must be considered, and they are indicated in Fig. 2C. Direction 3 is at the backside of the S–S bond, the bond which is cleaved, and is therefore the 3-atoms-in-a-line, "Walden inversion" direction. Direction 1 is down on one lobe of the lone-pair p-orbital, 4 is up toward its other lobe, 2 is backside to the C–S bond. Models show that the hindrance to attack increases in the order: direction $2 < 3 \sim 4 < 1$. Direction 2, the least hindered one, may be as little hindered as is attack on the S–S bond. However, attack from this direction gives a product, M—SR, with a 180° MSR angle, and this angle is actually 105°. Since sulfur has d-orbitals available for bonding, compromise directions are possible. The best direction for attack on the sulfur atom may be midway between 2 and 3; *i.e.*, from a direction that bisects the R–S–S valence angle. The optimum directions for attack are, therefore, the compromise direction 2a, and on the midpoint of the S–S bond. Both would be expected to show much less response to backside hindrance than the SN2 direction.

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

Photolysis of Nitrite Esters in Solution. I. Photochemistry of *n*-Octyl Nitrite

BY PETER KABASAKALIAN AND EDWARD R. TOWNLEY

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Complete photolysis of *n*-octyl nitrite in heptane has been found to give a 30% yield of 4-nitroso-1-octanol dimer, 2% yield of *γ*-nitrosoheptane dimer and 13% yield of *γ*-nitrosoheptane·4-nitroso-1-octanol dimer. The effects of photolysis solvent and temperature, concentration of *n*-octyl nitrite and oxygen upon the total yield of nitroso dimers have been studied. In the presence of oxygen, a 50% yield of *n*-octyl nitrate has been obtained.

Introduction

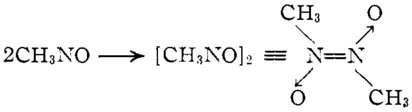
In the past, the photolysis studies of alkyl nitrites have been restricted to the obtaining of *qualitative* data on the *vapor* phase photolysis of alkyl nitrites. *t*-Butyl nitrite vapor photolysis was studied extensively by Thompson and Dainton,[1] Coe and Doumani,[2] Tarte,[3] and Gowenlock and Trotman.[4,5]

The principal product of the vapor phase photolysis of *t*-butyl nitrite is the *trans* isomer of the dimer of nitrosomethane. The formation of this product has been explained by reactions 1–4, which involve nitroso dimer formation by an *alkoxy radical decomposition mechanism* (reaction 2).

$$(CH_3)_3CONO + h\nu \longrightarrow (CH_3)_3CO\cdot + NO \quad (1)$$

$$(CH_3)_3CO\cdot \longrightarrow (CH_3)_2CO + CH_3\cdot \quad (2)$$

$$CH_3\cdot + NO \longrightarrow CH_3NO \quad (3)$$



(4)

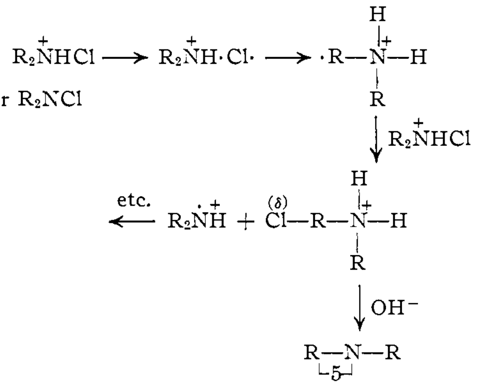
The only other tertiary nitrite studied has been *t*-amyl nitrite.[3,5] Tarte[3] has shown that ultraviolet radiation of wave lengths shorter than 330 mμ is required for the production of nitroso products.

Primary and secondary nitrites having straight chain lengths of up to five carbon atoms have also been photolyzed in the vapor phase,[5] but product analyses have been limited to the verification of the presence of the nitroso dimer moiety by ultraviolet spectrophotometry.

