

with a separation of about  $5,600 \text{ cm.}^{-1}$  between the peak maxima and the approximate oscillator strengths for these two transitions are 0.58 and 0.23, respectively. Even at low temperature, no fine structures could be observed within the experimental error. Most probably each absorption band represents a separate electronic transition.

A dilute solution of I in 4 parts ether and 1 part tetrahydrofuran<sup>12</sup> shows very strong fluorescence at  $77^\circ\text{K.}$  when illuminated with ultraviolet light. The fluorescence spectrum was photographed on a Steinheil spectrograph and the densitometer tracing of the spectral plate is reproduced in Fig. 2. The fluorescence of most organic molecules in condensed systems results from transitions from the fluorescent state down to the various vibrational levels of the ground state. Taking the normal state of I as zero, the position of the fluorescent level is  $16,500 \pm 50 \text{ cm.}^{-1}$  and the low lying vibrational levels are approximately located at 920 and  $1,600 \text{ cm.}^{-1}$ . The fluorescence of triphenylmethyl appears to be the mirror image of its absorption.<sup>9</sup>

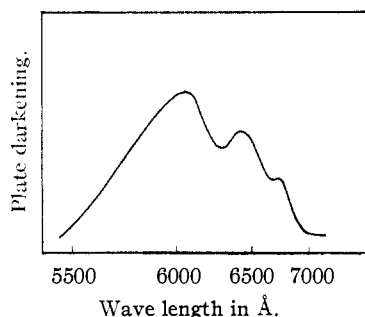


Fig. 2.—Fluorescence spectrum of triphenylboron sodium in 1:4 tetrahydrofuran-ether mixture.

Bent and Dorfman<sup>13</sup> prepared the disodium salt of tris- $\alpha$ -naphthylboron by treating tris- $\alpha$ -naphthylboron in ether solution with 40% sodium amalgam. It may be reported here that triphenylboron also forms dark green disodium salt by prolonged treatment with 40% sodium amalgam in tetrahydrofuran solution. The reversible color change similar to those reported for tris- $\alpha$ -naphthylboron disodium was also observed.

(12) This solvent mixture forms a rigid transparent medium at  $77^\circ\text{K.}$

(13) H. E. Bent and M. Dorfman, *THIS JOURNAL*, **54**, 2132 (1932).

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## Synthesis of Aureomycin Degradation Products. II

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Previous reports<sup>1,2</sup> have shown various phthalides and related compounds to be degradation products

(1) B. L. Hutchings, C. W. Waller, S. Gordon, R. W. Broschard, C. E. Wolf, A. A. Goldman and J. H. Williams, *THIS JOURNAL*, **74**, 3710 (1952).

(2) S. Kushner, J. H. Boothe, J. Morton II, J. Petisi and J. H. Williams, *ibid.*, **74**, 3710 (1952).

of aureomycin. These compounds have for the most part been synthesized for confirmation of structure. From a different portion of the aureomycin molecule some cyclopentane derivatives have been isolated,<sup>3</sup> two of which have been synthesized, namely, 1,3-cyclopentanedione and 1,2,4-cyclopentanetrione.

1,3-Cyclopentanedione was prepared from ethyl methyl  $\beta$ -keto adipate<sup>4</sup> by cyclizing its ethylene ketal<sup>5</sup> with sodium ethoxide followed by hydrolysis and decarboxylation.

1,2,4-Cyclopentanetrione was prepared by treating diethyl oxalate and diethyl acetonedicarboxylate in the presence of sodium ethoxide to yield 3,5-dicarbethoxy-1,2,4-cyclopentanetrione. On hydrolysis and decarboxylation the triketone was obtained.

Richter<sup>6</sup> has described the preparation of 2-carbethoxy-1,3-cyclopentanedione. This compound was prepared in our laboratory and showed none of the properties expected. It could not be hydrolyzed and decarboxylated to the dione, it could not be oxidized to succinic acid, and it showed two C-methyl groups.

Ruggli and Maeder<sup>7</sup> have also reported the preparation of 2-carbethoxy-1,3-cyclopentanedione by the cyclization of methyl ethyl  $\beta$ -keto adipate. They did not characterize the compound however and in our hands this reaction mixture after hydrolysis and decarboxylation did not yield 1,3-cyclopentanedione.

Ruggli and Doebel<sup>8</sup> prepared 2,4-dicarbethoxy-1,3-cyclopentanedione and have oxidized this with selenium dioxide to 3,5-dicarbethoxy-1,2,4-cyclopentanetrione. This compound, obtained in rather small amounts and not thoroughly purified or analyzed, melted approximately  $20^\circ$  below our best sample.

