TABLE IV

SODIUM SALTS OF THE MERCURY DERIVATIVES OF α-HY-
DROXYFLUOROCARBONMALONAMIDES

| [RC(O)-<br>(C₂O₂N₂H₂)]₂HgNa₂<br>R | M.p.,<br>°C. | Mercury,[a] %<br>Theory Found | | Nitrogen, %<br>Theory Found | |
|---|---|---|---|---|---|
| CF₃- | >360 | 32.57 | 32.11 | 9.12 | 8.95 |
| CF₃CF₂- | >360 | 28.01 | 27.63 | 7.84 | 7.79 |
| CF₃CF₂CF₂- | >360 | 24.57 | 24.19 | 6.87 | 6.63 |

[a] The mercury analysis was performed according to the procedure of Rauscher.[2]

2 hr. with the tip of the receiving condenser immersed in 25 ml. of standard hydrochloric acid. The solution was then steam distilled until the total volume in the receiving flask was 150 ml. This was titrated with standard sodium hydroxide solution, using methyl red indicator. The results indicated approximately two equivalents of ammonia for each equivalent of α-hydroxypentafluoroethylmalonamide.

After steam distillation, the alkaline residue was acidified with 50% sulfuric acid. The carbon dioxide that evolved was passed immediately through a calcium chloride drying tube and collected in a U-tube containing Ascarite. The weight of carbon dioxide corresponded approximately to one equivalent of the original α-hydroxypentafluoroethylmalonamide.

The acidic solution from above was extracted with ethyl ether and the ether removed. The colorless liquid that remained was very acid to pH paper. This liquid was added to 20 ml. of water containing 2.0 g. of silver oxide, the mixture refluxed for 30 minutes, filtered and the water evaporated under reduced pressure. A white crystalline, ether soluble, silver salt remained. This compound did not contain nitrogen. A gravimetric silver chloride analysis of an aqueous solution of this salt indicated 35.70% silver. This salt was not identified further, although it was believed to be a silver salt of the corresponding α-hydroxy or α-keto acid.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TULANE UNIVERSITY]

# Dehydrogenation of Glyoximes[1]

BY J. H. BOYER AND U. TOGGWEILER

The dehydrogenation of certain quinonoid and non-quinonoid glyoximes with chlorine, sodium hypochlorite or dinitrogen tetroxide was investigated.

Aldoximes and vicinal dioximes but not ketoximes[2] undergo simple intramolecular dehydrogenation. Polymerization of nitrile oxides, from aldoximes, leads to the formation of furoxanes, together with other products. Furoxanes and ψ-o-dinitrosoaromatic compounds have been obtained from cyclic non-quinonoid and o-quinonoid glyoximes, respectively.

Moderately useful chemical reagents for the dehydrogenation of aldoximes and glyoximes are dinitrogen tetroxide,[3] sodium hypohalite[4] and alkaline ferricyanide.[3,5] Nitric acid and arsenic trioxide[6] have been used less frequently and nitrous acid,[7] nitrogen trioxide[8] or amyl nitrite[9] inefficiently oxidizes aldoximes to nitrile oxides. In contrast, Caro's acid oxidizes both aldoximes and ketoximes to the corresponding nitro compounds.[10]

Hydroxamic acid chlorides resulted from combinations of aldoximes and chlorine[11] or nitrosyl chloride[12] while gem-chloro-nitroso compounds have been similarly obtained from ketoximes.[11,12] Dehydrochlorination of the hydroxamic acid chlorides occurs upon formation or upon mild treatment with alkali and the nitrile oxide thereby obtained polymerizes.[12]

The action of chlorine upon glyoximes has now been investigated. In agreement with the earlier work on monoximes, an immediate blue color characteristic of C-nitroso monomers developed upon combination of dialkyl glyoximes and chlorine in benzene or ethanol and disappeared upon warming. An intermediate gem-chloro-nitroso derivative apparently was formed. An unstable and impure colorless solid resulted from the combination of chlorine and decalin-2,3-dione dioxime and it gave a positive Beilstein test for halogen. Attempts to purify the compound were unsuccessful. In the treatment of benzil dioxime with chlorine a very dark color developed and faded rapidly. A high yield of diphenylfuroxane (I) was obtained, in sharp contrast to no yield of dialkyl furoxanes from corresponding dioximes.

