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.

Acknowledgments.—The authors wish to acknowledge the technical assistance of members of this Laboratory and in particular Mr. R. Armswood. The authors are indebted to Prof. D. H. R. Barton and Dr. E. B. Hershberg for their helpful interest in this work.

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-oximino-

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

toluene 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°, λ_{max}^{MeOH} 292 mμ (ϵ 7,300). The analytical sample was recrystallized twice from isopropyl ether; m.p. 137–137.5° (reported[8] 127–128°); λ_{max}^{MeOH} 291 mμ (ϵ 8,200), $\lambda_{max}^{CHCl_3}$ 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, λ_{max}^{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°, λ_{max}^{MeOH} 297 mμ (ϵ 6,500). The analytical sample was twice recrystallized from benzene–ether; m.p. 130–131°, λ_{max}^{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.

(7) D. B. Bruss and G. E. A. Wyld, *Anal. Chem.*, **29**, 232 (1957).

(8) R. Behrend and E. Konig, *Ber.*, **23**, 1773 (1890).

(9) E. Muller and H. Metzger, *ibid.*, **88**, 165 (1955).

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

Received March 4, 1961

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.

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

(2) P. Kabasakalian and E. R. Townley, *ibid.*, **84**, 2711 (1962), part I.

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

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.

TABLE I
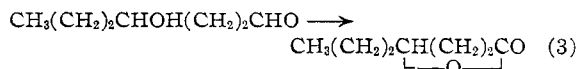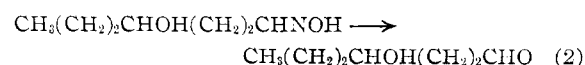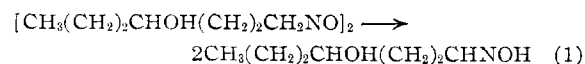### EFFECT OF CHAIN LENGTH ON YIELD OF NITROSO DIMER[a]

| Primary nitrites | | Secondary nitrites | | | | | | | | Tertiary nitrites | |
Starting material	Product ϵ	Starting material	Product ϵ	Starting material	Product ϵ	Starting material	Product ϵ	Starting material	Product ϵ	Starting material	Product ϵ
1-Octyl	4300	.....	..	.....	..	.....	..	.....	..	....	..
1-Heptyl	3400	2-Octyl	4400	.....	..	.....	..	.....	..	....	..
1-Hexyl	3400	2-Heptyl	4300	3-Octyl	3100	.....	..	.....	..	....	..
1-Pentyl	3000	2-Hexyl	3000	3-Heptyl	3000	4-Octyl	4000	5-Nonyl	3700	2-Methyl-2-hexyl	4600
1-Butyl	400	2-Pentyl	1300	3-Hexyl	1800	4-Heptyl	2700	.....	..	2-Methyl-2-pentyl	3700
1-Propyl	0	2-Butyl	700	3-Pentyl	500	.....	..	.....	..	2-Methyl-2-butyl	3600
1-Ethyl	0	2-Propyl	0	.....	..	.....	..	.....	..	2-Methyl-2-propyl	0

[a] For 100% yield of nitroso dimer ϵ ~9500, wave length maximum in the region of 290 mμ.