Although Gray and Williams[6] in their review article calculated $\Delta H = -8.5$ kcal. mole^{-1} for the internal hydrogen abstraction reaction 5 expected for long chain derivatives, rearrangements of this

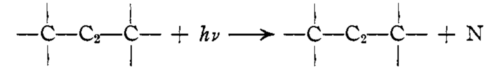
$$RCH_2(CH_2)_nCH_2O\cdot \longrightarrow R\dot{C}H(CH_2)_nCH_2OH \quad (5)$$

type have not been in fact demonstrated.[6] However, the isoelectric analog of alkoxyl radicals, $R_1R_2N\cdot$, undergoes internal hydrogen abstraction in the Hofmann-Loffler–Freytag reaction studied by Wawzonek[7] and Corey.[8]



(6)

Recently Barton,[9] *et al.*, have reported the formation of a hydroxy nitroso dimer as a direct result of the photolysis of the nitrite of 6β-hydroxycholestanyl acetate in benzene *solution* using filtered ultraviolet radiation (λ > 330 mμ) which did not work for Tarte.[3] The production of the nitroso dimer can be explained by reactions 7–10,



$$-\overset{H}{\underset{|}{\overset{|}{C}}}-C_2-\overset{ONO}{\underset{|}{\overset{|}{C}}}- + h\nu \longrightarrow -\overset{H}{\underset{|}{\overset{|}{C}}}-C_2-\overset{O\cdot}{\underset{|}{\overset{|}{C}}}- + NO \quad (7)$$

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[1] H. W. Thompson and F. S. Dainton, *Trans. Faraday Soc.*, **33**, 1546 (1937).

[2] C. S. Coe and T. F. Doumani, *J. Am. Chem. Soc.*, **70**, 1516 (1948).

[3] P. Tarte, *Bull. Soc. Roy. Sci. Liege*, **22**, 226 (1953).

[4] B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 4190 (1955).

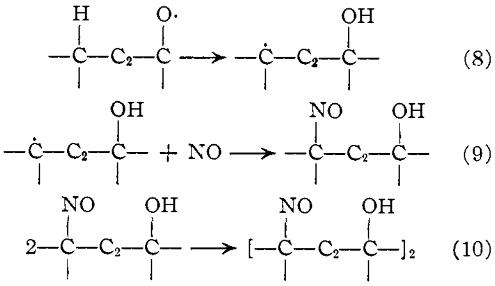
[5] B. G. Gowenlock and J. Trotman, *ibid.*, 1670 (1956).

[6] P. Gray and A. Williams, *Chem. Revs.*, **59**, 239 (1959).

[7] S. Wawzonek and T. P. Culbertson, *J. Am. Chem. Soc.*, **81**, 3367 (1959).

[8] E. J. Corey and W. R. Hertler, *ibid.*, **82**, 1657 (1960).

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



$$-\overset{H}{C}-C_2-\overset{O\cdot}{C}- \longrightarrow -\dot{C}-C_2-\overset{OH}{C}- \quad (8)$$

$$-\dot{C}-C_2-\overset{OH}{C}- + NO \longrightarrow -\overset{NO}{C}-C_2-\overset{OH}{C}- \quad (9)$$

$$2-\overset{NO}{C}-C_2-\overset{OH}{C}- \longrightarrow [-\overset{NO}{C}-C_2-\overset{OH}{C}-]_2 \quad (10)$$

which represent the formation of a nitroso dimer by an *alkoxy radical rearrangement mechanism* (reaction 8).

In spite of the easy preparation of alkyl nitrites from alcohols and the availability of suitable radiation sources (black light), the investigation of the photolysis of alkyl nitrites has not attracted the interest it deserves. This is due undoubtedly to the assumption that the photochemical behavior of alkyl nitrites is similar to their thermal behavior in as much as the initial thermal reaction 11 is identical with the initial photochemical reaction 1.

$$RCH_2ONO \xrightarrow[\Delta]{} RCH_2O\cdot + NO \qquad (11)$$

The thermal decomposition of alkyl nitrites usually yields predominantly the synthetically uninteresting alcohol and carbonyl analogs. The use of nitrites as radical sources has been little investigated since it presumably suffers from the difficulty that the nitric oxide produced is generally an efficient radical trap.