Earlier attempts to oxidize phenanthrene-9,10-quinone dioxime to ψ-9,10-dinitrosophenanthrene (II) failed.[13] Both this quinonoid glyoxime and o-benzquinone dioxime were successfully dehydrogenated by chlorine into the corresponding ψ-o-

(1) The financial support for this work was provided by the Office of Ordnance Research, U. S. Army, under contracts No. DA-01-ORD-331 and DA-01-ORD-428.

(2) A. Mailhe and F. de Godon, Bull. soc. chim., 23, 18 (1918), reported the formation of nitriles, hydrogen, olefins, ammonia and amines from dialkyl ketoximes over thorium or aluminum oxide catalysts at 350°.

(3) R. Scholl, Ber., 21, 506 (1888); 23, 3490 (1890).

(4) G. Panzio, Atti reale accad. sci. Torino, 41, 11/2 (1906); Chem. Zentr., 77, I, 1700 (1906); J. Meisenheimer, H. Lange and W. Lamparter, Ann., 444, 94 (1925); P. Robin, Ann. chim., 16, 77 (1921); E. M. Cherkasova and N. N. Mel'nikov, Zhur. Obshchei Khim., 19, 321 (1949); C. A., 43, 6569 (1949).

(5) R. Koreff, Ber., 19, 176 (1886).

(6) E. Beckmann, ibid., 22, 1588 (1889).

(7) E. Beckmann, ibid., 22, 1501 (1889).

(8) R. Ciusa and E. Parisi, Gazz. chim. ital., 55, 416 (1925).

(9) C. Minunni and R. Ciusa, Atti accad. Lincei, 14, II, 518 (1905).

(10) E. Bamberger, Ber., 35, 4293 (1902); E. Bamberger and R. Seligman, ibid., 35, 4299 (1902).

(11) E. Graf, Annales soc. español. fís. quím., 34, 91 (1936); C. A., 30, 4432 (1936).

(12) H. Rheinboldt and M. Dewald, Ann., 455, 300 (1927), for leading references.

(13) J. H. Boyer, R. F. Reinisch, M. J. Danzig, G. A. Stoner and F. Sahhar, THIS JOURNAL, 77, 5688 (1955).

dinitrosoaromatic compounds. A blue color was not detected in either reaction.

The action of dinitrogen tetroxide and sodium hypochlorite upon certain glyoximes was also investigated. In contrast to the formation of dimethylfuroxane from dimethylglyoxime and dinitrogen tetroxide in ether,[3] nioxime under similar conditions was transformed into a product to which the structure of a dinitrocyclohexenfuroxane has been tentatively assigned. In liquid dinitrogen tetroxide it underwent more extensive oxidation and adipic acid was obtained in working up the product. Nioxime and decalin-2,3-dione dioxime were oxidized by sodium hypochlorite into cyclohexenfuroxane (III) and octalin-2,3-furoxane (IV), respectively.
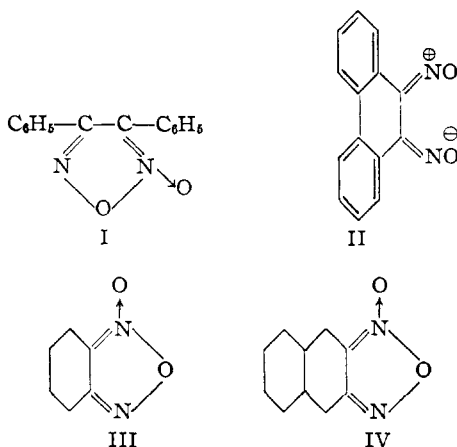


## Experimental[14]

**Preparation of the Glyoximes.**—According to a modified procedure of Ganapathi,[15] technical 2-decalone[16] was oxidized with selenium dioxide to 2,3-diketodecalin, b.p. 106–111° (3 mm.), m.p. 100–101° (lit.[15] m.p. 100–101°), 32% yield. The product was not extracted from the reaction mixture with ether[15] but was immediately isolated by distillation. Upon treatment with hot alkaline peroxide solution, 2,3-diketodecalin was converted into β,β'-tetramethylenesuccinic acid, m.p. 168–169° (lit.[15] m.p. 167°). When refluxed with o-phenylenediamine in acetic acid, the corresponding quinoxaline was obtained, m.p. 178–179° (lit.[17] 177°). With hydroxylamine, the diketone was transformed into the corresponding dioxime, m.p. 227–228° dec. (lit.[15] m.p. 229° dec.) which gave a characteristic rose, ethanol-insoluble complex with a nickel salt.

