examined, with the results shown in Table III. The cryoscopic molecular weight determinations were carried out in 1,4-dioxane, purified according to the method of Eigenberger.[13] Two concentrations were used, and the average value obtained did not differ by more than 3% from the individual results.

Summary

The hypothetical intermediates of the stepwise polymerization of ethylene oxide, namely, the pure synthetic polyoxyethylene glycols, have been shown to react with ethylene oxide in the presence of a catalyst to give higher polymers. This reaction takes place even with the eighteen-membered glycol. It has also been shown that the polymerization products from ethylene oxide are capable of reacting further with the monomer. On the basis of this and other evidence, it is concluded that ethylene oxide polymerizes by a stepwise series of reactions.

MONTREAL, CANADA RECEIVED JUNE 8, 1940

---

[13] Eigenberger, *J. prakt. Chem.*, [2] **130**, 75 (1931).

[CONTRIBUTION FROM THE RESEARCH DIVISION OF THE COMMERCIAL SOLVENTS CORPORATION]

β-Dioximes and Trialkylisoxazoles from Nitroparaffins

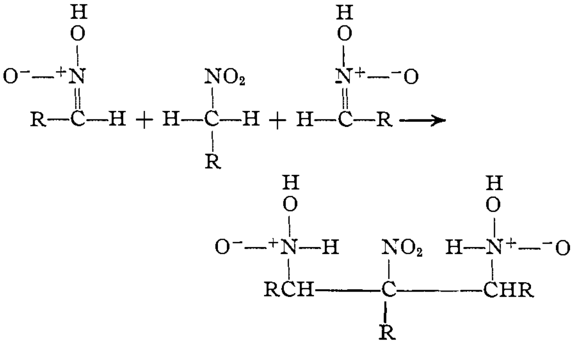
BY SAMUEL B. LIPPINCOTT

Early investigators[1,2] in the field of nitroparaffins discoverd a very interesting reaction in which trialkylisoxazoles are produced from primary nitroparaffins of more than one carbon atom in the presence of basic substances. By employing milder conditions than those used by the earlier investigators a new compound has been isolated from each of the nitroparaffins, nitroethane, 1-nitropropane and 1-nitrobutane. Upon refluxing with dilute acids each of these new compounds yields one mole of hydroxylamine and one mole of trialkylisoxazole. This fact, together with the analyses of the compounds, has led to the conclusion that they are β-dioximes of the general formula $RC(=NOH)CHRC(=NOH)R$. Dunstan and his co-workers suspected that derivatives of the β-dioximes were precursors of the trialkylisoxazoles but they were unable to isolate any such products. They therefore proposed a mechanism for the reaction that did not include any such intermediate. The following mechanism is now proposed.

Step 1.—In the presence of mild bases the nitroparaffin exists in the two forms, normal and *aci*.

$$RCH_2NO_2 \rightleftarrows RCH{=}NOOH$$

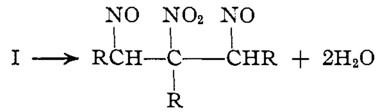
Step 2.—A condensation takes place in which two molecules of the *aci*-form unite with one molecule of the normal form.



$$\mathrm{R{-}\overset{\overset{O^{-}{-}{}^{+}\overset{HO}{N}}{\|}}{C}{-}H + H{-}\underset{R}{\overset{NO_2}{C}}{-}H + H{-}\overset{\overset{\overset{HO}{N^{+}}{-}{}^{-}O}{\|}}{C}{-}R \longrightarrow R\overset{O^{-}{-}{}^{+}\overset{HO}{N}{-}H}{CH}{-}\underset{R}{\overset{NO_2}{C}}{-}\overset{H{-}\overset{HO}{N^{+}}{-}{}^{-}O}{CHR}}$$

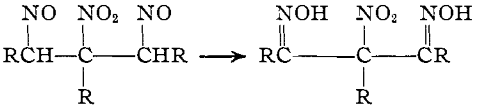
I

Step 3.—This molecule loses two molecules of water.