TABLE II
PRIMARY AND SECONDARY NITRITE PHOTOLYSIS PRODUCT COMPOSITION

Product	2-Propyl	2-Butyl	3-Pentyl	1-Butyl	2-Pentyl	3-Hexyl	4-Heptyl	2-Hexyl	3-Heptyl	4-Octyl	5-Nonyl
1-Nitrosoethane dimer	..	7.4%	4.7%	..	....	7%	....	....	....	....	....
1-Nitrosopropane dimer	..	....	....	..	8%	7%	8%	....	....	....	....
1-Nitrosobutane dimer	..	....	....	..	....	....	....	1%	4%	....	....
1-Nitroso-4-butanol dimer	..	....	....	4%	....	....	....	....	....	....	....
1-Nitroso-4-pentanol dimer	..	....	....	..	6%	....	....	....	....	....	....
1-Nitroso-4-hexanol dimer	..	....	....	..	....	5%	....	....	....	....	....
1-Nitroso-4-heptanol dimer	..	....	....	..	....	....	19%	....	....	....	....
2-Nitroso-5-hexanol dimer	..	....	....	..	....	....	....	31%	....	....	....
2-Nitroso-5-heptanol dimer	..	....	....	..	....	....	....	....	28%	....	....
2-Nitroso-5-octanol dimer	..	....	....	..	....	....	....	....	....	42%	....
2-Nitroso-5-nonanol dimer	..	....	....	..	....	....	....	....	....	....	38%
2-Propanol	23%	....	....	..	....	....	....	....	....	....	....
2-Butanol	..	31%	....	..	....	....	....	....	....	....	....
3-Pentanol	..	....	33%	..	....	....	....	....	....	....	....
1-Butanol	..	....	....	27%	....	....	....	....	....	....	....
2-Pentanol	..	....	....	..	32%	....	....	....	....	....	....
3-Hexanol	..	....	....	..	....	38%	....	....	....	....	....
4-Heptanol	..	....	....	..	....	....	32%	....	....	....	....
2-Hexanol	..	....	....	..	....	....	....	6.3%	....	....	....
3-Heptanol	..	....	....	..	....	....	....	....	5.8%	....	....
4-Octanol	..	....	....	..	....	....	....	....	....	7.2%	....
5-Nonanol	..	....	....	..	....	....	....	....	....	....	6.7%
2-Propanone	30%	....	....	..	....	....	....	....	....	....	....
2-Butanone	..	29%	....	..	....	....	....	....	....	....	....
3-Pentanone	..	....	28%	..	....	....	....	....	....	....	....
1-Butanal	..	....	....	22%	....	....	....	....	....	....	....
2-Pentanone	..	....	....	..	36%	....	....	....	....	....	....
3-Hexanone	..	....	....	..	....	17%	....	....	....	....	....
4-Heptanone	..	....	....	..	....	....	16%	....	....	....	....
2-Hexanone	..	....	....	..	....	....	....	8.1%	....	....	....
3-Heptanone	..	....	....	..	....	....	....	....	5.6%	....	....
4-Octanone	..	....	....	..	....	....	....	....	....	15%	....
5-Nonanone	..	....	....	..	....	....	....	....	....	....	8.9%
Methanal	..	....	....	0%	....	....	....	....	....	....	....
Ethanal	0%	7.4%	....	..	8.2%	....	....	0.9%	....	....	....
Propanal	..	0%	17%	..	....	7.0%	....	....	4.0%	....	....
Butanal	..	....	....	..	0%	7.0%	8.3%	....	....	0%	....
Pentanal	..	....	....	..	....	....	....	0%	0%	0%	0%

The Barton reaction products were not characterized except the one obtained from the photolysis of 4-heptyl nitrite. This was characterized by reactions 1–3.

$$[CH_3(CH_2)_2CHOH(CH_2)_2CH_2NO]_2 \longrightarrow$$
$$2CH_3(CH_2)_2CHOH(CH_2)_2CHNOH \quad (1)$$
$$CH_3(CH_2)_2CHOH(CH_2)_2CHNOH \longrightarrow$$
$$CH_3(CH_2)_2CHOH(CH_2)_2CHO \quad (2)$$

$$CH_3(CH_2)_2CHOH(CH_2)_2CHO \longrightarrow$$
$$CH_3(CH_2)_2\underset{\llcorner-O-\lrcorner}{CH(CH_2)_2CO} \quad (3)$$

The products of these reactions are known.[4]

The nitroso dimers (lacking hydroxyl groups) obtained from the photolysis of 3-pentyl, 2-butyl,

(4) (a) P. Bagard, Bull. soc. chim. France, [4] 1, 307 (1907); (b) A. S. Perlin and C. B. Purves, Can. J. Chem., 31, 227 (1935); (c) D. Papa, E. Schwenk and H. F. Ginsberg, J. Org. Chem., 16, 253 (1951).

