pearance of persulfate in solution of mixed substrates.

Discussion

It is apparent from the above results that the diminution of the rate is due not to the trapping of free radicals, but instead to the formation, by the competing reductant[5], of a stronger intermediate complex with the active oxidizing species than that which isopropyl alcohol forms with the oxidant. The rather unusual conclusions drawn recently by Edwards[6] concerning the "inhibition" of persulfate oxidations by the addition of a sequestering agent (ethylenediamine tetraacetic acid, disodium salt) to eliminate traces of transition metal ions (mainly Cu^{++}), are almost certainly erroneous for the same reason: The sequestering agent is itself preferentially oxidized[7] by the persulfate, and the active oxidizing species (possibly sulfur tetroxide, $\bar{O}_3S:\ddot{O}^+$) is probably tied up, thus retarding the rate of disappearance of persulfate.[8] It appears, therefore, that the "inhibition" of the reaction by this compound has little or nothing to do with the elimination of trace metal catalysis in persulfate oxidations.

Further evidence against a radical–chain mechanism for the persulfate oxidation of alcohols is the rather high activation energy[9] (26 kcal./mole), and the fact that molecular oxygen[10] has no effect whatever on the rate[11]; even in the silver ion-catalyzed persulfate cleavage of glycols, strong evidence has been presented by Greenspan and Woodburn[12] that the reaction does not involve free radicals.

Turning to Wiberg's rate expression[1] for these

(5) The competing organic compound is erroneously referred to as the "inhibitor" in Wiberg's paper (ref. 1).

(6) D. L. Ball, M. M. Crutchfield, and J. O. Edwards, *J. Org. Chem.*, **25**, 1599 (1960).

(7) It was, indeed, found that persulfate slowly oxidized the sequestering agent (ref. 6).

(8) We assume that $S_2O_8^-$ and SO_4 and their derivatives in the solution all titrate iodometrically as equivalent oxidizing agents, in the same fashion as do *t*-Bu-hypochlorite and the chromate esters.

(9) L. S. Levitt and E. R. Malinowski, *J. Am. Chem. Soc.*, **77**, 4517 (1955).

(10) E. Howard, Jr., and L. S. Levitt, *ibid.*, **75**, 6170 (1953).

(11) Nor has oxygen any effect on the rate of the persulfate oxidation of toluene. See A. Kailen and L. Olbrich, *Monatsh.*, **47**, 449 (1926).

(12) F. P. Greenspan and H. M. Woodburn, *J. Am. Chem. Soc.*, **76**, 6345 (1954).

oxidations, we note that this equation does not involve the constant k_3, which represents the rate of direct attack of the HO·radical on the alcohol molecule. Since this reaction is depicted as the only one in which an intact alcohol molecule participates, one might expect little or no variation of the rate when secondary alcohols other than 2-propanol are oxidized under the same conditions by persulfate.[13] This is not what is observed experimentally, however, since the structure of the alcohol has a marked effect on the rate,[14] as shown by the above-mentioned rate constants for 2-propanol and 2-butanol.

In any case, the proposed radical–chain mechanism does not in any way lead to the remarkable dependence of the initial first-order rate constant on the *initial* concentrations of alcohol and persulfate, which we have shown[15] to be of the form $k = k_{max}[ROH]_0[S_2O_8^-]_0/(b + [ROH]_0)(c + [S_2O_8^-]_0)$ where b and c are empirical constants. As already pointed out in our previous article,[15] there is a close, but not exact, analogy between this rate expression and that for enzyme kinetics, thus strongly suggesting the existence of at least one equilibrium step in the reaction sequence, leading to the formation of a reactive intermediate complex which decomposes irreversibly to the observed oxidation products. In the case of a secondary alcohol this can be formulated

$$R_2CHOH + S_2O_8^- \rightleftharpoons Complex \longrightarrow R_2CO + 2HSO_4^-$$
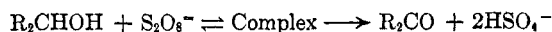
The intermediate complex is very likely one of the possible persulfate esters.[16]

(13) It is true that the rate constants k_4 and k_5 do appear in Wiberg's rate equation and these represent reactions of radicals formed by abstraction of a hydrogen atom from the carbinol carbon of the secondary alcohol. However, the bond dissociation energies of all these secondary alcohol radical species, and hence their reactivities, are nearly identical.