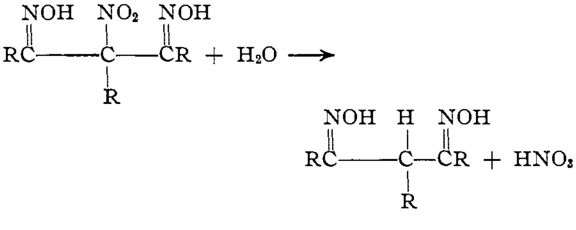
$$\mathrm{I \longrightarrow R\overset{NO}{CH}{-}\underset{R}{\overset{NO_2}{C}}{-}\overset{NO}{C}HR + 2H_2O}$$

Step 4.—The nitroso groups rearrange to isonitroso or oxime groups.



$$\mathrm{R\overset{NO}{CH}{-}\underset{R}{\overset{NO_2}{C}}{-}\overset{NO}{C}HR \longrightarrow R\overset{\overset{NOH}{\|}}{C}{-}\underset{R}{\overset{NO_2}{C}}{-}\overset{\overset{NOH}{\|}}{C}R}$$

Step 5.—Under the influence of the negative oxime groups the nitro group is lost by hydrolysis.



$$\mathrm{R\overset{\overset{NOH}{\|}}{C}{-}\underset{R}{\overset{NO_2}{C}}{-}\overset{\overset{NOH}{\|}}{C}R + H_2O \longrightarrow R\overset{\overset{NOH}{\|}}{C}{-}\underset{R}{\overset{H}{C}}{-}\overset{\overset{NOH}{\|}}{C}R + HNO_3}$$

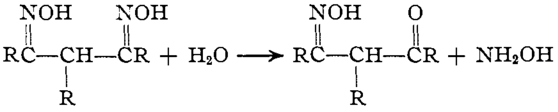
---

[1] Dunstan and Dymond, *J. Chem. Soc.*, **59**, 410 (1891).

[2] Dunstan and Goulding, *ibid.*, **77**, 1262 (1900).

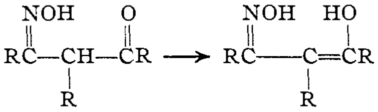
This step is the reversal of the nitration reaction and, so far as the writer is aware, such a hydrolysis has not been reported in the literature. Nitric acid was found in the reaction mixture but never in a 1:1 ratio with the β-dioxime. Its presence is not offered as proof of this mechanism but simply as additional evidence.

Step 6.—One of the oxime groups is lost by hydrolysis.



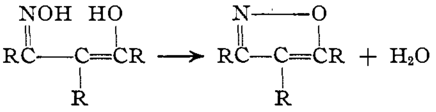
$$\overset{NOH}{\overset{\|}{RC}}-\underset{\underset{R}{|}}{CH}-\overset{NOH}{\overset{\|}{CR}} + H_2O \longrightarrow \overset{NOH}{\overset{\|}{RC}}-\underset{\underset{R}{|}}{CH}-\overset{O}{\overset{\|}{CR}} + NH_2OH$$

Step 7.—The keto group enolizes.



$$\overset{NOH}{\overset{\|}{RC}}-\underset{\underset{R}{|}}{CH}-\overset{O}{\overset{\|}{CR}} \longrightarrow \overset{NOH}{\overset{\|}{RC}}-\underset{\underset{R}{|}}{C}=\overset{HO}{\overset{|}{CR}}$$

Step 8.—The ring is closed with elimination of water.



$$\overset{NOH}{\overset{\|}{RC}}-\underset{\underset{R}{|}}{C}=\overset{HO}{\overset{|}{CR}} \longrightarrow \overset{N\text{———}O}{\overset{\|\qquad\quad|}{RC-\underset{\underset{R}{|}}{C}=CR}} + H_2O$$

The decomposition of β-dioximes to give hydroxylamine and isoxazoles is a well-known reaction found in many text-books of organic chemistry. If it is carried out in an acid medium, the hydroxylamine is in the form of a stable hydroxylammonium salt. The reaction also takes place by heating the dioxime alone or an aqueous solution[3] or, as reported below, by heating an alkaline solution. In these cases, however, the hydroxylamine is unstable.

Experimental

3-Methyl-2,4-pentanedione Dioxime.—One mole of nitroethane, one mole of mono-*n*-propylamine and one-quarter mole of water were mixed in a glass-stoppered bottle and allowed to stand at room temperature for three weeks. During the first part of this period it was necessary to cool the mixture occasionally by placing the bottle in a pan of cold water. At the end of the reaction period the mixture was diluted to 250 cc. with water and placed in a refrigerator at about 5° for a day. A solid separated from the mixture. This was collected on a filter paper, washed with water and dried; yield 7 g., or 15% of the theoretical. The product was recrystallized from methanol several times. The white crystalline solid melted at 132.2 ± 0.1°. It was insoluble in water.