TABLE III

TERTIARY NITRITE PHOTOLYSIS PRODUCT COMPOSITION

Product	2-Methyl-2-propyl	2-Methyl-2-butyl	2-Methyl-2-pentyl	2-Methyl-2-hexyl	2,5-Dimethyl-2-hexyl
Nitrosomethane dimer	0%	..	..	..	..
Nitrosoethane dimer	..	40%	..	..	..
Nitrosopropane dimer	..	..	45%	..	..
5-Nitroso-2-methyl-2-hexanol dimer	..	..	..	49%	..
5-Nitroso-2,5-dimethyl-2-hexanol	..	..	..	..	39%
2-Propanone	15%	39%	45%	0%	0%
2-Butanone	..	0%	..	..	..
2-Pentanone	..	..	0%	..	..
2-Hexanone	..	..	..	0%	..
2-Methyl-2-hexanone	..	..	..	..	0%
2-Methyl-2-propanol	46%	..	..	..	..
2-Methyl-2-butanol	..	28%	..	..	..
2-Methyl-2-pentanol	..	..	44%	..	..
2-Methyl-2-hexanol	..	..	..	28%	..
2,5-Dimethyl-2-hexanol	..	..	..	..	33%

2-methyl-2-butyl and 2-methyl-2-pentyl nitrites were characterized by reaction 4. The products

$$[RCH_2NO]_2 \longrightarrow 2RCHNOH \qquad (4)$$

of reaction 4 are known compounds.[5] The other products of the photolyses were alcohols, aldehydes and ketones which were characterized by standard procedures.[5]

The yield reported for 5-nitroso-2,5-dimethyl-2-hexanol monomer is the peak value obtained when only a fraction of the nitrite had been converted to photolytic products. The concentration of this tertiary nitroso monomer reached a limiting value early in the photolysis and remained there throughout the reaction. All other product yields are for complete photolysis runs.

Discussion

A. Nitroso Products. 1. Primary Nitrites.— Photolysis of decreasing chain length primary alkyl nitrites resulted in essentially identical yields of nitroso dimers (Table I) until the minimum straight chain length of four carbon atoms (1-butyl nitrite) was reached. At this point a sharp drop in yield of nitroso dimer was noted. The lower yield is the result of the more difficult intramolecular hydrogen abstraction reaction of a primary hydrogen atom as compared to a secondary hydrogen atom. 1-Propyl and ethyl nitrites do not yield any nitroso dimer in solution; this is in sharp contrast to their behavior in the vapor phase.[6] No nitroso dimers were formed via the alkoxy radical decomposition reaction from the straight chain primary nitrites. The minimum straight chain length requirement (of four carbon atoms) for the Barton reaction was again noted[2,3] for primary nitrites.

2. Secondary Nitrites. a. 2-Series.—The photolysis behavior of secondary nitrites in the 2-series was similar to that of primary nitrites. The total nitroso dimer product yield remained essentially constant until the minimum straight chain length of four carbon atoms was reached in 2-

(5) R. L. Shriner, R. C. Fuson and D. J. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956.

(6) P. Tarte, Bull. Soc. Roy. Sci. Liege, 22, 226 (1953).