Because of its potentially important contribution to free radical chemistry in solution and to organic syntheses, we have undertaken the study of the *liquid* phase photolysis of organic nitrite esters to determine (1) the structural factors involved in the production of nitroso compounds by both the *alkoxy radical decomposition mechanism* and the *alkoxy radical rearrangement mechanism* (the Barton reaction) and (2) the behavior of alkoxy radicals in *solution*.

As a representative initial study, we wish to describe here the photochemistry of the primary alkyl nitrite, *n*-octyl nitrite. The effects of nitrite concentration, photolysis solvent and temperature and presence of oxygen on the yield of nitroso dimer are reported as well as the quantitative description of the nature of the products under optimum conditions for nitroso dimer formation.

Results

Because of the photochemical[10] and thermal[11-13] stability of simple nitroso dimers and in particular the nitroso dimer formed in the photolysis of *n*-octyl nitrite, the study of the effects of photolysis solvent and temperature, nitrite concentration and oxygen on the yield of nitroso dimer was reduced to a simple comparison of the molar absorptivity of the strong ultraviolet absorption band at 294 mμ of the photolyzed solutions.[14]

TABLE I
EFFECT OF SOLVENT ON PHOTOCHEMICAL YIELD OF NITROSO DIMER[a]

	Product[b]		By-product[c]
Solvent	ϵ (294 mμ)	$E^{1\%}_{1\,\text{cm.}}$ (294 mμ)	$E^{1\%}_{1\,\text{cm.}}$ (225 mμ)
Heptane	4270	134	6
Benzene	4300	135	30
Acetonitrile	4300	135	48 (225 mμ)
Freon #113	4000	126	49 (225 mμ)
Acetone	3400	107	59 (225 mμ)
Toluene	3120	98	63 (245 mμ)
Chlorobenzene	3030	95	55
Acetic acid	2360	74	51 (220 mμ)
Ethyl acetate	2070	65	63 (225 mμ)
Methanol	1910	60	115 (230 mμ)
Methylene chloride	1880	59	53
1,2-Dichloroethane	1850	58	53
Carbon tetrachloride	930	29	51
Dioxane	320	10	109 (220 mμ)
Dimethylformamide	0	0	79
Chloroform	0	0	59
Pyridine	0	0	71

[a] Photolysis run at 18°. [b] Product $E^{1\%}_{1\,\text{cm.}}$(294 mμ) = 300 for 100% yield. [c] $E^{1\%}_{1\,\text{cm.}}$ values without wave lengths assigned do not have a maximum.

The best yields of nitroso dimer were obtained in solvents (Table I) having poor radical chain transfer characteristics. Solvents which gave poorer yields of nitroso dimers, gave increasingly better yields of by-products which had ultraviolet absorption bands in the 220–230 mμ region. Since evidence was obtained that the same by-product was not formed in all cases, none was fully characterized. From Table I, heptane appears to be the best solvent for nitroso dimer formation if one uses minimum production of the 220–230 mμ ultraviolet absorbing by-products as an additional criterion.

The effect of temperature on the photolysis reaction was studied in heptane. The yield of nitroso dimers was reduced drastically at −55° (ϵ 250) while at 60° (ϵ 4,500) it was only slightly better than at room temperature (ϵ 4,300). Photolysis in toluene gave similar results.

The yield of nitroso dimer formed in the photolysis reaction at room temperature in heptane was found to be independent of the concentration of *n*-octyl nitrite in the range measured (0.008 to 0.32 mole/liter).

The presence of oxygen during the photolysis changed the major product to *n*-octyl nitrate. No nitroso dimers were formed. Because studies on the octyl nitrate indicated that it too was photochemically and thermally stable during the photolysis runs, the study of the effects of photolysis solvent and temperature and the effect of nitrite concentration was reduced to a simple comparison of the molar absorptivity of the strong infrared absorption band of the nitrate moiety[15] at 6.1 μ.

The yield of *n*-octyl nitrate was found to be dependent on the photolysis solvent and tempera-

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(10) H. Metzer and E. Muller, *Chem. Ber.*, **90**, 1185 (1957).

(11) L. G. Donaruma, *J. Org. Chem.*, **23**, 1338 (1950).