Nioxime was commercially available.

In the preparation of γ-benzil dioxime, the directions of Auwers and Meyer[18] were modified. To 190 ml. of 60% ethanol, 21 g. (0.1 mole) of benzil and 6.8 g. (0.1 mole) of hydroxylamine hydrochloride were added. The reaction mixture was refluxed for 3 hours, cooled, poured into 400 ml. of water, treated with sodium hydroxide until homogeneous and acidified with 6 N hydrochloric acid. Crude β-benzil monoxime, m.p. 106–107° (lit.[18] 113–114°), 17 g. (75%), slowly precipitated. Five grams (0.02 mole) of β-benzil monoxime dissolved in 100 ml. of 20% aqueous sodium hydroxide solution containing 10 g. of hydroxylamine hydrochloride was kept at room temperature for 6 hours. The sodium salt of γ-benzil dioxime was isolated by filtration,

dissolved in 250 ml. of water, neutralized with finely powdered Dry Ice, filtered with suction, and washed with ice-cold water. The resulting dioxime recrystallized from 95% ethanol upon cooling in a Dry Ice–acetone slurry and was dried over sulfuric acid. The purified γ-benzil dioxime, 3.0 g. (60%), melted at 164–165° (lit.[18] m.p. 164–166°), but resolidified and upon further heating was converted into the β-isomer, m.p. 210–211° (lit.[18] m.p. 206°).

A nickel complex was not obtained from γ-benzil dioxime upon adding nickelous nitrate to a hot alcoholic solution of the dioxime. Under similar conditions a nickel complex of the α-isomer was obtained.

Freshly distilled aniline saturated with α-benzil dioxime,[18] m.p. 240–241° (lit.[18] m.p. 237°), was refluxed for one hour.[19] Solid **β-benzil dioxime** separated quantitatively upon cooling and was filtered and washed with dilute hydrochloric acid and cold water. The β-dioxime did not form a complex with nickel salts. It recrystallized twice from dilute ethanol as colorless leaflets, m.p. 210–211° (lit.[18] m.p. 206°), which contained alcohol of crystallization.

**Oxidation of Glyoximes with Chlorine.**—Chlorine gas was bubbled into 10 ml. of an ethanol or benzene solution of 1.0 g. (0.004 mole) of α- (poorly soluble), β- or γ-benzil dioxime until the solution became colorless. The temperature was kept under 40°. Upon cooling, diphenylfuroxane separated and was recrystallized from 90% ethanol from which it separated as colorless needles, 0.8 g. (80%), m.p. 117–118° (lit.[6] m.p. 114–115°).

In a similar manner o-benzoquinone dioxime and phenanthrene-9,10-quinone dioxime, m.p. 199–200°,[13] were oxidized to ψ-o-dinitrosobenzene, m.p. 72–73°,[20] (75% yield) and ψ-9,10-dinitrosophenanthrene, respectively. Upon a recrystallization from ethanol or benzene, ψ-9,10-dinitrosophenanthrene separated as colorless needles, m.p. 234–235°, in 80% yield.

*Anal.* Calcd. for $C_{14}H_8N_2O_2$: C, 71.20; H, 3.40; N, 11.88. Found: C, 71.05; H, 3.24; N, 11.67.

**Oxidation of Glyoximes with Sodium Hypochlorite.**—A solution of sodium hypochlorite was prepared by bubbling chlorine gas into 20% aqueous sodium hydroxide until the solution was neutral or slightly acidic. This solution was added dropwise to a well-stirred, cold (0–10°) solution of 4.0 g. (0.03 mole) of nioxime in 10% aqueous alcoholic sodium hydroxide. The solution lost its original yellow color as colorless needles of the furoxane separated. The precipitate was recrystallized from low-boiling ligroin, from which cyclohexenfuroxane separated as colorless needles, m.p. 44–45°, 3.0 g. (76%).