pentyl nitrite. The yield of Barton reaction product again dropped sharply for the same reason as for 1-butyl nitrite. However, a nitroso dimer, 1-nitrosopropane dimer, also was formed by the radical decomposition mechanism. There are two possible radical decomposition reactions—one gives the propyl radical and ethanal (5) and the other a methyl radical and butanal (6). There was no evidence for the production of methyl
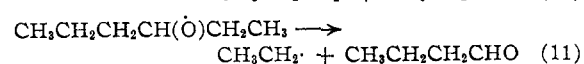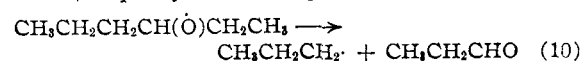
$$CH_3CH_2CH_2CH(\dot{O})CH_3 \longrightarrow$$
$$CH_3CH_2CH_2\cdot + CH_3CHO \quad (5)$$
$$CH_3CH_2CH_2CH(\dot{O})CH_3 \longrightarrow\!\!\!\!/$$
$$CH_3\cdot + CH_3CH_2CH_2CHO \quad (6)$$
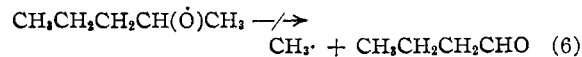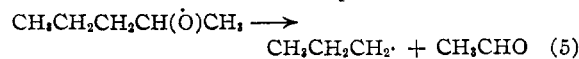
radicals (no butanal). The next lower member of this series, 2-butyl nitrite, did not give any Barton reaction product but a small yield of 1-nitroso-ethane dimer (7). Again there was no evidence for the production of methyl radicals (no propanal (8)). With 2-propyl nitrite, the nitroso dimer
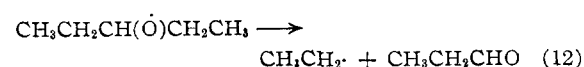
$$CH_3CH_2CH(\dot{O})CH_3 \longrightarrow CH_3CH_2\cdot + CH_3CHO \quad (7)$$
$$CH_3CH_2CH(\dot{O})CH_3 \longrightarrow\!\!\!\!/ CH_3\cdot + CH_3CH_2CHO \quad (8)$$
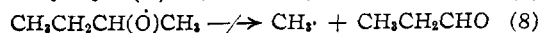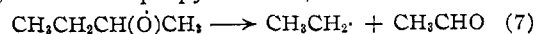
yield dropped to zero. There was no evidence for the decomposition of the 2-propoxy radical into a methyl radical and ethanal (9).

$$CH_3CH(\dot{O})CH_3 \longrightarrow\!\!\!\!/ CH_3\cdot + CH_3CHO \quad (9)$$
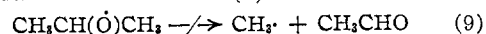
b. 3-Series.—3-Hexyl nitrite (chain of four carbon atoms) gave the same low Barton reaction yield of hydroxy nitroso dimer as 1-butyl and 2-pentyl nitrites. However, 1-nitrosopropane and nitrosoethane dimers also were formed (via the two possible radical decomposition reactions 10 and 11, respectively). The next lower member of this series, 3-pentyl nitrite, gave no Barton reaction

$$CH_3CH_2CH_2CH(\dot{O})CH_2CH_3 \longrightarrow$$
$$CH_3CH_2CH_2\cdot + CH_3CH_2CHO \quad (10)$$
$$CH_3CH_2CH_2CH(\dot{O})CH_2CH_3 \longrightarrow$$
$$CH_3CH_2\cdot + CH_3CH_2CH_2CHO \quad (11)$$

product; instead a low yield of nitrosoethane dimer was obtained by the radical decomposition mechanism 12.

$$CH_3CH_2CH(\dot{O})CH_2CH_3 \longrightarrow$$
$$CH_3CH_2\cdot + CH_3CH_2CHO \quad (12)$$

c. 4-Series.—4-Heptyl nitrite gave the highest yield (*ca.* 3X) of hydroxy nitroso dimer *via* the Barton reaction for compounds involving intramolecular hydrogen abstraction on a primary hydrogen atom. The higher yield is due to the symmetrical choice of two methyl groups. 1-Nitrosopropane dimer *via* the radical decomposition mechanism was also produced.

d. Rearrangement *vs.* Decomposition.—In order to determine whether nitroso dimer formation *via* the radical decomposition mechanism accompanied the more favorable Barton reactions involving intramolecular hydrogen abstraction on a secondary hydrogen atom, the photolysis products of 2-hexyl, 3-heptyl, 4-octyl and 5-nonyl nitrites were studied. 5-Nonyl nitrite which could give the Barton reaction *via* the symmetrical choice of two secondary hydrogen atom locations gave no evidence of nitroso dimer formation by the radical decomposition mechanism. 4-Octyl nitrite behaved similarly; however, 3-heptyl and 2-hexyl nitrites afforded 1-nitrosobutane dimer by the radical decomposition mechanism. In both cases only one alkyl radical, the larger butyl, was formed in the cleavage reaction in yields smaller than those obtained by the other secondary nitrites mentioned above.