A product obtained from a mixture of nitroethane, diethylamine and water was shown by mixed melting points to be the same compound as that described above.

Anal. Calcd. for $C_6H_{12}O_2N_2$: N, 19.44; NH_2OH, 0.229 g. per g. of sample. Found: N, 19.64; NH_2OH, 0.232 g. per g. of sample.

The analysis for hydroxylamine was carried out by refluxing a weighed sample with an excess of dilute sulfuric acid and determining the hydroxylamine content by Raschig's method.[4] The calculated value for hydroxylamine was based on the assumption that only one mole of hydroxylamine would be produced from one mole of dioxime.

4-Ethyl-3,5-heptanedione Dioxime.—One mole of 1-nitropropane, one mole of mono-*n*-butylamine and 0.3 mole of water were mixed in a glass-stoppered bottle and allowed to stand at room temperature for five weeks during which time crystals separated from the mixture. Sufficient water was added to make the total volume 500 cc. and the mixture was placed in a refrigerator at approximately 5° for a day. The product was collected on filter paper, washed with water and dried; yield 35 g., or 57% of the theoretical. The nitrate ion content of the water layer was determined by precipitation of nitron nitrate[5] taking the precautions necessary to eliminate interference from nitrous acid. It was found to be equivalent to 6.08 g. of nitric acid. The ratio of moles of nitric acid to moles of dioxime was, therefore, 0.5.

After recrystallization from methanol several times the white crystalline product melted at 135.4 ± 0.1°. It was insoluble in water.

A product obtained from 1-nitropropane with *n*-propylamine was shown by mixed melting points to be the same compound as that described above.

Anal. Calcd. for $C_9H_{18}O_2N_2$: N, 15.05; NH_2OH, 0.178 g. per g. of sample. Found: N, 15.19; NH_2OH, 0.179 g. per g. of sample.

5-*n*-Propyl-4,6-nonanedione Dioxime.—One mole of 1-nitrobutane and one mole of mono-*n*-butylamine were mixed in a glass-stoppered bottle and allowed to stand at room temperature for six weeks. One-quarter mole of water was added and the mixture allowed to stand for two weeks, during which time a solid crystallized from the mixture. The mixture was placed in a refrigerator at approximately 5° for a day and then was filtered. A second crop of crystals was obtained by chilling the mother liquor. The product was washed with a little cold methanol; yield 28 g., or 37% of the theoretical.

The product was recrystallized from methanol several times. The pure white crystals melted at 116.6 ± 0.2° and were insoluble in water.

Anal. Calcd. for $C_{12}H_{24}O_2N_2$: N, 12.28; NH_2OH, 0.145 g. per g. of sample. Found: N, 12.19; NH_2OH, 0.152 g. per g. of sample.

3,4,5-Trimethylisoxazole.—Due to the small amount of 3-methyl-2,4-pentanedione dioxime produced no attempt was made to prepare pure trimethylisoxazole from it. However, the odor of this product was very noticeable when a small amount of the dioxime was refluxed with dilute sulfuric acid and, as noted above, the hydroxylamine

---

(3) Tafel and Pfeffermann, *Ber.*, **36**, 219 (1903).

(4) W. W. Scott, "Standard Methods of Chemical Analysis," 5th ed., Vol. I, D. Van Nostrand Company, New York, N. Y., 1938, p. 645.

(5) W. W. Scott, *ibid.*, Vol. I, p. 635.

determination indicated that the conversion was practically quantitative.

3,4,5-Triethylisoxazole.—4-Ethyl-3,5-heptanedione dioxime (100 g.) and 3 *N* sulfuric acid (200 cc.) were refluxed for four hours. The layers of the reaction mixture were separated and the oil layer was washed with a little water. It weighed 84 g. This was distilled under vacuum yielding 80.5 g. of product, 98% of the theoretical. The hydroxylamine content of the water layer and washings was determined by Raschig's method. It was found to be 17.8 g., which is the theoretical amount. The hydroxylamine was further identified by conversion to acetoxime. Triethylisoxazole is a colorless liquid; b. p. (761) 215.3 ± 0.2°, d^{20}_{20} 0.9363, $n^{20}\text{D}$ 1.45803.

