

poule at 7° for 6720 min. without change in the specific rotation or production of trimethylamine.

**Attempted Racemization of Trimethyl- $\beta$ -phenylisopropylammonium Iodide (II).**—(–)II, prepared by methylation of  $\beta$ -phenylisopropylamine with methyl iodide and aqueous sodium carbonate, was recrystallized from alcohol as colorless needles, m.p. 202–203° (reported<sup>7</sup> m.p. 204–205°). A solution of 0.305 g. ( $10^{-3}$  mole) of II in 7 cc. of 0.15 *N* sodium hydroxide with  $[\alpha]_D -3.9$  was heated at 81° for 6720 min. The reaction mixture, smelling strongly ammoniacal, contained an oil which was extracted with ether. The residue from the dried, concentrated ether solution was dissolved in 0.5 cc. of carbon tetrachloride and treated with bromine until permanently colored. Evaporation of the solvent left a solid which was crystallized from ethanol to give 1-phenyl-1,2-dibromopropane, m.p. 65–66.5° (reported<sup>8</sup> m.p. 65–66°), showing no depression of m.p. on admixture with authentic material.

Concentration of the aqueous portion of the reaction mixture gave solid material which was extracted with chloroform. Evaporation of the chloroform left crystalline starting material,  $[\alpha]_D -3.9$  ( $c$  4.4, 0.15 *N* sodium hydroxide).

(7) K. Freudenberg and F. Nikolai, *Ann.*, **510**, 223 (1934).

(8) W. H. Perkin, *J. Chem. Soc.*, **32**, 660 (1877).

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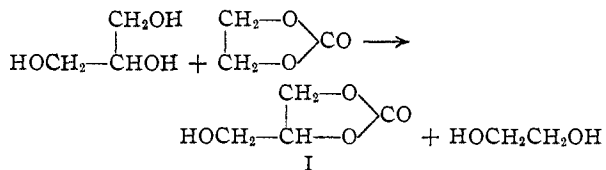
NEW YORK 27, NEW YORK RECEIVED NOVEMBER 16, 1951

### Thermal Decomposition of Glyceryl Carbonates

By HERMAN A. BRUSON AND THOMAS W. RIENER

RECEIVED OCTOBER 6, 1951

While attempting to prepare glyceryl monocarbonate (I) by heating equimolar proportions of glycerol and ethylene carbonate to effect an ester exchange it was noticed that after the ethylene

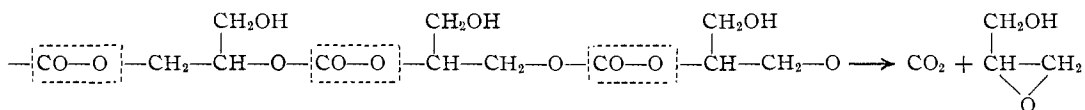


glycol had been removed by vacuum distillation there remained in the still-pot a thick, balsam-like, resinous material which, upon further distillation *in vacuo*, decomposed almost entirely to yield glycidol  $\text{CH}_2\text{—CH—CH}_2\text{OH}$ .



This unexpected reaction affords a convenient method for preparing glycidol in 60–85% yields directly from glycerol.

When an open chain dialkyl carbonate such as for example diethyl carbonate was used in place of the cyclic ethylene carbonate as above (1:1 mole ratio), the alcoholysis did not readily take place without the use of a catalyst because of the immiscibility of diethyl carbonate with glycerol at the boiling point of the mixture. The use of an alkaline cat-



alyst, however, such as sodium or sodium methoxide together with rapid stirring caused a more rapid alcoholysis of the mixture, with formation of a glyceryl carbonate. This product, however, upon further distillation *in vacuo*, gave considerable non-

distillable resin and only a very mediocre yield (7%) of glycidol.

Since it was possible that the alkaline catalyst might exert a deleterious influence upon the yield of glycidol in this decomposition, an attempt was made to prepare glyceryl carbonate by heating glycerol with diphenyl carbonate in the absence of a catalyst, and distilling off under reduced pressure the phenol formed. This reaction is reported<sup>1</sup> to give a crystalline glyceryl tricarboxylate  $\text{C}_9\text{H}_{10}\text{O}_9$ , melting at 148°, when the mole ratio of glycerol to the diphenyl carbonate used is 2:3; and to give liquid or resinous glyceryl carbonates containing free hydroxyl groups when an excess of glycerol is employed. We have confirmed this work and isolated the crystalline glyceryl tricarboxylate in pure form. This compound when subjected to vacuum distillation yielded no glycidol but decomposed instead to form a resinous material together with traces of acrolein, and gases which did not condense in a Dry Ice trap at  $-80^\circ$ .