(12) J. Schwartz, *J. Am. Chem. Soc.*, **79**, 4353 (1957).

(13) L. Batt and B. G. Gowenlock, *Trans. Faraday Soc.*, **56**, 1022 (1960).

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

(15) J. F. Brown, *J. Am. Chem. Soc.*, **77**, 6341 (1955). Although *ca.* 600–650 for the 6.1 μ band were reported in this reference, much higher molar absorptivities were obtained in the present study. Using carbon tetrachloride as a solvent, the following results were obtained: ethyl nitrate (ϵ 914), butyl nitrate (ϵ 852), isoamyl nitrate (ϵ 870), octyl nitrate (ϵ 1090) and cholesteryl nitrate (ϵ 1130).

TABLE II

EFFECT OF CONCENTRATION,[a] SOLVENT AND TEMPERATURE[a] ON THE PHOTOCHEMICAL YIELD OF OCTYL NITRATE

Concn. mole/liter	Product ε (6.1μ)[b]	Solvent	Product ε (6.1μ)
0.318	548	Heptane	562
.159	562	Freon 113	506
.0795	585	Acetonitrile	433
.0318	565	Toluene	407
.0159	579	Benzene	386
.00795	454	Acetone	120
		Methanol	43

Temp.°	Product ε (6.1μ)
−55	252
18	562
60	450

[a] Photolysis run in heptane. [b] ε (6.1μ) = 1090 for 100% yield.

ture and independent of the nitrite concentration (Table II) in the range studied. The best results were obtained in heptane at room temperature.

The principal product obtained from the photolysis of *n*-octyl nitrite (in the absence of oxygen) in heptane solution was 4-nitroso-1-octanol dimer. Analysis of the photolysis solution by means of quantitative paper chromatography showed that it was formed in 30% yield in addition to lesser quantities of *y*-nitrosoheptane dimer, 2%, and of the mixed *y*-nitrosoheptane · 4-nitroso-1-octanol dimer, 13% (Table III). These results are in good agreement with the total yield of the three nitroso dimers as determined by ultraviolet spectral analysis.

TABLE III

NITROSO DIMERS FROM OCTYL NITRITE PHOTOLYSIS IN HEPTANE

Dimer	Found,[a] %
y-Nitrosoheptane	2.1
y-Nitrosoheptane·4-nitroso-1-octanol	12.7
4-Nitroso-1-octanol	29.8
Total	44.6

	Nitroso dimer equilibrium constant[b]	
Equil. constant	Photolysis mixt.	Equilibrated mixt.
K	2.5	3.0

[a] Analysis by quantitative paper chromatography. [b] Equilibrium constant as defined by eq. 25.

The crude 4-nitroso-1-octanol dimer crystallized directly out of the heptane photolysis solution and was isolated in 26% yield. The nitroso heptane and the mixed nitrosoheptane · 4-nitroso-1-octanol dimers were very much more soluble in heptane and were isolated only after concentrating and chromatographing the residue after removal of the nitroso octyl dimer.

Although the photolysis of *n*-octyl nitrite in benzene solution afforded a good yield of nitroso dimer as determined by ultraviolet spectral analysis (Table IV), repeated attempts to isolate crystalline 4-nitroso-1-octanol dimer, as was obtained from heptane, resulted in the isolation of oily residues that could not be crystallized.

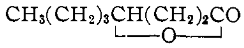
The 4-nitroso-1-octanol dimer was characterized by reactions 12 through 15.

$$[CH_3(CH_2)_3CHNO(CH_2)_2CH_2OH]_2 \xrightarrow[\Delta]{} 2CH_3(CH_2)_3CNOH(CH_2)_2CH_2OH \quad (12)$$

$$CH_3(CH_2)_3CNOH(CH_2)_2CH_2OH \xrightarrow[H_2SO_4]{CrO_3} CH_3(CH_2)_3CO(CH_2)_2COOH \quad (13)$$

$$CH_3(CH_2)_3CO(CH_2)_2COOH \xrightarrow{NaBH_4} CH_3(CH_2)_3CHOH(CH_2)_2COONa \quad (14)$$