(14) B. W. Levitt and L. S. Levitt, Abstracts of Papers, Chicago Meeting, American Chemical Society, 5-P, September, 1958.

(15) E. R. Malinowski and L. S. Levitt, *J. Am. Chem. Soc.*, **80**, 5334 (1958).

(16) L. S. Levitt, *J. Org. Chem.*, **20**, 1297 (1955); see also ref. 9.

Photolysis of Nitrite Esters in Solution
VI.   Nitroso Dimers from Alicyclic Nitrites

PETER KABASAKALIAN AND EDWARD R. TOWNLEY

*Chemical Research and Development Division,
Schering Corporation, Bloomfield, New Jersey*

In a previous publication[1] it was established that cyclohexyl nitrite failed to undergo the Barton reaction.[2] The present study was undertaken to

(1) P. Kabasakalian and E. R. Townley, Part V, *J. Am. Chem. Soc.*, **84**, 2724 (1962).

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

determine whether this was a common property of alicyclic nitrites.

Experimental

Material, Apparatus, and Photolysis Procedure.—These were as described in Part I,[3] Part II,[4] and Part III.[5] The alicyclic nitrites were photolyzed for about 2 hr. at 18° in 200 ml. of deaerated benzene, using a high pressure mercury arc lamp with a Pyrex filter. The course of the reaction (disappearance of alicyclic nitrite) was followed spectrophotometrically using the characteristic nitrite peaks in the 320–380-mμ region.

Analytical Methods. Total Nitroso Dimer.—The Cary Model 14 recording ultraviolet spectrophotometer was used for the quantitative determination of the total nitroso dimer.[3] The absorbance of the photolyzed benzene solution at the end of the photolysis was measured at the characteristic absorption maximum of the nitroso dimer moiety (ϵ ca. 9500) near 290 mμ after appropriate dilution (ca. 1:4000) in methanol.

Cleavage Nitroso Dimer.—The nitroso dimer from the cleavage reaction yielded a stable dialdoxime after the following treatment. An aliquot of the benzene photolysis solution was concentrated to an oil by flash evaporation of the solvent. The oil was treated with an aqueous solution of hydroxylamine hydrochloride and sodium hydroxide (with sufficient ethanol added to effect solution) on a steam bath for 2 hr. The dioxime was isolated *via* methylene chloride extraction, the solvent evaporated, and the resulting residue dissolved in ethanol. Under the same conditions, the nitroso dimer from the rearrangement reaction yielded a ketoxime. The dialdoxime was determined *polarographically*[6] using the Sargent Model XXI recording polarograph. The reductions were carried out in aqueous ethanol (7:3 v./v.) containing 0.1 M hydrochloric acid–potassium chloride buffer. Only the dialdoximes were reduced in this system ($E_{1/2}$ ca. -1.07 v. *vs.* S.C.E.). The diffusion currents were compared with those of authentic dialdoximes.

Characterization.—The nitroso dimers were characterized to verify the structure of the suspected product. The nitroso dimers from the cleavage reaction were characterized as the α,ω-dioximino derivative while the nitroso dimers from the rearrangement reaction were characterized as the 1,4-cycloalkyldione derivative.

