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

Photolysis of Nitrite Esters in Solution. IV. Nitroso Products from Radical Decomposition Mechanism

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No nitroso dimers were formed from the photolytic reaction in benzene of the primary nitrites (substituted methyl nitrites) when the substituents were methyl, ethyl and isopropyl groups. When the substituent was *t*-butyl, nitroso monomer and methanal were formed by the alkoxy radical decomposition mechanism. Photolysis of secondary nitrites (alkyl substituted ethyl nitrites) resulted in alkoxy radical cleavage products (ethanal and nitroso compounds) in increasing amounts when the substituents were ethyl, isopropyl and *t*-butyl.

Introduction

In previous publications[1,2] the photolysis of primary and secondary nitrites was reported to yield nitroso dimers by the alkoxy radical decomposition mechanism as well as by the Barton[3] reaction (alkoxy radical rearrangement mechanism). In the present paper the photolyses of nitrite esters which could not undergo the Barton reaction were studied to determine the effect of alkyl substituent on the ease of the alkoxy radical decomposition reaction in solution.

Results

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

TABLE I

EFFECT OF BRANCHING ON YIELD OF NITROSO DIMER

Primary nitrites		Secondary nitrites	
Starting material	Product[a] ε	Starting material	Product[a] ε
Ethyl	0	2-Propyl	0
Propyl	0	2-Butyl	700
2-Methyl-1-propyl	0	3-Methyl-2-butyl	3000
2,2-Dimethyl-1-propyl	0	3,3-Dimethyl-2-butyl	0

[a] For 100% yield ε(294 mμ) ∼ 9,500.

The photolysis product compositions found for these primary and secondary nitrites are shown in Table II.

The yields reported for 2-nitroso-2-methylpropane are peak values obtained when only a fraction of the nitrite had been converted to photolytic products. The concentration of 2-nitroso-2-methylpropane reached a limiting value early in the photolysis and remained there throughout the reaction. All the other yields represent products from complete photolysis runs. The alcohols, aldehydes and ketones were determined by vapor phase chromatography.

Discussion

A. Primary Nitrites.—When R is methyl or ethyl, the alkoxy radical, $RCH_2O\cdot$, produced during the photolyses of the corresponding primary nitrites, principally undergoes a disproportionation reaction in benzene, yielding alcohol and aldehyde products. When R is isopropyl or *t*-butyl, alkoxy radical decomposition also occurs yielding methanal and the isopropyl and *t*-butyl radical, respectively. No nitroso monomer, dimer or isomeric oxime was formed during the photolysis of 2-methyl-1-propyl nitrite indicating that for inexplicable reasons the isopropyl radical in this case does not undergo reaction with nitric oxide. The *t*-butyl radical formed during the 2,2-dimethyl-1-propyl nitrite photolysis, combines with nitric oxide to yield 2-nitroso-2-methylpropane monomer. The inequality of the 2-nitroso-2-methylpropane and methanal yields is due to the instability of this tertiary nitroso monomer under the experimental conditions. No evidence for the formation of hydroxamic acid, reaction 1, was found as recently reported by

$$(CH_3)_3CNO + CH_2O \not\longrightarrow (CH_3)_3CN(OH)CHO \quad (1)$$

Robinson, *et al.*,[4] in the alicyclic case, for 5α-androstane-3α,17β-diol 3α-acetate 17β-nitrite, testosterone 17β-nitrite, 19-nortestosterone 17β-nitrite, estradiol 3-benzoate 17β-nitrite and estradiol 3-methyl ether 17β-nitrite.

B. Secondary Nitrites.—Photolysis of secondary nitrites, 1-alkyl-1-ethyl nitrites, gave alcohol and ketone products *via* disproportionation reactions, similar to their primary analogs. However, the alkoxy radical decomposition occurred not only when the alkyl substituent was isopropyl and *t*-butyl, but also when it was ethyl. When the substituents were ethyl and isopropyl groups, nitrosoethane and 2-nitrosopropane dimers, respectively, were produced together with ethanal. The nitroso dimer yield roughly corresponded to the ethanal yield. Again there was an inequality between the 2-nitroso-2-methylpropane and the ethanal yields in the photolysis of 3,3-dimethyl-2-butyl nitrite. However, in this case, a large amount of isobutene (40%) was detected by vapor phase chromatography which could account for the disappearing tertiary nitroso monomer *via* reaction 2. Kraus and Calvert[5] have reported that in the presence of nitric oxide, the normal products of the photolysis

$$(CH_3)_3CNO \longrightarrow (CH_3)_3C{=\!=}CH_2 + HNO \quad (2)$$

of di-*t*-butyl ketone, isobutane and 2,2,3,3-tetramethylbutane were absent while the yield of isobutene was doubled. They suggested that reaction 2 accounted for this.

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[1] P. Kabasakalian, E. R. Townley and M. D. Yudis, *J. Am. Chem. Soc.*, **84**, 2716 (1962), part II.