$$CH_3(CH_2)_3CHOH(CH_2)_2COONa \xrightarrow{H^+}$$



$$CH_3(CH_2)_3\underbrace{CH(CH_2)_2CO}_{O} \quad (15)$$

The nitroso dimer was thermally isomerized to 4-oximino-1-octanol which in turn was oxidized and concomitantly hydrolyzed to form 4-ketoöctanoic acid. Reduction with sodium borohydride gave the 4-hydroxyoctanoic acid salt which on acidification lactonized to give the lactone of 4-hydroxyoctanoic acid. All the products of reactions 13, 14 and 15 are known compounds.[16]

No evidence for substitution on the 2- and 3-positions of the products was obtained using polarographic[17] (α-keto-acids) and ultraviolet absorption spectroscopy (β-ketoacids) detection methods. No evidence for substitution on the 5-, 6-, 7- and 8-position of the products was obtained by infrared absorption spectroscopy which showed that only a five-membered lactone ring was obtained in reaction 15. Thus, all the evidence eliminated the possibility of a probability distribution of substitution around the favored 4-position.

Two more nitroso dimers were isolated in appreciable amounts (Table III) from the photolysis of *n*-octyl nitrite in heptane. These were the dimers of *y*-nitrosoheptane[18] and *y*-nitrosoheptane·4-nitroso-1-octanol mixed dimer. *y*-Nitrosoheptane dimer was found to be a mixture of 48%, 39% and 12%, respectively, of the 2-, 3- and 4-isomers. Muller and Metzer[19] have reported the formation of dimeric *x*-nitrosoheptane during the photolysis in the liquid phase of heptane, nitric oxide and chlorine. The result of equilibrating a mixture of *y*-nitrosoheptane and 4-nitroso-1-octanol dimers also is shown in Table III.

Table IV lists the amount of the products formed in the photolysis of *n*-octyl nitrite in benzene.

TABLE IV

OCTYL NITRITE PHOTOLYSIS[a] PRODUCT COMPOSITIONS[b]

Product	Found (% of theory)	Product	Found (% of theory)
4-Nitroso-1-octanol		Acidic	<1
dimer	45	Basic	<1
1-Octanol	25	Formaldehyde	<1
1-Octanal	15	Heptane	<1
1-Octyl nitrate	<1	1-Heptene	<1
1-Octyl nitrite	<1	Tetradecane	<1
4-Oximino-1-octanol	<1		

[a] Photolysis run in benzene at 18° for 2 hours. [b] Product analysis as determined by instrumental methods.

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(16) D. Papa, E. Schwenk and H. F. Ginsberg, *J. Org. Chem.*, **14**, 726 (1949).

(17) O. H. Muller and J. P. Baumberger, *J. Am. Chem. Soc.*, **61**, 590 (1939).

(18) This was characterized by converting it to the *y*-oximinoheptane and comparing it with the known 1-, 2-, 3- and 4-oximinoheptanes.

(19) E. Muller and H. Metzer, *Chem. Ber.*, **88**, 165 (1955).