*Anal.* Calcd. for $C_6H_8N_2O_2$: C, 51.42; H, 5.75; N, 19.99. Found: C, 51.64; H, 5.74; N, 19.41.

In a similar manner, decalin-2,3-dione dioxime was oxidized to octalin-2,3-furoxane as colorless needles from ligroin, 60% yield, m.p. 84–85°.

*Anal.* Calcd. for $C_{10}H_{14}N_2O_2$: C, 61.84; H, 7.26; N, 14.43. Found: C, 61.39; H, 6.96; N, 14.10.

In a similar preparation of ψ-9,10-dinitrosophenanthrene the reaction mixture was kept under 50°. The product recrystallized from ethanol or benzene as colorless needles, m.p. 234–235°, 75% yield.

**Oxidation of Glyoximes with Dinitrogen Tetroxide.**—To 40 ml. of an ethereal solution of 2.15 g. (0.015 mole) of nioxime, m.p. 189–190°, 1.3 ml. (0.04 mole) of liquid dinitrogen tetroxide was added as the mixture was maintained at 0°. As the dioxime dissolved the solution became blue-green. Stirring was continued for 20 minutes. Evaporation of the ether left a residue which recrystallized from ethanol as colorless needles, 2.4 g., m.p. 115–116° dec. Elemental analysis suggested that the product was a dinitrocyclohexenfuroxane.

*Anal.* Calcd. for $C_6H_6N_4O_6$: C, 31.31; H, 2.63; N, 24.35. Found: C, 31.30; H, 2.87; N, 24.36.

The oxidation of phenanthrene-9,10-quinone dioxime by dinitrogen tetroxide in ether was carried out in a similar manner. Recrystallized ψ-9,10-dinitrosophenanthrene, m. p. 233–234°, was obtained in 70% yield.

Nioxime, m.p. 189–190°, was oxidized in pure liquid dinitrogen tetroxide at 0° over a period of 10 minutes to adipic

(14) Semi-micro analyses by Micro-tech Laboratory, Skokie, Ill. Melting points are corrected.

(15) K. Ganapathi, *J. Ind. Chem. Soc.*, **15**, 407 (1938).

(16) Technical 2-decalone was available from Dehydag, Düsseldorf, Germany. It was a mixture of cis- and trans-2-decalone and contained 10% 2-decalol.

(17) K. Ganapathi, *Current Science*, **6**, 448 (1938); *C. A.*, **32**, 4973 (1938).

(18) K. Auwers and V. Meyer, *Ber.*, **22**, 537, 705 (1889).

(19) O. L. Brady and H. M. Perry, *J. Chem. Soc.*, 3308 (1931).

(20) P. A. S. Smith and J. H. Boyer, *Org. Syntheses*, **31**, 14 (1951).

acid, m.p. and mixture m.p. 150–151°, 21% yield. A similar oxidation of cyclohexanone oxime gave adipic acid in 12% yield.

Trace amounts of diphenylfuroxane were obtained from the oxidation of benzil dioxime with dinitrogen tetroxide.

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# Cationic Polymerization of Ethylene Oxide. I. Stannic Chloride

BY D. J. WORSFOLD AND A. M. EASTHAM

The polymerization of ethylene oxide by stannic chloride in ethylene chloride solution at ordinary temperatures produces polymer of molecular weight below 5000, dioxane and small amounts of dioxolane. Two polymer molecules are formed for each molecule of stannic chloride; dioxane formation is an alternative reaction at the active end of the growing chain. The rate of disappearance of oxide is controlled by the propagation step and is given by the expression $k(\text{oxide})^{0.45}(\text{SnCl}_4)^{1.2}$ obtained from initial rates. Chain termination occurs with catalyst destruction and without transfer at a rate which appears to be first order in catalyst. A mechanism by which propagation occurs through an intermediate oxonium ion is proposed to account for the results.

The polymerization of ethylene oxide may be effected with either acidic or basic catalysts to give linear polyethers with a considerable range of molecular weights. The base-catalyzed reaction has been studied comprehensively by Perry and Hibbert[1] and is of the polycondensation type, but with the exception of a study by Meerwein, et al.,[2] of trialkyl oxonium ions and their reactions with epichlorohydrin, and some remarks by Emeleus and Stone[3] on the reaction of boron trifluoride with ethylene oxide, little work has been reported on the acid-catalyzed polymerization. This paper describes the results of some studies on the polymerization of ethylene oxide by stannic chloride, and is followed by one describing the polymerization by boron fluoride. Of the Friedel–Crafts catalysts tested, only these two gave polymeric products; aluminum, titanium and germanium chlorides are ineffective.