1,3-Cyclopentanedione and 1,2,4-cyclopentanetrione are quite acidic, the former having a  $pK_a$  of 4.5 and the latter a  $pK_a$  of 3.0. The ultraviolet absorption spectra of the dione show maxima at  $257 \text{ m}\mu$  ( $E$  29,400) in 0.1  $N$  sodium hydroxide and at  $242 \text{ m}\mu$  ( $E$  20,700) in 0.1  $N$  hydrochloric acid. The

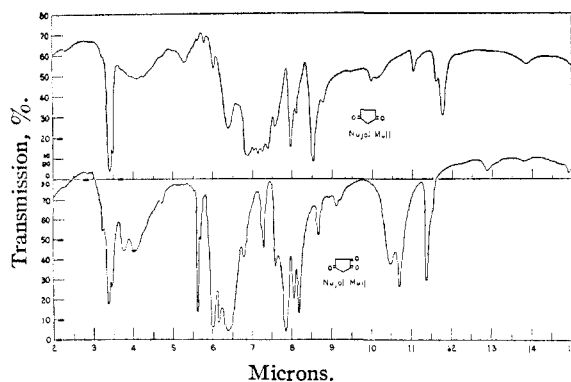


Fig. 1.—Infrared absorption spectra of 1,3-cyclopentanedione and 1,2,4-cyclopentanetrione.

(3) C. W. Waller, *et al.*, *ibid.*, **74**, 4978 (1952).

(4) J. C. Bardhan, *J. Chem. Soc.*, 1848 (1936).

(5) H. Schintz and G. Schappi, *Helv. Chim. Acta*, **30**, 1488 (1947).

(6) R. Richter, *ibid.*, **32**, 1123 (1949).

(7) P. Ruggli and A. Maeder, *ibid.*, **26**, 1476 (1943).

(8) P. Ruggli and K. Doebel, *ibid.*, **29**, 600 (1946).

trione shows maxima at 310  $m\mu$  ( $E$  13,450) in 0.1  $N$  sodium hydroxide and at 267  $m\mu$  ( $E$  10,850) in 0.1  $N$  hydrochloric acid. The infrared absorption spectra of the two compounds are shown in Fig. 1.

### Experimental

**1,3-Cyclopentanedione.**—A mixture of 5.8 g. of ethyl methyl  $\beta$ -ketoacrylate, 2.53 g. of ethylene glycol, 0.01 g. of *p*-toluenesulfonic acid monohydrate and 10 cc. of dry benzene was refluxed four hours using a water separator. The solution was stirred with solid sodium bicarbonate and anhydrous sodium sulfate and decanted onto dry sodium ethoxide (from 0.69 g. of sodium) in a nitrogen atmosphere. About 20 cc. of dry benzene and 20 cc. of dry ether were used to wash the inorganic salts and the mixture was refluxed 45 minutes. After acidification with acetic acid and addition of 15 cc. of concentrated hydrochloric acid, the mixture was filtered and the organic solvents distilled off. The aqueous solution was refluxed 1.5 hours and concentrated to dryness *in vacuo*. The oily residue was evaporatively distilled at 120° (0.5 mm.), and the oily distillate partially crystallized from ethyl acetate. The product was sublimed at 120° (0.5 mm.) to yield 0.211 g. (7.5%) of 1,3-cyclopentanedione, m.p. 151.5–152.5°, which showed no depression upon admixture with the degradation product. *Anal.* Calcd. for  $C_5H_6O_2$ : C, 61.2; H, 6.2. Found: C, 61.0; H, 6.3. The ultraviolet and infrared absorption spectra were identical with those of the degradation product.

**3,5-Dicarbethoxy-1,2,4-cyclopentanetrione.**—A mixture of 2.5 cc. of ethyl oxalate, 3.45 cc. of diethyl acetonedicarboxylate and sodium ethoxide (from 0.8 g. of sodium), in 100 cc. of dry benzene and 25 cc. of dry ether was refluxed under nitrogen for 1.75 hours. The cooled solution was poured into 150 cc. of cold 10% sulfuric acid and the water layer was extracted with ethyl acetate. The combined organic layers were evaporated, and by crystallization from ethyl acetate and sublimation of the residue a total yield of 1.42 g. (28%) was obtained, m.p. 159–162° with gas. *Anal.* Calcd. for  $C_{11}H_{12}O_7$ : C, 51.6; H, 4.7. Found: C, 51.5; H, 4.7.

**1,2,4-Cyclopentanetrione.**—A mixture of 0.22 g. of the above diester was refluxed 90 minutes in 30 cc. of concentrated hydrochloric acid and the solution was concentrated to dryness. The residue was sublimed twice at 90° and 0.5 mm. giving 0.06 g. (62%) of a white solid, m.p. 172.5–173° with decomposition starting at 167°. There was no depression upon admixture with the degradation product from aureomycin. *Anal.* Calcd. for  $C_5H_4O_3$ : C, 53.6; H, 3.6. Found: C, 53.8; H, 3.9. The ultraviolet<sup>3</sup> and infrared spectra of the degradation product and 1,2,4-cyclopentanetrione were identical.

