made by photolyzing an organic nitrite ester, 3-phenyl-1-propyl nitrite, which was not expected to yield nitroso dimer products by either the alkoxy radical decomposition[1] or the alkoxy radical rearrangement mechanism[1] using the best solvents previously indicated.[1] Benzene was found to be the best solvent using the criterion of minimum production of solvent nitroso dimer products. It was henceforth used as the solvent of choice in all the photolysis studies.

The photolysis of 1-phenylmethyl and 3-phenyl-1-propyl nitrites in benzene did not yield any nitroso dimer. This was expected since the alkyl chain did not contain the minimum number of four carbon atoms required to undergo the Barton reaction (nitroso dimer formation by the alkoxy radical rearrangement mechanism). However, 2-phenyl-1-ethyl nitrite gave an unexpected high yield (43%) of ω-nitrosotoluene dimer.

The phenylethoxy radical formed during the photolysis undergoes radical decomposition to form the relatively stable benzyl radical and methanal (reaction 1). The benzyl radical subsequently couples with nitric oxide yielding monomeric ω-nitrosotoluene which readily dimerizes. This is the first reported case of nitroso dimer formation during the photolysis of a primary nitrite in solution *via* the alkoxy radical decomposition mechanism. It is not apparent why the yield of ω-nitrosotoluene dimer and methanal was not identical.


(1)

No evidence was found for the Barton reaction involving hydrogen abstraction on the *2*-position of the phenyl ring (reaction 2). However, (2-methylphenyl)-methyl nitrite gave an appreciable yield (Table I) of nitroso dimer *via* the radical rearrangement reaction 3.


(2)


(3)

The other products, 2-phenyl-1-ethanol (14%) and 2-phenyl-1-ethanal (14%), obtained from the photolysis of 2-phenyl-1-ethyl nitrite (Table II) were formed by disproportionation.

4-Phenyl-1-butyl and 5-phenyl-1-pentyl nitrites gave nitroso dimers *via* the Barton reaction. The products were 4-nitroso-4-phenyl-1-butanol and 4-nitroso-5-phenyl-1-pentanol dimers, respectively. The formation of these nitroso dimers occurred by the pathway previously reported.[1] The lack of formation of any methanal in these reactions provided further evidence for the fact that simple primary alkoxy radicals do not undergo the radical decomposition reaction in solution to any appreciable extent at room temperature.

An opportunity for the formation of a five- and a seven-membered ring intermediate existed during the photolysis of 3-phenyl-1-propyl and 5-phenyl-1-

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[3] G. Komppa and W. Rohrmann, *Ann.*, **509**, 259 (1934).

[4] K. Russwurm and J. Schulz, *ibid.*, **308**, 175 (1899).

[5] B. G. Gowenlock and W. Luttke, *Quart. Revs.*, **12**, 321 (1958).

pentyl nitrites, respectively. However, no nitroso dimers were formed involving any but a six-membered ring intermediate in the Barton reaction, in spite of the ease with which the secondary hydrogen atoms involved could be abstracted as a result of their activation by the phenyl group.

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Experimental

Material.—The phenylalkyl nitrites were prepared according to the general method of Hunter and Marriott[6] from authentic starting alcohols and were vacuum distilled before use. Each of the distilled oils, although not characterized by elementary analysis, was identified as being a nitrite ester as shown by the strong doublet at about 6.0 and 6.25 μ in the infrared spectrum and by the highly specific envelope of low intensity bands from 310 to 385 mμ in the ultraviolet spectrum. When examined as thick films lack of absorption in the 2.8 to 3.0 μ region demonstrated the absence of alcoholic impurities. Vapor-phase chromatographic analysis indicated the presence of less than 0.5% impurity. A glass bead column containing 0.5% Carbowax 400 was used in the Perkin-Elmer model 154C vapor fractometer. The nitrite esters were injected at 50 to 60° and the temperature raised at the rate of 5°/min.

The benzene was dried by refluxing over anhydrous magnesium sulfate.

Apparatus, Photolysis Procedure and Analytical Methods.—The apparatus, photolysis procedure and analytical methods were described in Part I. The amount of ω-oximinotoluene was determined by titrating the ω-oximinotoluene as a weak acid according to the method of Bruss and Wyld.[7]

ω-Nitrosotoluene Dimer.—Photolysis of 4.30 g. of 2-phenyl-1-ethyl nitrite yielded 1.4 g. (40%) of crude ω-nitrosotoluene dimer, m.p. 110–115°, $\lambda_{\max}^{\mathrm{MeOH}}$ 292 mμ (ε 7,300). The analytical sample was recrystallized twice from isopropyl ether; m.p. 137–137.5° (reported[8] 127–128°); $\lambda_{\max}^{\mathrm{MeOH}}$ 291 mμ (ε 8,200), $\lambda_{\max}^{\mathrm{CHCl_3}}$ 295 mμ (ε 9,250) (reported[9] 296 mμ (ε 12,200)). The product exhibits infrared absorption (in Nujol) at 8.62 μ and 8.73 μ (nitroso dimer); no hydroxyl bands were evident.

