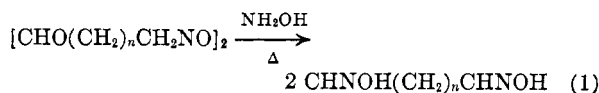


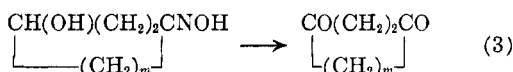
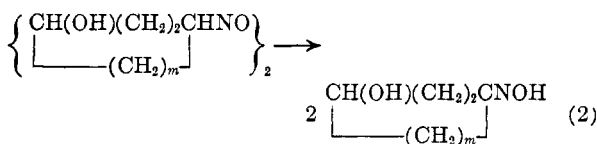
hexyl, and cycloheptyl nitrites yielded *linear* nitroso aldehyde dimers, 4-nitrosobutanal, 5-nitrosopentanal, 6-nitrosohexanal, and 7-nitrosoheptanal dimers, respectively, by the cleavage mechanism. These were not directly characterized since they were not particularly stable. The presence of an aldehyde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



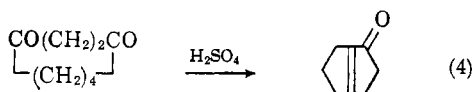
conversion of the nitroso dimer group to an *aldoxime* concomitantly with the formation of the oxime derivative on the aldehyde group.

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



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-cycloöctanedione ($m = 4$)^{11,12} were formed, respectively. The 1,4-cycloöctanedione was further characterized by an intramolecular condensation reaction 4 to form the known bicyclo[3.3.0]-1(5)-octen-2-one.^{11,12}



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 nitrites⁵ 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. Cycloöctyl nitrite photolysis did not produce any detectable nitroso dimer by

the ring fission process. Gray¹³ has reported ring fission during the pyrolysis of cyclohexyl nitrite to form 6-nitroso-1-hexanol.

Cycloheptyl and cycloöctyl 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 Cope¹⁴ 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).

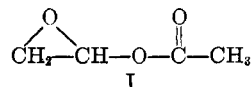
Synthesis of Vinyl Acetate Epoxide

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The reaction of vinyl acetate with hydrogen peroxide has been reported to yield glycoaldehyde.¹ The reaction presumably proceeded through an intermediate epoxide or hemiacetal 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.



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).

action with aqueous sodium thiosulfate, nor did it absorb hydrogen chloride from ether solution.

Treatment of I with aqueous acid or base causes rapid hydrolysis to glycolaldehyde and acetic acid. Acetoxyacetaldehyde itself is known to hydrolyze readily in water.⁴ The hydrolysis of I also appears to occur slowly in the absence of acid or base. Thus, a freshly prepared aqueous solution of I could be titrated slowly with 0.1 N sodium hydroxide, while a similar solution aged twenty-four hours could be titrated rapidly. The equivalent weight by titration was 105 (calcd. 102). These reactions indicate that the compound could be either I or acetoxyacetaldehyde. A comparison of their infrared and ultraviolet spectra as well as their refractive indices serves to distinguish between the two compounds.

The infrared spectrum of I contained bands at 3.35, 5.7, 6.8 (w), 7.0 (w), 7.35, 7.82, 8.2, 8.78 (w), 9.0, 9.25 (w), 9.55 (w), 9.9, 10.2, 10.4 (w), 10.75 (w), 11.25, 11.87, and 12.8 μ . The vinyl double bond absorption of vinyl acetate at 6.1 and 10.5 μ had disappeared. The strong peak at 9.0 μ was new. The acetate carbonyl absorption at 5.7 μ and the peak at 8.2 μ were present in both I and vinyl acetate.

The infrared spectrum of acetoxyacetaldehyde contained bands at 2.90 (w), 3.45 (w), 3.55 (w), 3.70 (w), 5.72–5.8 (broad), 7.10 (w), 7.3, 8.2, 8.7 (w), 9.2 (w), 9.50, 10.0 (w), 10.4 (w), 11.3 (w), 11.8 (w), and 12.8 μ (w). The peaks at 3.55 and 3.70 μ are assigned to the aldehyde C—H absorption. The peak for carbonyl CO absorption at 5.7–5.8 μ did not appear to be split as determined on a Perkin-Elmer Infracord.

The ultraviolet spectrum of acetoxyacetaldehyde has a peak at 287 m μ , ϵ (CCl₄) 9.3. At the same wave length, for I, ϵ 0.9.