Upon heating glycerol with diphenyl carbonate (1:1 mole ratio) and distilling off under reduced pressure the phenol formed, a still-pot residue was obtained which upon further distillation *in vacuo* gave a 60% yield of glycidol.

It is apparent that no glycidol is formed (or can be expected) if all three hydroxyl groups of the glycerol are esterified with carbonate radicals. Obviously, one primary hydroxyl group must be free if glycidol is to be obtained. Ethylene carbonate is superior to diphenyl carbonate because a smaller weight of it is required per mole of glycerol and the reaction is more rapid, giving less opportunity for side reactions and in general a higher yield.

Application of the reaction with ethylene carbonate to glycerol derivatives such as glycerol-mono- $\alpha$ -chlorohydrin and glyceryl- $\alpha$ -ethyl ether did not yield the respective epichlorohydrin or glycidyl ethyl ether. Likewise, an attempt to convert 1,2,6-hexanetriol into the epoxide  $\text{CH}_2\text{—CH—(CH}_2\text{)}_3$



$\text{CH}_2\text{OH}$  by heating with ethylene carbonate was unsuccessful.

Since one would expect monomeric glyceryl monocarbonate (I) to be a vacuum-distillable liquid that on prolonged heating might yield a polyester resin, and since the viscous character of the still-pot residue which is obtained in the transesterification of glycerol with ethylene carbonate (1:1 mole ratio) is that of a polymeric resinous material; it is believed that the reaction involves the formation of a poly-(glyceryl-1,2-dicarbonate) which subsequently loses carbon dioxide on further heating with formation of glycidol as

### Experimental

**Raw Materials.**—The glycerol used was anhydrous, vacuum-distilled C.P. grade. The ethylene carbonate was

(1) German Patent 252,758 (1912), Chem. Fabrik Dr. Rudolf Scheuble and Dr. A. Hochstetter; *Chem. Zentr.*, **83**, II, 1756 (1912).

prepared by heating ethylene chlorohydrin with sodium bicarbonate,<sup>2</sup> and was distilled twice in vacuum before use. It analyzed better than 99% pure.

**Preparation of Glycidol.**—In a 200-cc. flask attached to an 8' long packed column arranged for vacuum distillation, a mixture of 92 g. of glycerol (1 mole) and 95 g. of ethylene carbonate (1.08 moles) was heated gradually during the course of 90 minutes to 145° under 75 mm. vacuum; then during 75 minutes at 135–155° under 34–36 mm. vacuum, and finally during 90 minutes at 155–240° under 10–15 mm. vacuum. In the early stages of the heating, ethylene glycol (60 g.) came over in the receiver until the vapor temperature at 11 mm. was 80°. The thick liquid residue during the final heating at 155–240° in vacuum (5–10 mm.) gradually decomposed to give a colorless liquid which distilled over below 60° at 5 mm. Yield of crude glycidol was 64 g. (86%). Upon redistillation, this boiled at 53–55° (10 mm.) and furnished 47 g. (63.5%) of pure product,  $n_D^{20}$  1.4346.

It was identified by means of its phenylurethan<sup>3</sup> derivative, m.p. 60–61° and by treatment with piperidine<sup>3</sup> to give 1-piperidinopropane-diol-2,3 melting at 83°.

In contrast to the above, a stirred mixture of 236 g. of diethyl carbonate (2 moles), 184 g. of glycerol (2 moles) and 1 g. of sodium methoxide when heated at 90–100° under a short column until no more ethyl alcohol distilled over, gave a sirupy residue, which upon distillation *in vacuo* yielded 16 g. of distillate, b. p. 70–80° (13–16 mm), from which 10 g. of glycidol (7% yield) could be recovered upon redistillation (b.p. 62–64° (10–11 mm.)).

**Glyceryl Tricarbonate.**—A mixture of 100 g. of glycerol (1.087 moles) and 350 g. of diphenyl carbonate (1.63 moles) was heated *in vacuo* (6–8 mm.) at 135–45° under an 8' column arranged for vacuum distillation. During a heating period of 9.5 hours, 267 g. of phenol (2.84 moles) distilled over into the receiver. The still-pot residue was a sirup which, in part, gradually solidified after standing for several days. It was mixed at room temperature with an equal volume of glacial acetic acid which dissolved most of the impurities, leaving behind 77 g. of crystalline product. After recrystallization from hot glacial acetic acid, it formed colorless crystals, m.p. 146–148°.

A 40-g. sample of this crystalline glyceryl tricarbonate was subjected to vacuum distillation as described above for the preparation of glycidol. After heating at 230–240° at 7 mm. for 1.5 hours, it showed no decomposition. At 300–320° decomposition set in. An acrid smelling liquid (1 g.) containing acrolein collected in the Dry Ice trap, and 7 g. of distillate in the vacuum receiver; neither of which contained glycidol.