3. Tertiary Nitrites.—In the case of tertiary nitrites, the first member of the series, *t*-butyl nitrite, failed to produce any nitrosomethane dimer; this is in sharp contrast to its photolysis behavior in the vapor phase.[6–10] Evidently, the methyl radical formed as a result of the radical decomposition reaction typical of tertiary alkoxy radicals, as evidenced by the production of 2-propanone, does not survive long enough to react with nitric oxide. The methyl radical probably reacts with the benzene solvent predominantly by addition (13) and to a lesser extent by hydrogen abstraction (14) reactions as reported by Levy, Steinberg and Szwarc.[11] 2-Methyl-2-butyl and 2-methyl-2-pentyl nitrites produced nitrosoethane

$$CH_3\cdot + C_6H_6 \longrightarrow CH_3C_6H_6\cdot \qquad (13)$$
$$CH_3\cdot + C_6H_6 \longrightarrow CH_4 + C_6H_5\cdot \qquad (14)$$
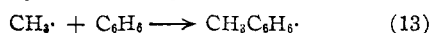
and 1-nitrosopropane dimers, respectively, in good yields by the radical decomposition mechanism together with an equal amount of 2-propanone. There was no evidence for the formation of methyl radicals (15) during the tertiary alkoxy radical

$$CH_3CH_2C(CH_3)_2O\cdot \longrightarrow\!\!/\!\!\longrightarrow CH_3\cdot + CH_3CH_2COCH_3 \quad (15)$$
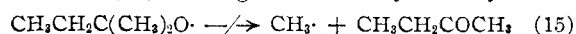
decompositions. Additionally there was but little evidence for the Barton reaction in the case of 2-methyl-2-pentyl nitrite. Evidently the tertiary alkoxy radical decomposition reaction is preferred to a Barton reaction involving intramolecular hydrogen abstraction of a primary hydrogen atom.

When the length of the longest alkyl chain was increased so that the Barton reaction would involve a secondary hydrogen atom (2-methyl-2-hexyl

nitrite) or a tertiary hydrogen atom (2,5-dimethyl-2-hexyl nitrite) the Barton reaction occurred to the exclusion of the tertiary alkoxy radical decomposition. The yield of 2-propanone dropped to zero and good yields of 5-nitroso-2-methyl-2-hexanol dimer and 5-nitroso-2,5-dimethyl-2-hexanol, respectively, were obtained. This is the first reported case of tertiary nitroso monomer formation *via* the Barton reaction.
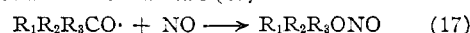
The tertiary nitroso monomer was produced only when the light radiation in the 680 mμ region, in which the tertiary nitroso product has a weak absorption band, was eliminated by a suitable light filter. Anderson, Crumpler and Hammick[12] have reported the photochemical decomposition of tertiary nitroso compounds using radiation in the 680 mμ region.

B. Factors Effecting Dominance of Different Modes of Alkoxy Radical Reaction.—The various types of reactions which alkoxy radicals (formed
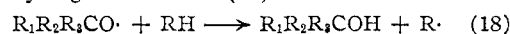
$$R_1R_2R_3CONO + h\nu \longrightarrow R_1R_2R_3CO\cdot + NO \quad (16)$$
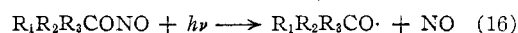
in the photolytic reaction 16) undergo are[13]

