[CONTRIBUTION FROM THE WALKER LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

The Synthesis of 3-Chloro-2-chloromethyl-1-propene from Pentaerythritol[1]

BY ARAM MOORADIAN[1a] AND J. B. CLOKE

The present work on 3-chloro-2-chloromethyl-1-propene (I), $H_2C{=}C(CH_2Cl)_2$, was undertaken in connection with a study of certain chlorinated ethylenic hydrocarbons and nitriles to be reported in a later paper. Kleinfeller[2] first announced the preparation of a mixture of (I) and 1,3-dichloro-2-chloromethyl-1-propene (II) in 70% yield by the action of sodium amalgam on 5 g. lots of 1,3-dichloro-2-nitro-2-chloromethylpropane, $O_2N{-}C(CH_2Cl)_3$. Although Kleinfeller reported the separation of (I) and (II) in the pure state, he failed to state the yield of each. For obvious reasons, his method does not recommend itself for the preparation of the compound in significant quantities.

More recently, a mixture of (I) and the isomeric 1,3-dichloro-2-methyl-1-propene (III) $ClCH{=}C(CH_3)CH_2Cl$, which may exist in *cis* and *trans* forms, was obtained by the pyrolysis of 1,2,3-trichloro-2-methylpropane,[3] and also by the chlorination of isobutene and methallyl chloride.[4,5,6] However, no account has yet appeared on the separation of this mixture. It would appear that this might be accomplished through the hydroxy derivatives.

Since the foregoing methods are unsatisfactory for the synthesis of (I) in quantity and in the pure state, several alternative methods were investigated. A satisfactory preparation involves the decomposition of tris-(chloromethyl)-acetic acid (1,3-dichloro-2-chloromethyl-2-propanecarboxylic acid) (IV) in the presence of hot quinoline, whereby 75–85% yields of (I) are obtained. It may be assumed that the first stage in the reaction is the decarboxylation of (IV) to give 1,3-dichloro-2-chloromethylpropane (V), which then undergoes a dehydrohalogenation to give (I)

$$\underset{\text{(IV)}}{(ClCH_2)_3CCO_2H} \longrightarrow \underset{\text{(V)}}{(ClCH_2)_3CH} \longrightarrow \underset{\text{(I)}}{(ClCH_2)_2C{=}CH_2}$$

Our synthesis of (I), like that of Kleinfeller,[2] points to the symmetrical structure (I) rather than (III). That this is the case, at least for the bulk of the compound, is borne out by its relatively sharp and higher boiling point and by its hydrolysis in the presence of calcium carbonate to give the glycol, $(HO{-}CH_2)_2C{=}CH_2$ (VI); for the unsymmetrical compound (III), as shown by Pogorshelski[7] is saponified by 10% potassium carbonate solution to give the β-chloro-alcohol, $ClCH{=}C(CH_3)CH_2OH$, in which the halogen attached to the doubly linked carbon is not replaced by hydroxyl. Furthermore, (I) has a higher melting point (−15 to −13°) than (III) (below −65),[8] which is also in harmony with the symmetrical structure. Measurements of the dipole moment of (I)[9] were inconclusive on account of certain experimental difficulties. The question of the rearrangement of (I) into (III) has not yet been investigated.

The tris-(chloromethyl)-acetic acid (IV) or *sym*-trichloropivalic acid, presumably a new compound, was obtained by the nitric acid oxidation of pentaerythrityl trichlorohydrin (VII), which, in turn, was prepared from pentaerythritol (VIII) by the use of thionyl chloride and pyridine

$$\underset{\text{(VIII)}}{(HOCH_2)_4C} \longrightarrow \underset{\text{(VII)}}{(ClCH_2)_3CCH_2OH} \longrightarrow \underset{\text{(IV)}}{(ClCH_2)_3CCO_2H}$$