1,4-Dioximinobutane.—A 2.70-g. sample of cyclobutyl nitrite was photolyzed in 200 ml. of trichlorotrifluoroethane[7] at 5°. The nitroso dimer precipitated as a viscous gum: yield; 1.45 g.; $\lambda_{max}^{CH_3OH}$ 272 mμ (ϵ 9000). The product exhibits infrared absorption (in Nujol) at 3.69 μ (aldehydic C—H), 5.83 μ (aldehydic C=O) and 8.5 μ (nitroso dimer). A clear solution of 0.70 g. of the crude 4-nitrosobutanal dimer in 3 ml. of water, 2 ml. of 10% sodium hydroxide, and 0.175 g. of hydroxylamine hydrochloride was obtained by the dropwise addition of ethanol. After refluxing the solution for 30 min., the ethanol was removed by distillation and the 1,4-dioximinobutane allowed to crystallize; yield 0.68 g. (45% calculated from starting cyclobutyl nitrite), m.p. 168–170°. The product was identified by an infrared comparison with an authentic sample.[8]

1,5-Dioximinopentane.—Photolysis of cyclopentyl nitrite and work-up by the above procedure afforded a 32% yield of 1,5-dioximinopentane, m.p. 165° (lit.,[9] 171°). The material

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

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

(5) P. Kabasakalian, E. R. Townley, and M. D. Yudis, Part III, *ibid.*, **84**, 2718 (1962).

(6) H. Lund, *Acta Chem. Scand.*, **13**, 249 (1959).

(7) Although benzene has been the preferred photolysis solvent, the use of trichlorotrifluoroethane makes product isolation simple.

(8) G. Ciamician and C. U. Zanetti, *Ber.*, **22**, 1968 (1889).

(9) F. G. Fischer, H. Dull, and L. Ertel, *ibid.*, **65**, 1467 (1932).

was further identified by infrared comparison with an authentic sample.

1,6-Dioximinohexane.—Photolysis of cyclohexyl nitrite and work-up by the above procedure afforded a 1% yield of 1,6-dioximinohexane, m.p. 178° (lit.,[9] 184°). The material was further identified by infrared comparison with an authentic sample. Gas chromatography indicated that the predominant product from the photolysis was cyclohexanol (68%).

1,4-Cycloheptanedione.—A 7.2-g. sample of cycloheptyl nitrite was photolyzed in 200 ml. of trichlorotrifluoroethane at 5°. The nitroso dimer precipitated as a viscous gum; yield 4.3 g.; $\lambda_{max}^{CH_3OH}$ 288 mμ (ϵ 4300). The crude 4-nitroso-1-cycloheptanol dimer was heated at 75° for 24 hr. in a closed vessel to form 4-oximino-1-cycloheptanol; yield 4.3 g. A solution containing 4.5 g. of chromic anhydride in 150 ml. of 98% acetic acid was added dropwise over a period of 1 hr. to a solution of 3 g. of the crude 4-oximino-1-cycloheptanol in 150 ml. of acetic acid. The resulting mixture was allowed to stand overnight at room temperature, then concentrated under vacuum to 50 ml., and refluxed for 2 hr. after the addition of 250 ml. of acetone and 25 ml. of concentrated hydrochloric acid. The mixture was again concentrated to 50 ml., poured into water, and extracted with methylene chloride. Evaporation of the solvent yielded 2.5 g. of residue. Gas chromatography with a Perkin-Elmer Model 154C Vapor Fractometer indicated that the residue contained 36% 1,4-cycloheptanedione (21% calculated from starting cycloheptyl nitrite). The product was collected from the gas chromatograph by the usual technique and identified by an infrared comparison with an authentic sample.[10]

1,4-Cyclooctanedione.—Photolysis of cyclooctyl nitrite and work-up by the above procedure afforded a 16% yield of 1,4-cyclooctanedione.[11,12] The 1,4-cyclooctanedione was characterized by conversion into the known semicarbazone of bicyclo[3.3.0]-1(5)-octen-2-one, m.p. 232° dec. (lit.,[11] 232°). The material was further identified by infrared comparison with an authentic sample.

Results and Discussion

The yields of total nitroso dimers (as indicated by their molar absorptivity values at the wave length of maximum absorption near 290 mμ) resulting from the photolysis of alicyclic nitrites in benzene are shown in Table I together with the percentage of the total nitroso dimer formed by the alkoxy radical decomposition mechanism as determined by *polarography* and the alkoxy radical rearrangement mechanism (determined by difference).