1. Association with radicals (17)
$$R_1R_2R_3CO\cdot + NO \longrightarrow R_1R_2R_3ONO \qquad (17)$$

2. Hydrogen abstraction (18)
$$R_1R_2R_3CO\cdot + RH \longrightarrow R_1R_2R_3COH + R\cdot \quad (18)$$

3. Disproportionation (19)
$$R_1R_2HCO\cdot + R_1R_2HCO\cdot \longrightarrow$$
$$R_1R_2HCOH + R_1R_2CO \quad (19)$$
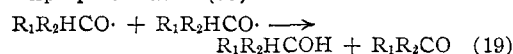
4. Rearrangement by hydrogen atom migration (20)
$$RCH_2(CH_2)_2CH_2O\cdot \longrightarrow R\dot{C}H(CH_2)_2CH_2OH \quad (20)$$
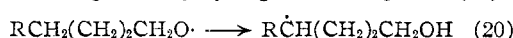
5. Decomposition by radical elimination (21)
$$R_1R_2R_3CO\cdot \longrightarrow R_1\cdot + R_2R_3CO \qquad (21)$$
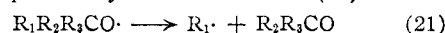
The relative importance of the different reactions depends on the nature of the particular alkoxy radical and its chemical and physical environment. The problem is one of kinetics; the kinetically favored reactions predominate. Hydrogen abstraction (18) can be suppressed by the use of benzene as solvent, while the reaction of association (17) cannot be suppressed since the free radical, nitric oxide, is formed in the photolytic reaction (16). This reaction with an activation energy of zero accounts for a quantum yield of less than unity. Unless there are other reactions faster than reaction 17, the quantum yield for the disappearance of alkyl nitrites will be very low. The reactions normally available are decomposition, hydrogen abstraction and disproportionation, whose activation energy ranges are 10 to 30, 5 to 10, and 0 kcal./mole, respectively. Their relative importance (when using a particular light source) depends principally on (1) the alkoxy radical (RO·) concerned, (2) the temperature and (3) the concentration of the parent molecule from which hydrogen may be abstracted.

1. Decomposition.—The cleavage reaction of alkoxy radicals in solution reported in this study parallels the thermochemical data of Gray and Williams[13] (Table IV). Primary alkoxy radicals

(7) B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 1670 (1956).

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

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

(10) B. G. Gowenlock and T. Trotman, *J. Chem. Soc.*, 4190 (1955).

(11) M. Levy, M. Steinberg and M. Szwarc, *J. Am. Chem. Soc.*, **76**, 3439 (1954).

(12) K. D. Anderson, C. J. Crumpler and D. L. Hammick, *J. Chem. Soc.*, 1679 (1935).

(13) P. Gray and A. Williams, *Chem. Revs.*, **59**, 239 (1959).

and secondary alkoxy radicals which can only eliminate a methyl radical did not undergo cleavage while other secondary and tertiary radicals did cleave when the Barton reaction was not favored. During the *t*-butyl nitrite photolysis, hydrogen abstraction under suppressed conditions and decomposition by the difficult elimination of a methyl radical were the only means available to consume the *t*-butoxy radical. The low quantum yield of 0.08 (compared to 0.25 for 1-octyl nitrite) attests to the slowness of these reactions compared to the association reaction (17). The order of ease of radical elimination found in this study decreased in the manner: *n*-butyl > *n*-propyl, ethyl >> methyl.

TABLE IV

THERMOCHEMISTRY AND STABILITY OF ALKOXY RADICALS

Radical	Min. enthalpy required for decompn., kcal. mole^{-1}	Decompn. obsd. in soln.
$C_2H_5O\cdot$	13	No
$p\text{-}C_4H_9O\cdot$	11	No
$p\text{-}C_3H_7O\cdot$	10	No
$s\text{-}C_3H_7O\cdot$	10	No
$s\text{-}C_4H_9O\cdot$	5	Yes
$t\text{-}C_4H_9O\cdot$	5	Yes