[2] P. Kabasakalian, E. R. Townley and M. D. Yudis, *ibid.*, **84**, 2718 (1962), part III.

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

[4] C. H. Robinson, O. Gnoj, A. Mitchell, R. Wayne, E. Townley, P. Kabasakalian, E. P. Oliveto and D. H. R. Barton, *J. Am. Chem. Soc.*, **83**, 1771 (1961).

[5] J. W. Kraus and J. G. Calvert, *ibid.*, **79**, 5921 (1957).

TABLE II

NITRITE PHOTOLYSIS PRODUCT COMPOSITION

	Starting nitrite							
Product	Ethyl	Propyl	2-Methyl-1-propyl	2,2-Dimethyl-1-propyl	2-Propyl	2-Butyl	3-Methyl-2-butyl	3,3-Dimethyl-2-butyl
Nitrosomethane dimer	0%	..	..	....	0%	..	..	....
Nitrosoethane dimer	..	0%	..	....	..	7%	..	....
2-Nitrosopropane dimer	..	..	0%[a]	....	..	..	31%	....
2-Nitroso-2-methylpropane	..	..	..	7.5%	..	..	..	8.5%[b]
Methanal	0%	0%	18%	35%	..	..	..	....
Ethanal	40%	..	..	....	0%	10%	46%	64%
Propanal	..	40%	..	....	..	..	..	....
2-Methyl-1-propanal	..	..	12%	....	..	..	..	....
2,2-Dimethyl-1-propanal	..	..	..	5.7%	..	..	..	....
2-Propanone	..	..	..	....	30%	..	..	....
2-Butanone	..	..	..	....	..	29%	..	....
3-Methyl-2-butanone	..	..	..	....	..	..	2%	....
3,3-Dimethyl-2-butanone	..	..	..	..	..	..	..	7.4%
Ethanol	34%	..	..	....	..	..	..	....
Propanol	..	29%	..	....	..	..	..	....
2-Methyl-1-propanol	..	..	27%	....	..	..	..	....
2,2-Dimethyl-1-propanol	..	..	..	8.1%	..	..	..	....
2-Propanol	..	..	..	....	23%	..	..	....
2-Butanol	..	..	..	....	..	31%	..	....
3-Methyl-2-butanol	..	..	..	....	..	..	18%	....
3,3-Dimethyl-2-butanol	..	..	..	....	..	..	..	16%

[a] No isomeric oxime found. [b] 40% yield of isobutene found.

Levy and Copeland[6] reported that reaction 2 is accompanied by reaction 3 and that the thermal

$$2HNO \longrightarrow N_2O + H_2O \qquad (3)$$

decomposition of 2,2′-azoisobutane in the presence of nitric oxide yielded 2-nitroso-2-methylpropane, isobutene and nitrous oxide. Again there was no evidence for the formation of hydroxamic acid, reaction 4.

$$(CH_3)_3CNO + CH_3CHO \not\longrightarrow (CH_3)_3CN(OH)COCH_3 \qquad (4)$$

Secondary alkoxy radicals undergo the radical decomposition reaction with greater ease than do the corresponding primary alkoxy radicals, as evidenced by the greater yield of aldehyde cleavage product. The yield of ethanal increased as the alkyl radical from the radical decomposition reaction of secondary alkoxy radicals varied from ethyl to isopropyl and *t*-butyl. This order is identical with the well known order of stability of simple alkyl radicals, *i.e.*, tertiary > secondary > primary.

Experimental

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

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(6) J. B. Levy and B. K. W. Copeland, *J. Am. Chem. Soc.*, **82**, 5314 (1960).

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Photolysis of Nitrite Esters in Solution. V. Photochemistry of Cyclohexyl Nitrites

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Photolysis of alkyl cyclohexyl nitrites in benzene indicated that only the conformationally favored disubstituted cyclohexane derivatives, the ones vicinally substituted, capable of forming six-membered ring intermediates gave 30–40% yields of nitroso dimers. Cyclohexyl alkyl nitrite photolyses gave further evidence in the support of the basic prerequisite of a six-membered ring intermediate in the Barton reaction.

Introduction

Four previous publications[1] in this series have established that the photolysis of primary, secondary and tertiary alkyl nitrites produces simple nitroso compounds by the *alkoxy radical decomposition mechanism* and hydroxy nitroso compounds by the *alkoxy radical rearrangement mechanism* (the Bar-

(1) (a) P. Kabasakalian and E. R. Townley, *J. Am. Chem. Soc.*, **84**, 2711 (1962), part I; (b) P. Kabasakalian, E. R. Townley and M. D. Yudis, *ibid.*, **84**, 2716 (1962), part II; (c) *ibid.*, **84**, 2718 (1962), part III; (d) P. Kabasakalian and E. R. Townley, *ibid.*, **84**, 2723 (1962), part IV.