## Experimental

**Materials.**—Ethylene oxide was purified by low temperature distillation, by distillation at −78° from dried sodium hydroxide pellets and finally by drying over barium oxide, all under vacuum.

Stannic chloride was fractionally distilled from tin metal, then twice distilled under vacuum.

Solvents were fractionated from phosphorus pentoxide. Ethylene chloride was treated with aluminum chloride, washed and dried before fractionating.

**Method.**—Polymerizations were carried out in an all-glass vacuum system and the rate of reaction in ethylene chloride solution followed by the decrease in vapor pressure of the reaction mixture. The relationship between oxide concentration and vapor pressure was linear and hence readily determined from known mixtures.

Stannic chloride and water were measured out by allowing the liquid, at controlled temperature, to evaporate into bulbs of known volume until equilibrium was established. The quantity was then determined from the vapor pressure of the liquid.

Ethylene oxide and ethyl chloride were measured in the gas phase, but the less volatile solvents were pipetted into a trap containing phosphorus pentoxide and degassed before distilling into the reaction vessel.

Catalyst, water if any, and solvent in that order were condensed into the reaction vessel and brought to reaction temperature. Ethylene oxide was then rapidly distilled in from

a small side arm on the main reaction vessel. Magnetic stirring established equilibrium within three minutes.

Ethyl chloride was employed as solvent when reaction products were to be determined because it could be separated readily by distillation. Ethylene chloride was used for most of the kinetic studies because of its lower vapor pressure.

Reaction products were isolated by treating a 10% solution of ethylene oxide with one mole per cent. stannic chloride at 20°. Solvent, excess oxide and volatile products were removed by distillation, leaving a white wax having an infrared spectrum identical with that of a polyethylene glycol of similar melting point. The volatile product was found, by mass spectrometer analysis, to consist of 92% dioxane and 8% 2-methyl-1,3-dioxolane.

**Molecular Weights.**—Molecular weights were determined viscometrically in ethylene chloride, using Ostwald viscometers with flow times of about two hundred seconds at 20°. For molecular weights less than 1000 the relationship

$$\eta_{sp}/c = 0.048 + 0.000204\,M$$

was used where $c$ is in base moles per liter. This expression was obtained using commercial polyglycols whose molecular weights were determined by end-group analysis and by the depression of the benzene freezing point.

Molecular weights above 1000 were given by the expression

$$\eta_{sp}/c = 0.160 + 0.000089\,M$$

which was obtained from commercial polyglycols whose molecular weights were first determined in carbon tetrachloride using the viscometric data of Fordyce and Hibbert.[4]

Polymer samples were obtained from the reaction mixture by quenching aliquots in aqueous alcohol, evaporating on a steam-bath, then drying for two or three hours under vacuum at 70°.

## Results

When molar solutions of ethylene oxide were treated in ethylene chloride with a monomer–catalyst ratio of 100:1, reaction stopped before all oxide was consumed. Addition of monomer did not regenerate the reaction but a higher initial concentration of catalyst caused it to go to completion. Apparently stannic chloride is consumed in the reaction; the alternative possibility that the catalyst itself contained some unidentified co-catalyst which was consumed seems unlikely. Because of the consumption of stannic chloride it was necessary to use initial rates to obtain the reaction order. The results are shown in Figs. 1–2 and lead to the kinetic equation

$$-d(C_2H_4O)/dt = k(C_2H_4O)^{0.45}(\text{SnCl}_4)^{1.2} \qquad (1)$$

(1) S. Perry and H. Hibbert, THIS JOURNAL, **62**, 2599 (1940).

(2) H. Meerwein, U. Eisenmenger and H. Matthiae, Ann., **560**, 150 (1950).

(3) F. G. A. Stone and H. J. Emeleus, J. Chem. Soc., 2755 (1950).

(4) R. Fordyce and H. Hibbert, THIS JOURNAL, **61**, 1912 (1939).