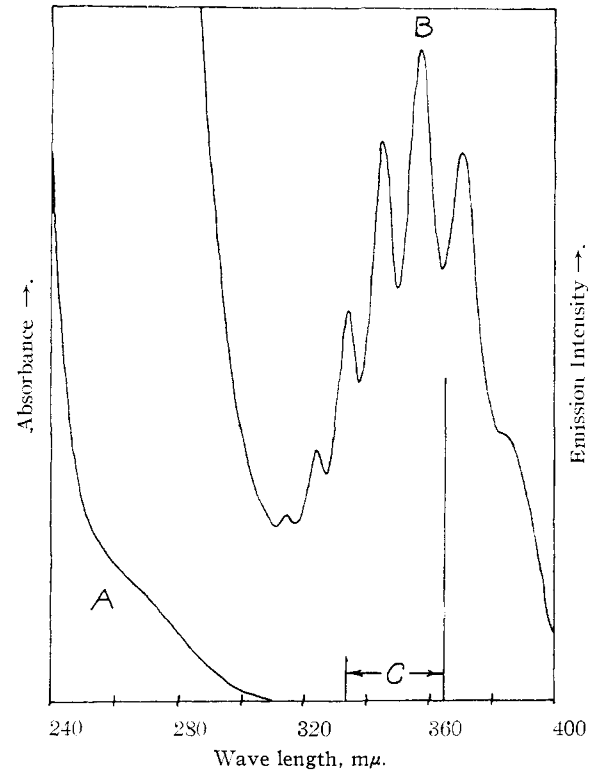


Fig. 1.—A, absorption spectrum of octyl nitrate in methanol; B, absorption spectrum of octyl nitrite in methanol; C, emission spectrum of mercury arc lamp.

Discussion

Photolysis of *n*-octyl nitrite in solution using a high pressure mercury arc lamp with a Pyrex filter (the use of a quartz filter did not significantly change the rate of photolyses) which limited the radiation to wave lengths greater than 300 mμ was possible because of the multiplicity of weak absorption bands ($\epsilon \sim 80$) of organic nitrite esters[20] in the 320–380 mμ region (Fig. 1).

In order to determine whether the products obtained during the photolysis reactions could be attributed solely to the photolytic initiation reaction, *n*-octyl nitrite was subjected to thermal stability studies and was found to be thermally stable under the photolytic conditions.

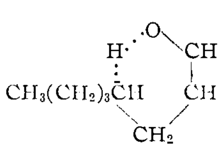
Quantum yield studies ($\Phi = 0.76$) and the lack of a nitrite concentration effect indicate that the free radical reactions probably are not of a chain nature. The initial photolytic reaction is given by reaction 16.

$$CH_3(CH_2)_6CH_2ONO + h\nu \longrightarrow CH_3(CH_2)_6CH_2O\cdot + NO \quad (16)$$

Reaction 17 accounts for the fact that the quantum yield is less than unity.[21]

$$CH_3(CH_2)_6CH_2O\cdot + NO \longrightarrow CH_3(CH_2)_6CH_2ONO \quad (17)$$

Reactions 8, 9 and 10 denote the pathway to the nitroso dimer product. The initial reaction is an intramolecular hydrogen abstraction by the primary octoxy radical which requires the formation of a six-membered ring intermediate (A).


A

The rearranged alkoxy radical adds nitric oxide to give the monomeric 4-nitroso-1-octanol which readily dimerizes to yield the major product of the photochemical reaction. The formation of the nitroso dimer is in sharp contrast to the oxime obtained in the steroid series by Barton and Beaton.[22] Evidently, the nitroso dimer in the steroid series is rather unstable as contrasted to the present case. Studies on the 4-oximino-1-octanol prepared from the dimer of 4-nitroso-1-octanol indicated that the oxime was thermally and photochemically stable under the photolysis conditions. Therefore the almost complete absence of oxime in the photolysis product (Table IV) indicated that the oxime is not formed directly during the photolysis, but when it is produced it must be formed indirectly through the nitroso monomer. The nitroso dimer does convert to the oxime upon standing at room temperature (k_1(benzene) = 0.016/day and k_1(methanol) = 0.014/day).

The vanishing yield of nitroso dimer at the low temperature indicates that other unknown reactions successfully compete with the Barton reaction.

The minor products, 1-octanol and 1-octanal, are probably formed by reactions 18 and 19, a hydrogen abstraction[6] and a disproportionation reaction[6,21,23] respectively.

$$CH_3(CH_2)_6CH_2O\cdot + RH \longrightarrow CH_3(CH_2)_6CH_2OH + R\cdot \quad (18)$$

$$2CH_3(CH_2)_6CH_2O\cdot \longrightarrow CH_3(CH_2)_6CH_2OH + CH_3(CH_2)_6CHO \quad (19)$$

These reactions do not involve the efficient radical trap, nitric oxide. The dependence of the yield of nitroso dimer on the photolysis solvent probably is due to reaction 18 which is predicated on the ease with which the solvent, RH, loses a hydrogen atom in a radical reaction.