**Glycidol from Glyceryl Dicarboxylate.**—A mixture of 149 g. of diphenyl carbonate (0.697 mole) and 64.3 g. of glycerol (0.7 mole) was heated at 135–140° in vacuum at 5–7 mm. for five hours during which time 129 g. of phenol or 98.5% of the theoretical amount, distilled over into the receiver. The viscous still-pot residue was then heated at 185–190° for 3 hours at 5–7 mm. vacuum, yielding 35.5 g. of colorless liquid distillate. Upon redistillation this gave 31 g. (60% yield) of glycidol, b.p. 55–57° (10 mm.), identified by means of its piperidine derivative.<sup>3</sup>

(2) G. Steimmig and M. Wittwer, U. S. Patent 1,907,891 (1933).

(3) T. H. Rider and A. J. Hill, *THIS JOURNAL*, **52**, 1527, 1530 (1930).

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## Precision Actinometry at Low Light Intensities with Malachite Green Leucocyanide

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RECEIVED JANUARY 14, 1952

The quantitative measurement of low intensities of ultraviolet light, less than  $10^{13}$  quanta/sec., offers many experimental difficulties. Calibrated thermopile or phototube systems of high sensitivity with which such measurements can be made are not available in many laboratories and recourse to

chemical actinometry must be made. Uranyl oxalate solutions are used universally for the measurement of light intensities.<sup>1</sup> However, this actinometer is not ideally suited for the measurement of very low intensities since exposure times necessary to obtain the desired accuracy in these experiments are very great. The use of monochloroacetic acid photolysis<sup>2</sup> as an actinometer is restricted to experiments utilizing 2537 Å. radiation. It is generally unsatisfactory because of the large temperature coefficient of the quantum yield and the dark reaction for which correction must be made in the long experiments necessary at low intensities.

Harris, Kaminsky and Simard have made an important contribution to the problem of measurement of very small light intensities.<sup>3</sup> These authors reported that the photolysis of malachite green leucocyanide, *p,p'*-didimethylaminotriphenylacetone, in ethyl alcohol solution resulted in the formation of an intensely colored dye with a quantum efficiency of 100%. The quantum yield of 1.00 was independent of the initial leucocyanide concentration, the intensity of the absorbed light, the temperature of the solution, and the wave length of absorbed light in the region 2480 to 3300 Å. The colored ion formed in the reaction, presumably  $[(CH_3)_2NC_6H_4]_2C(C_6H_5)^+$ , was found to be stable in acidified alcohol and identical to the colored ion of malachite green salts in the same solvent. The great sensitivity of this proposed actinometer makes it particularly suited for the measurement of very low light intensities. However, two important factors have prevented its general use. (1) No completely satisfactory method of preparation and purification of the leucocyanide has been available. (2) The reliability of the quantum yield determinations of Harris, *et al.*, has been questioned. These authors reported  $1.07 \pm 0.06$  for the quantum yield of chloride ion formation in monochloroacetic acid photolysis<sup>3</sup>; this value was obtained by a comparison method using malachite green leucocyanide photolysis as a reference standard. A value of 1.05 for the quantum yield of monochloroacetic acid photolysis was reported earlier by Rudberg.<sup>4</sup> Recent redeterminations of this quantum yield indicate that the correct value is 0.32 at 25°.<sup>2</sup> These conflicting results make uncertain the accuracy of the quantum yields of malachite green leucocyanide photolysis reported by Harris, *et al.*<sup>2,5</sup> In the present report these two major limitations to the general use of the leucocyanide actinometer for measurement of low light intensities are eliminated. An improved method of preparation and purification of malachite green leucocyanide has been developed and is presented in this report. The quantum yield results of Harris and co-workers from photolysis of leucocyanide solutions have been confirmed by two independent methods.

(1) W. G. Leighton and G. S. Forbes, *THIS JOURNAL*, **52**, 3139 (1930); G. S. Forbes and L. J. Heidt, *ibid.*, **56**, 2363 (1934).

(2) R. N. Smith, P. A. Leighton and W. G. Leighton, *ibid.*, **61**, 2299 (1939); L. B. Thomas, *ibid.*, **62**, 1879 (1940).

(3) L. Harris, J. Kaminsky and R. G. Simard, *ibid.*, **57**, 1151, 1154 (1935).

(4) E. Rudberg, *Z. Physik*, **24**, 247 (1924).

(5) W. A. Noyes, Jr., and P. A. Leighton, "Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 83.