The photolysis of cyclobutyl, cyclopentyl, cyclo-

TABLE I

ALICYCLIC NITRITE PHOTOLYSIS[a] NITROSO DIMER YIELD

| Starting Nitrite	λ_{max}^{b}	ϵ	Product Yield,[c] %	Cleavage, %	Rearrangement,[d] %
Cyclobutyl	272	4400	46	100	0
Cyclopentyl	278	5400	57	100	0
Cyclohexyl	280	300	3	100	0
Cycloheptyl	288	2500	26	20	80
Cyclooctyl	288	2000	21	0	100

[a] Photolysis run in benzene at 18°. [b] Run in methanol—mμ. [c] Approximate yield based on an average ϵ 9500 for 100% yield. [d] Calculated by difference.

(10) A. C. Cope, T. A. Liss, and G. W. Wood, *J. Am. Chem. Soc.*, **79**, 6287 (1957).

(11) A. C. Cope, S. W. Fenton, and C. F. Spencer, *ibid.*, **74**, 5884 (1952).

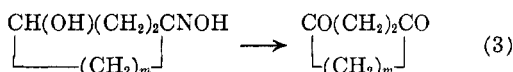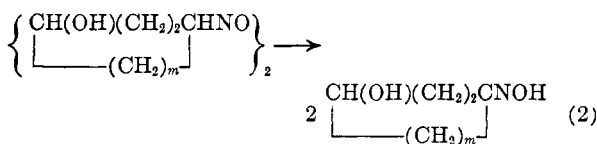(12) A. C. Cope and W. R. Schmutz, *ibid.*, **72**, 3056 (1950).

hexyl, and cycloheptyl nitrites yielded *linear* nitroso aldehyde dimers, 4-nitrosobutanal, 5-nitrosopentanal, 6-nitrosohexanal, and 7-nitrosoheptanal dimers, respectively, by the cleavage mechanism. These were not directly characterized since they were not particularly stable. The presence of an aldehyde group was indicated by infrared absorption bands at 3.6 μ (C—H) and 5.8 μ (C=O). These nitroso dimers were characterized by reaction 1, the

$$[CHO(CH_2)_nCH_2NO]_2 \xrightarrow[\Delta]{NH_2OH} 2\ CHNOH(CH_2)_nCHNOH \quad (1)$$
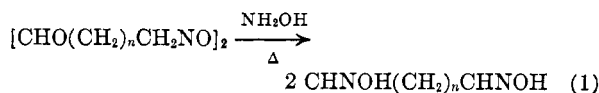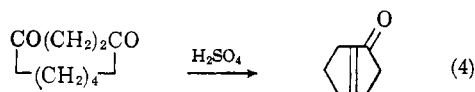
conversion of the nitroso dimer group to an *aldoxime* concomitantly with the formation of the oxime derivative on the aldehyde group.

The known 1,4-dioximinobutane ($n = 2$),[8] 1,5-dioximinopentane ($n = 3$),[9] 1,6-dioximinohexane ($n = 4$),[9] and 1,7-dioximinoheptane ($n = 5$)[9] were formed, respectively.

The photolysis of cycloheptyl and cyclooctyl nitrites yielded *cyclic* nitroso alcohol dimers, 4-nitroso-1-cycloheptanol and 4-nitroso-1-cyclooctanol dimers, respectively, by the rearrangement mechanism. These were characterized by reaction 2 and 3, thermal isomerization of the hydroxy

$$\left\{ \begin{matrix} CH(OH)(CH_2)_2CHNO \\ \underline{\qquad} (CH_2)_m \underline{\qquad} \end{matrix} \right\}_2 \longrightarrow$$
$$2\ \begin{matrix} CH(OH)(CH_2)_2CNOH \\ \underline{\qquad} (CH_2)_m \underline{\qquad} \end{matrix} \quad (2)$$