When RH was heptane, the solvent products, *y*-nitroso-heptane dimer and *y*-nitrosoheptane·4-nitroso-1-octanol mixed dimer, were isolated. These were formed by reactions 20, 21, 22, and 23. The reactions shown illustrate the reactions of 2-nitrosoheptane, the major component of *y*-nitrosoheptane.

$$CH_3(CH_2)_6CH_2O\cdot + CH_3(CH_2)_4CH_2CH_3 \longrightarrow CH_3(CH_2)_6CH_2OH + CH_3(CH_2)_4\dot{C}HCH_3 \quad (20)$$

$$CH_3(CH_2)_4\dot{C}HCH_3 + NO \longrightarrow CH_3(CH_2)_4CHNOCH_3 \quad (21)$$

$$2CH_3(CH_2)_4CHNOCH_3 \longrightarrow [CH_3(CH_2)_4CHNOCH_3]_2 \quad (22)$$

$$CH_3(CH_2)_4CHNOCH_3 + CH_3(CH_2)_3CHNO(CH_2)_2CH_2OH \longrightarrow [CH_3(CH_2)_4CHNOCH_3]\cdot[CH_3(CH_2)_3CHNO(CH_2)_2CH_2OH] \quad (23)$$

Hydrogen abstraction on the heptane solvent produced the *y*-heptyl radical which coupled with

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[20] H. E. Ungnade and R. A. Smiley, *J. Org. Chem.*, **21**, 993 (1956).

[21] J. B. Levy, *J. Am. Chem. Soc.*, **75**, 1801 (1953).

[22] D. H. R. Barton and J. M. Beaton, *ibid.*, **82**, 2641 (1960).

[23] H. E. De La Mare and W. E. Vaughan, *J. Chem. Ed.*, **34**, 10 (1957).

nitric oxide to give monomeric *y*-nitrosoheptane. Since monomeric 4-nitroso-1-octanol also was being formed continually during the photolysis, the *y*-nitroso-heptane had an opportunity to combine with it to form the *y*-nitrosoheptane·4-nitroso-1-octanol mixed dimer. The mixed nitroso dimer was not fully characterized since it continued to dissociate into the *y*-nitrosoheptane and 4-nitroso-1-octanol dimers *via* reaction 24. An equilibrium constant, *K*, calculated from the amounts of nitroso dimers found (employing quantitative paper chromatography) using eq. 25, was found to be 2.5 which approximates the value (3.0) determined by equilibrating an equimolar mixture of the *y*-nitrosoheptane and 4-nitroso-1-octanol dimers (Table III).

$$[CH_3(CH_2)_4CHNOCH_3]_2 + [CH_3(CH_2)_3CHNO(CH_2)_2CH_2OH]_2 \rightleftarrows 2[CH_3(CH_2)_4CHNOCH_3]\cdot[CH_3(CH_2)_3CHNO(CH_2)_2CH_2OH] \quad (24)$$

$$K = \frac{([CH_3(CH_2)_4CHNOCH_3]\cdot[CH_3(CH_2)_3CHNO(CH_2)_2CH_2OH])^2}{([CH_3(CH_2)_4CHNOCH_3]_2)([CH_3\text{-}(CH_2)_3CHNO(CH_2)_2CH_2OH]_2)} \quad (25)$$

Hydrogen abstraction of the secondary hydrogen atoms of heptane statistically should have given 40, 40 and 20%, respectively, of the 2-, 3- and 4-nitroso isomers. Experimentally, 48, 39 and 12%, respectively, were found indicating the greater reactivity of the 2-position hydrogen atoms due to an additional factor, hyperconjugation. Fredericks and Tedder[24] have reported rather compelling evidence that radicals with the structure $CH_3\text{–}\dot{C}H\text{–}CH_2\text{–}$ are more stable than radicals with the structure $\text{–}CH_2\text{–}\dot{C}H\text{–}CH_2\text{–}$, presumably because of hyperconjugative stabilization. The decreased reactivity of the C_4-hydrogen atom may be due to steric factors. Chambers and Ubbelohde[25] have suggested that paraffins assume crumpled configurations in which some of the secondary C–H bonds may be protected by other parts of the molecule from radical attack.