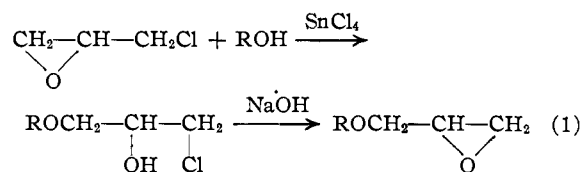
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## Synthesis of Polyglycidyl Ethers

BY SAUL G. COHEN AND HOWARD C. HAAS

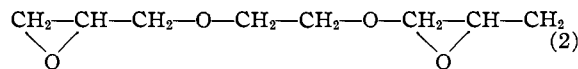
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Monoglycidyl ethers are generally prepared<sup>1</sup> by treating a large excess of an alcohol with epichlorohydrin in the presence of a small amount of stannic chloride and converting the glycerol  $\alpha$ -monochlorohydrin ether which is formed to the glycidyl ether by the action of concentrated aqueous sodium hydroxide solution.



(1) Shell Chemical Corporation Technical Booklet SC: 49-35.

Although the reaction of epichlorohydrin with polyhydric alcohols is discussed, in the literature,<sup>2-7</sup> little information is available on the preparation and isolation of polyglycidyl ethers of the type



by this reaction. The use of excess epichlorohydrin in such a reaction is prohibited because of its rapid polymerization which is catalyzed by acids.

The addition of epichlorohydrin to a polyhydric alcohol in the presence of stannic chloride, one mole of epichlorohydrin per mole of hydroxyl group, led to polyglycidyl ethers in satisfactory yield. This was accomplished, however, only if the conversion of the polychlorohydrin to the polyepoxide was carried out in the presence of a water-immiscible solvent which extracted the polyglycidyl ether as it was formed. Otherwise a vigorous alkali-catalyzed polymerization occurred resulting in almost complete conversion of the polyepoxide to non-volatile products. An example of the procedure is the following preparation of 1,2-bis-(2,3-epoxypropoxy)-ethane, the diglycidyl ether of ethylene glycol.

### Experimental

Ethylene glycol (distilled, 31 g., 0.5 mole) and 0.3 g. of stannic chloride were placed in a three-necked flask equipped with a stirrer, reflux condenser and dropping funnel. The solution was heated to 85–90° and 92.5 g. (1 mole) of epichlorohydrin (Shell) was added over a 16-hour period. Heating was continued for an additional 24 hours after which time no low boiling materials were distilled off under vacuum indicating that the epichlorohydrin had reacted completely. The reaction mixture was cooled and diluted with 100 ml. of ether. Eighty grams of 50% sodium hydroxide was added with vigorous stirring while the reaction was held at ice-bath temperature. The ether solution was decanted from the dense aqueous phase, dried over anhydrous sodium sulfate and fractionated through a 3 ft. column. After stripping off the ether, a small fraction was collected, b.p. 89–90° (10 mm.),  $n_D^{20}$  1.4490. A second larger fraction was collected at 128–131° (10 mm.),  $n_D^{20}$  1.4530. A considerable amount of non-volatile residues remained in the distillation flask. Both fractions were colorless oils which gave positive Beilstein tests indicating halogen impurities. Analysis of the second fraction for oxirane oxygen by hydrochloric acid consumption<sup>8</sup> gave a value of 97% diepoxide; analysis of fraction 1 indicated 88% monoepoxide. Fraction 2 was fractionated and yielded 18 g. of material, b.p. 119° (2–3 mm.),  $d_4^{20}$  1.1182,  $n_D^{20}$  1.4498,  $M_D$  41.80. *Anal.* Calcd. for  $C_8H_{14}O_4$ : C, 55.15; H, 8.1. Found<sup>9</sup>: C, 54.80; H, 8.1.

By use of Eisenlohr's atomic refractivities and a value of 0.22 for the three-membered epoxide ring (calculated from  $M_D$  and  $d$  of epichlorohydrin),  $M_D$  was calculated for the diglycidyl ether and found to be 41.76.

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- (2) J. Nivière, *Compt. rend.*, **156**, 1628 (1913).
- (3) O. Loehr, German Patent 510,422 (October 18, 1930).
- (4) O. Schmidt and E. Meyer, U. S. Patent 1,922,459 (August 15, 1933).
- (5) W. Schneider and A. Fröhlich, U. S. Patent 2,280,722 (April 21, 1942).
- (6) M. DeGroote and B. Keiser, U. S. Patent 2,411,029 (November 12, 1946).
- (7) M. S. Kharasch and W. J. Nudenberg, *J. Org. Chem.*, **8**, 189 (1943).
- (8) S. Siggia, "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 108.
- (9) Analyses were performed by Dr. C. K. Fittz, Boston, Massachusetts.