Anal. Calcd. for $C_{14}H_{14}N_2O_2$: C, 69.50; H, 5.83; N, 11.54. Found: C, 69.34; H, 6.06; N, 11.62.

4-Nitroso-4-phenyl-1-butanol Dimer.—4-Phenyl-1-butyl nitrite (4.0 g.) was photolyzed. After the reaction mixture was concentrated to a dark viscous residue, formation of 4-nitroso-4-phenyl-1-butanol was demonstrated by ultraviolet spectral analysis, $\lambda_{\max}^{\mathrm{MeOH}}$ 294 mμ (ε 3500). Attempts to isolate the pure dimer resulted in isomerization to yield crude 4-oximino-4-phenyl-1-butanol. The photolysis product was characterized by conversion to 3-benzoylpropionic acid, m.p. 115–116.5°[3] (0.8 g., 20% yield from nitrite ester).

4-Nitroso-5-phenyl-1-pentanol Dimer.—5-Phenyl-1-pentyl nitrite (1.02 g.) was photolyzed. The reaction solution was concentrated to a dark viscous oil which became semi-solid on standing. Vigorous shaking with 75 ml. of a 2:1 mixture of benzene–ether precipitated solid material which after refrigerating overnight and filtering afforded 197 mg. (18%) of crude 4-nitroso-5-phenyl-1-pentanol dimer, m.p. 120–123°, $\lambda_{\max}^{\mathrm{MeOH}}$ 297 mμ (ε 6,500). The analytical sample was twice recrystallized from benzene–ether; m.p. 130–131°, $\lambda_{\max}^{\mathrm{MeOH}}$ 297 mμ (ε 7,000). The product exhibits infrared absorption (in Nujol) at 3.04, 3.13 (CO–H) and 8.54 μ (*trans*-nitroso dimer).

Anal. Calcd. for $C_{22}H_{30}N_2O_4$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.64; H, 8.10; N, 7.35.

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(6) L. Hunter and J. A. Marriott, *J. Chem. Soc.*, 285 (1936).

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[CONTRIBUTION FROM THE CHEMICAL RESEARCH AND DEVELOPMENT DIVISION, SCHERING CORPORATION, BLOOMFIELD, N. J.]

Photolysis of Nitrite Esters in Solution. III. Photochemistry of Primary, Secondary and Tertiary Alkyl Nitrites

BY PETER KABASAKALIAN, EDWARD R. TOWNLEY AND MILTON D. YUDIS

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Complete photolysis of primary, secondary and tertiary alkyl nitrites in benzene indicated that a minimum chain length of five carbon atoms attached to the nitrite grouping is required for appreciable yields of secondary nitroso dimers *via* the Barton reaction. In the case of primary and secondary nitrites, a chain length of four carbon atoms attached to the nitrite grouping gave drastically reduced yields of primary nitroso dimer *via* the Barton reaction. Nitroso dimers also were formed *via* the alkoxy radical decomposition mechanism in the case of certain secondary and tertiary alkyl nitrites.

Introduction

Recently the Barton reaction[1] affording hydroxy nitroso dimers was studied using simple primary nitrites, *n*-octyl nitrite,[2] and aromatic alkyl nitrites.[3]

In the present paper, an attempt has been made to relate the general applicability of the Barton reaction to simple flexible primary, secondary and tertiary alkyl nitrite molecules.

Results

The yields of nitroso dimers (as indicated by their molar absorptivity values at 294 mμ) obtained from the photolysis of alkyl nitrites in benzene are listed in Table I.

The photolysis product compositions (% of theory) found for primary and secondary nitrites are shown in Table II while those for tertiary nitrites are shown in Table III. Where there was more than one nitroso dimer product, the Barton reaction product (hydroxy nitroso dimer) was calculated by obtaining the difference between the total nitroso dimers and the simple nitroso dimers from the cleavage reactions.

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(1) D. H. R. Barton, J. M. Beaton, L. E. Geller and M. M. Pechet, *J. Am. Chem. Soc.*, **82**, 2640 (1960).

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(3) P. Kabasakalian, E. R. Townley and M. D. Yudis, *ibid.*, **84**, 2716 (1962), part II.