When nitric oxide is not involved in the reactions, the secondary photolytic reactions of octyl nitrite should be identical with the known reactions which primary alkoxy radicals undergo. Reactions 18, 19 and 26, hydrogen abstraction, disproportionation and decomposition, respectively, are primary alkoxy radical reactions in the vapor phase reported by Vaughan, *et al.*[26] The *n*-heptyl radical formed in reaction 26 could then possibly undergo a hydrogen abstraction (27), disproportionation, (28) or a coupling reaction (29) to yield, heptane, heptene and tetradecane, respectively. None of these products, nor formaldehyde (or paraformaldehyde) was detected when the photolysis was carried out in benzene (Table IV). The possibility that the *n*-heptyl radical might have reacted with nitric oxide (30) was eliminated when adsorption chromatography could not detect either 1-nitrosoheptane dimer (31) or 1-nitrosoheptane·4-nitroso-1-octanol mixed dimer (32) in the octyl nitrite photolysis carried out in benzene. Evidently, simple primary alkoxy radicals do not undergo the radical decomposition reaction in the liquid phase to any appreciable extent at room temperature.

$$CH_3(CH_2)_5CH_2CH_2O\cdot \longrightarrow CH_3(CH_2)_5CH_2\cdot + CH_2O \quad (26)$$

$$CH_3(CH_2)_5CH_2\cdot + RH \longrightarrow CH_3(CH_2)_5CH_3 + R\cdot \quad (27)$$

$$2CH_3(CH_2)_5CH_2\cdot \longrightarrow CH_3(CH_2)_5CH_3 + CH_3(CH_2)_4CH{=}CH_2 \quad (28)$$

$$2CH_3(CH_2)_5CH_2\cdot \longrightarrow CH_3(CH_2)_{12}CH_3 \quad (29)$$

$$CH_3(CH_2)_5CH_2\cdot + NO \longrightarrow CH_3(CH_2)_5CH_2NO \quad (30)$$

$$2CH_3(CH_2)_5CH_2NO \longrightarrow [CH_3(CH_2)_5CH_2NO]_2 \quad (31)$$

$$CH_3(CH_2)_5CH_2NO + CH_3(CH_2)_3CHNO(CH_2)_2CH_2OH \longrightarrow [CH_3(CH_2)_5CH_2NO]\cdot[CH_3(CH_2)_3CHNO(CH_2)_2CH_2OH] \quad (32)$$

Since the solvent heptane yielded heptane nitroso dimers during the photolysis of *n*-octyl nitrite, the molar absorptivity of the photolyzed solutions listed in Table I is not a good indication of the yield of 4-nitroso-1-octanol dimer. Toluene solvent gave a 20% yield of ω-nitrosotoluene dimer. Benzene did not yield any other nitroso dimer as determined by adsorption chromatography; however, crystalline 4-nitroso-1-octanol dimer could not be isolated from this solvent.

Octyl nitrate was found to be the major product when oxygen was present during the photolysis. Reactions 33 and 34 proposed by Hanst and Calvert[27] may account for the formation of *n*-octyl nitrate.

$$2NO + O_2 \longrightarrow 2NO_2 \quad (33)$$

$$CH_3(CH_2)_6CH_2O\cdot + NO_2 \longrightarrow CH_3(CH_2)_6CH_2ONO_2 \quad (34)$$

The photochemical stability of octyl nitrate under the radiation conditions used in the octyl nitrite photolysis is due to the fact that the ultraviolet absorption band of the octyl nitrate is displaced to lower wave lengths (less than 300 mμ) in comparison to the octyl nitrite absorption bands (Fig. 1).

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Experimental

Materials.—*n*-Octyl nitrite obtained from Eastman Organic Chemical Department was distilled under vacuum before use. Its infrared spectrum was examined for identity; gas chromatographic analysis showed less than 0.5% impurities. The photolysis solvents were dried by refluxing over anhydrous magnesium sulfate.

Apparatus.—The 200-ml. capacity water-jacketed photolysis vessel contained a water-jacketed mercury arc lamp well and a nitrogen sparger. A 200 watt Hanovia 654A-36 ultraviolet lamp was utilized as the radiation source. The

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

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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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