$$\begin{matrix} CH(OH)(CH_2)_2CNOH \\ \underline{\qquad} (CH_2)_m \underline{\qquad} \end{matrix} \longrightarrow \begin{matrix} CO(CH_2)_2CO \\ \underline{\qquad} (CH_2)_m \underline{\qquad} \end{matrix} \quad (3)$$

nitroso dimers to a hydroxy *ketoxime* and subsequent oxidation and concomitant hydrolysis to the 1,4-cycloalkyldione. The known 1,4-cycloheptanedione ($m = 3$)[10] and 1,4-cyclooctanedione ($m = 4$)[11,12] were formed, respectively. The 1,4-cyclooctanedione was further characterized by an intramolecular condensation reaction 4 to form the known bicyclo[3.3.0]-1(5)-octen-2-one.[11,12]

$$\begin{matrix} CO(CH_2)_2CO \\ \underline{\qquad} (CH_2)_4 \underline{\qquad} \end{matrix} \xrightarrow{H_2SO_4} \quad \text{(structure)} \quad (4)$$

Cyclobutyl and cyclopentyl nitrites did not undergo the Barton reaction; the formation of the prerequisite six-membered ring intermediate was physically impossible. However, nitroso dimers were produced by the alkoxy radical decomposition mechanism in yields (*ca.* 50%) very much higher than those (*ca.* 5%) for simple aliphatic secondary nitrites[5] probably due to ring strain. In the cyclohexyl and cycloheptyl nitrite photolysis, the alkoxy radical decomposition mechanism produced nitroso dimers in yields (*ca.* 5%) similar to those of secondary aliphatic nitrites. Cyclooctyl nitrite photolysis did not produce any detectable nitroso dimer by

the ring fission process. Gray[13] has reported ring fission during the pyrolysis of cyclohexyl nitrite to form 6-nitroso-1-hexanol.

Cycloheptyl and cyclooctyl nitrites undergo the Barton reaction. These transannular free radical rearrangements behave like their straight chain counterparts and do not seem to be influenced by ring size or "proximity effects" found by Cope[14] and Prelog,[15] for transannular rearrangements involving hydride shifts. The uniqueness of the six-membered intermediate in the Barton reaction must be due to the geometric requirements for both the alkoxy radical rearrangement reaction and the coupling of the subsequent radical with nitric oxide. These two 1,5-shifts in opposite directions (hydrogen to oxygen; nitric oxide to carbon) probably occur simultaneously.

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

(13) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).
(14) A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *J. Am. Chem. Soc.*, **82**, 6366 (1960).
(15) J. D. Dunitz and V. Prelog, *Angew. Chem.*, **72**, 896 (1960).

Synthesis of Vinyl Acetate Epoxide

BERT S. GORTON AND JAMES A. REEDER

Research Division, Electrochemicals Department, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware

The reaction of vinyl acetate with hydrogen peroxide has been reported to yield glycoaldehyde.[1] The reaction presumably proceeded through an intermediate epoxide or hemiacylal which was hydrolyzed to the aldehyde during isolation. We have found that vinyl acetate epoxide (I) can be isolated if conditions are chosen to minimize hydrolysis.

$$\underset{I}{\overset{O\qquad\qquad O}{\overset{/\backslash\quad\quad\quad\;\|}{CH_2\!-\!CH\!-\!O\!-\!C\!-\!CH_3}}}$$
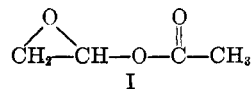
The chemical behavior of I is similar to that of its isomer acetoxyacetaldehyde.[2,3] It gives an immediate silver mirror with Tollens reagent and reacts with phenylhydrazine reagents to give derivatives of acetoxyacetaldehyde. On the other hand, it does not undergo reactions characteristic of epoxides. It did not produce an alkaline re-

(1) N. A. Milas, U. S. Patent 2,402,566 (1946).
(2) H. M. Dawson and J. Marshall, *J. Chem. Soc.*, **105**, 388 (1914).
(3) W. F. Gresham, U. S. Patent 2,286,034 (1942).