2. Hydrogen Abstraction.—The second normally present free radical reaction, *hydrogen abstraction*, was the predominant reaction in the case of *t*-butyl nitrite but of secondary importance for the higher members of the tertiary nitrite series. Intramolecular hydrogen abstraction (rearrangement by hydrogen atom migration) by an alkoxy radical is not as rare as Gray and Williams[13] report. In fact, it is the most favored reaction of alkoxy radicals in solution where the solvent (benzene) is reluctant to undergo hydrogen abstraction reactions provided the geometric requirements of the Barton reaction are fulfilled. The Barton reaction is an alkoxy radical rearrangement reaction by hydrogen atom migration, followed by association with nitric oxide. With primary, secondary and even tertiary nitrites, the Barton reaction involving internal hydrogen abstraction of either secondary or tertiary hydrogen atoms is the predominant alkoxy radical reaction in benzene. When only primary hydrogen atoms are available for the rearrangement reaction, disproportionation and decomposition reactions replace the Barton reaction as the predominant one in primary (and secondary) and tertiary alkoxy radicals reactions, respectively. With solvents such as heptane favorably disposed toward hydrogen abstraction reactions, intermolecular hydrogen abstraction competes with the Barton reaction as evidenced by solvent products (2) and the increased quantum yield ($\Phi = 0.76$).

In order to determine the selectivity of radical attack in an instance where there is a choice of abstracting a tertiary and a primary δ-hydrogen and in a case involving competition between a secondary and a primary δ-hydrogen, 2-ethyl-4-methyl-1-pentyl and 2-ethyl-1-hexyl nitrites, respectively, were prepared and photolyzed. In both cases there was no evidence for primary hydrogen abstraction.

3. Disproportionation.—The third normally present free radical reaction, *disproportionation*, is restricted to primary and secondary alkoxy radicals. It is always favored over the decomposition reactions of primary and secondary alkoxy radicals involving the elimination of simple straight chain alkyl radicals and over the rearrangement reaction when the geometric and structural requirements of the Barton reaction are not fulfilled. At all other times it is present to an appreciable extent.

Experimental

Material, apparatus, photolysis procedure and analytical methods are as described in Parts I and II.

1-Nitroso-4-heptanol Dimer.—4-Heptyl nitrite (25 ml.) was photolyzed in 200 ml. of heptane. After the reaction solution was decanted from an oily residue in the photolysis cell, the light yellow oil was removed with methylene chloride. The methylene chloride was removed under vacuum and the 3.1 g. of residue was dissolved in 100 ml. of isoöctane. After standing at $-15°$ for 96 hours, 730 mg. of crude 1-nitroso-4-heptanol dimer was filtered off and dried, m.p. 68–70°, λ_{max}^{MeOH} 287 mμ, (ϵ 9170). The analytical sample was recrystallized from benzene–isoöctane; m.p. 74–75°, λ_{max}^{MeOH} 287 mμ, (ϵ 9350). The product exhibits infrared absorption (in Nujol) at 2.93 μ (CO–H) and 8.25 μ (*trans*-nitroso dimer).

Anal. Calcd. for $C_{14}H_{30}O_4N_2$: C, 57.90; H, 10.41; N, 9.65. Found: C, 58.06; H, 9.77; N, 9.49.

5-Nitroso-2,5-dimethyl-2-hexanol.—2,5-Dimethyl-2-hexyl nitrite (2.0 g.) was photolyzed in benzene using a Corning No. 5874 light filter. The decrease in nitrite ester was followed spectrophotometrically during the photolysis while the increase in tertiary nitroso monomer was followed polarographically. The blue color of the nitroso monomer was observed soon after the initiation of the photolysis and was visible during the course of the reaction.

In the procedure for the polarographic analysis, an aliquot from the photolysis solution was added to aqueous methanol to afford a solution that was finally 10% benzene, 20% water, 70% methanol and 0.2 *M* lithium chloride. A half-wave for 5-nitroso-2,5-dimethyl-2-hexanol was observed at -0.86 v. (S.C.E.). The yield from nitrite ester to tertiary nitroso monomer was calculated by comparison with the current constant obtained from 2-nitroso-2-ethylpropane[14]; $K = 3.86$ μa./mM, $E_{1/2} = -0.81$ v. measured in the same system. The yield of nitroso monomer reported in Table III is the peak value obtained when only a fraction of the nitrite had been converted to photolytic products.

The nitroso monomer continuously degraded to unknown products and therefore was not characterized.

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