Experimental

Vinyl Acetate Epoxide (I).—To a filtered solution of 24 g. of perbenzoic acid⁵ in 400 ml. of chloroform was added 15 ml. of vinyl acetate. The mixture was stored at 5° for 6 days. The solution was decanted from the precipitate of benzoic acid and then extracted with 40 ml. of a saturated aqueous solution of potassium bicarbonate. The chloroform layer was dried over anhydrous sodium sulfate and the solvent stripped off under vacuum at 0° in a spinning band still. The residual liquid was then distilled in the spinning band to give 4 g. (25%) of colorless liquid distilling at 35–40°/5 mm., 140°/760 mm., n_{25}^D 1.4071, d_{25}^{25} 1.13 g./ml. (NOTE: the compound should be handled with care until its explosive properties have been determined.)

Anal. Calcd. for C₄H₆O₃: C, 47.06; H, 5.92; O, 47.02. Found: C, 46.62, 46.62; H, 5.84, 5.97; O, 46.70, 47.15.

Vapor phase chromatography (silicone grease on Celite) indicated that the sample contained 99% I and 1% acetic acid. For comparison, the b.p. of acetoxyacetaldehyde is reported as 108–112°/760 mm.² and 90°/50 mm.³

(4) C. D. Hurd and E. M. Filachione, *J. Am. Chem. Soc.*, **61**, 1156 (1939).

(5) G. Brown, "Organic Syntheses," Coll. Vol. I, Wiley, New York, N. Y., 1941, p. 431.

The phenylhydrazone of acetoxyacetaldehyde was prepared by treating I with phenylhydrazine acetate according to the standard procedure.⁶ Its melting point was 126° (lit., 128°²).

The *p*-nitrophenylhydrazone of acetoxyacetaldehyde, prepared from I, melted at 300°.

Anal. Calcd. for C₁₀H₁₁N₃O₄: C, 50.65; H, 4.64. Found: C, 51.11; H, 4.73.

Acetoxyacetaldehyde.—To 38.0 g. of 1,2-diacetoxy-1-ethoxyethane⁷ was added 3.6 g. of water and one drop of concentrated hydrochloric acid. The water was immiscible. The mixture was stirred vigorously at room temperature for 15 hr. At the end of this period, a homogeneous solution was obtained and distilled through a 15-in. spinning band column at 50 mm. The first distillate, 38–45°, was a mixture of acetic acid and ethyl acetate (approx. 11.3 g.). A second fraction which distilled at 75° was the acetoxyacetaldehyde, n_{25}^D 1.4220, d_{25}^{25} 1.21 g./ml. (yield, approx. 5.2 g.). The material is hygroscopic.

Anal. Calcd. for C₄H₆O₃: C, 47.06; H, 5.92; O, 47.02. Found: C, 46.80, 46.64; H, 6.25, 6.10; O, 46.90, 47.03.

The acetoxyacetaldehyde on being shaken with an aqueous solution of semicarbazide hydrochloride formed a semicarbazone which was recrystallized from water to give white crystals, m.p. 170–172° (lit. 170°).⁷

Anal. Calcd. for C₈H₈N₂O₃: C, 37.8; H, 5.69; N, 26.4. Found: C, 37.90; H, 5.70; N, 26.14.

(6) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, 1956, p. 131.

(7) Criegee, "Neuere Methoden Preparativen Organische Chemie," Vol. II, 266.

Tetrachloro-*o*-benzoquinone by Direct Oxidation of Pentachlorophenol

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It is generally accepted that *o*-benzoquinones are formed only if there are two *ortho* substituents attached to the benzene ring, such as in catechol and *o*-aminophenols.^{1,2} Reed³ recently oxidized pentachlorophenol with nitric acid in trifluoroacetic acid and trifluoroacetic anhydride at –20° and obtained 2,3,4,5,6-pentachloro-4-pentachlorophenoxy-2,5-cyclohexadienone in 64% yield. Baral⁴ reported oxidation of pentachlorophenol with fuming nitric acid under two experimental conditions, the only isolated product being chloranil in 16.6 and 40% yield.

We found⁵ that fuming nitric acid, unlike the system used by Reed,³ did not react with penta-

(1) J. Cason, *Org. Reactions*, IV, 313 (1948).

(2) Z. E. Jolles in E. H. Rodd, Ed., "Chemistry of Carbon Compounds," Vol. IIIB, Elsevier Publishing Co., New York, 1956, p. 689.

(3) R. Reed, Jr., *J. Am. Chem. Soc.*, **80**, 219 (1958).

(4) M. E. Baral, *Bull. soc. chim. France*, [3] **27**, 2710 (1902).

(5) While this manuscript was in preparation, A. L. Rocklin disclosed the preparation of tetrachloro-*o*-benzoquinone by nitric acid oxidation of pentachlorophenol, U.S. Patent 2,920,082 (1960).