Anal. Calcd. for $C_9H_{15}NO$: N, 9.15. Found: N, 9.17.

Triethylisoxazole was also prepared by dissolving 4-ethyl-3,5-heptanedione dioxime in dilute sodium hydroxide solution and steam distilling. The product separated from the distillate.

3,4,5-Tri-*n*-propylisoxazole.—5-*n*-Propyl-4,6-nonanedione dioxime (45.2 g.) and 2 *N* sulfuric acid (270 cc.) were refluxed for six hours. The layers of the reaction mixture were separated and the oil layer was washed with a little water. The oil layer weighed 40 g. This was vacuum distilled, yielding 36 g. or 96% of the theoretical. The aqueous layer and washings were combined and analyzed for hydroxylamine; yield, 6.3 g., or 96% of the theoretical. Tripropylisoxazole is a water white liquid, b. p. 255.5 ± 0.2°, d^{20}_{20} 0.9128, $n^{20}\text{D}$ 1.46088.

Summary

1. 3-Methyl-2,4-pentanedione dioxime, 4-ethyl-3,5-heptanedione dioxime and 5-*n*-propyl-4,6-nonanedione dioxime have been prepared from nitroethane, 1-nitropropane and 1-nitrobutane, respectively.

2. The dioximes named above were converted to the corresponding trialkylisoxazoles and hydroxylamine.

3. A mechanism for the conversion of primary nitroparaffins to isoxazoles has been proposed.

Terre Haute, Indiana Received July 12, 1940

[Contribution from the Chemical Laboratory of Iowa State College]

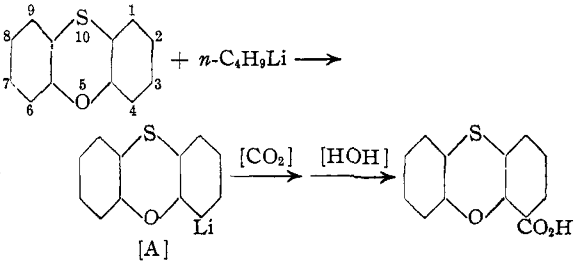
The Metalation of Phenoxathiin

By Henry Gilman, Marian W. Van Ess, H. B. Willis and C. G. Stuckwisch

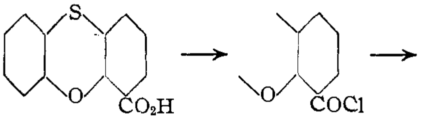
The initial purpose of this study was to investigate the possibility of synthesizing dibenzofuran derivatives from phenoxathiin compounds by the removal of sulfur.

Metalation.—Carbonation of the *n*-butyllithium metalation product of phenoxathiin gave an acid which melted at 168–169°. Decarboxylation of this acid to phenoxathiin showed that there was no cleavage of the oxygen or sulfur bridge. Suter and co-workers[1a] had previously prepared 2-phenoxathiincarboxylic acid, and found it to melt at 260–262°; and Mauthner's[2] 3-phenoxathiincarboxylic acid melts at 223°. Accordingly, the acid obtained by metalation must have the carboxyl group in either the 1- or 4-position. By analogy with earlier extensive studies[3] one might have predicted that metalation would have involved the 1- or 4-position. However, because anomalous orientations in metalations have been noted with sulfides,[4] all four possible positions might have been involved originally On the assumption that metalation probably took place in the 4-position, two different ring-closures were tried for the synthesis of 4-phenoxathiincarboxylic acid. These were unsuccessful, and are described in the Experimental Part.

The acid was shown to be 4-phenoxathiincarboxylic acid by an indirect procedure involving



comparison with the chlorophenoxathiins. Inasmuch as three of the four possible chlorophenoxathiins were known, and among them 4-chlorophenoxathiin, we converted our acid to a chloro derivative by the following sequence of reactions



---

[1] (a) Suter, McKenzie and Maxwell, This Journal, **58**, 717 (1936); (b) Suter and Maxwell, "Organic Syntheses," Vol. 18, 1938, p. 64.

[2] Mauthner, *Ber.*, **39**, 1340 (1906).

[3] Gilman and Bebb, This Journal, **61**, 109 (1939).

[4] Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1938); Gilman, Jacoby and Pacevitz, *ibid.*, **3**, 120 (1938); Gilman and Webb, This Journal, **62**, 987 (1940).