The reaction of pentaerythritol with thionyl chloride had been studied previously by other workers. In the first work, Orthner[10] obtained only a disulfite derivative which Bougault[11] had prepared by the action of sulfur monochloride on (VIII). More recently Govaert and Hansens[12] treated pentaerythritol with both thionyl chloride and thionyl bromide in the presence and absence of both pyridine and diethylaniline in the expectation of obtaining the mono-, di- or trihalogen derivatives, but they reported a quantitative yield of the disulfite only and no halogenated products. The reference to this work was found, perhaps fortunately, only after we had obtained the tetra-, tri-, di- and possibly the mono-chlorine substitution products of VIII by the same reaction

$$\underset{\text{(VIII)}}{C(CH_2OH)_4} \longrightarrow \underset{\text{(IX)}}{ClCH_2C(CH_2OH)_3} \longrightarrow$$

$$\underset{\text{(X)}}{(ClCH_2)_2C(CH_2OH)_2} \longrightarrow \underset{\text{(VII)}}{(ClCH_2)_3CCH_2OH} \longrightarrow \underset{\text{(XI)}}{C(CH_2Cl)_4}$$

As had been reported by the earlier workers, we obtained the disulfite compound when the reac-

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[2] Kleinfeller, *Ber.*, **62B**, 1590 (1929).

[3] Rogers and Nelson, THIS JOURNAL, **58**, 1027 (1936).

[4] Burgin, Engs, Groll and Hearne, *J. Ind. Eng. Chem.*, **31**, 1413 (1939).

[5] Burgin, Hearne, Rust, *ibid.*, **33**, 385 (1941); Suter and Bordwell, THIS JOURNAL, **65**, 507 (1943).

[6] Dyakonov, *J. Gen. Chem.*, U.S.S.R., **10**, 402 (1940).

[7] Pogorshelski, *J. Russ. Phys.-Chem. Soc.*, **36**, 1129–1184 (1904); *Chem. Zentr.*, **76**, 668 (1905).

[8] Mooradian, "Thesis," R.P.I., 1941; Mooradian and Cloke, communication in preparation for THIS JOURNAL.

[9] De Lalla, "Thesis," Rensselaer Polytechnic Institute, 1941, with Dr. O. M. Arnold.

[10] Orthner, *Ber.*, **61B**, 116 (1928).

[11] Bougault, *Compt. rend.*, **123**, 188 (1896).

[12] Govaert and Hansens, *Natuurw. Tijdschr.*, **21**, 215 (1940); *Chem. Abs.* **34**, 3680 (1940).

tion was carried out in the absence of organic base. Previous to our work, the only successful method for the preparation of (VII) involved the action of hydrochloric acid on (VIII), whereby small yields of (VII) and the three other possible products (IX), (X) and (XI) were obtained.[13]

Experimental Part

Pentaerythrityl Trichlorohydrin (VII).—To a mechanically stirred, externally ice-cooled slurry of 408 g. (3 moles) of pentaerythritol (Niacet Co.) and 711 g. (9 moles) of pyridine (Barrett) contained in a flask, a weight of 1071 g. (9 moles) of thionyl chloride was added drop by drop at such a rate that the white mist appearing in the flask did not rise up into the condenser. After about one-third of the thionyl chloride had been added at this rate, the remainder was dropped in quite rapidly. When the addition was complete, the whole was heated under a reflux condenser until no more sulfur dioxide was evolved. After cooling, an equal volume of water was added, whereby, on standing, a water layer and water-insoluble layer appeared. The water layer was decanted and extracted three times with benzene. It was then extracted continuously with ether in a special apparatus.[14]

The combined benzene extract and water insoluble layer was fractionated under diminished pressure and gave 50–80 g. of crude pentaerythrityl chloride b. p. 95–110° at 12 mm., 305–341 g. (53–59%) of pentaerythrityl trichlorohydrin, b. p. 127.5–129° at 12 mm., m. p. 65.5° (cor.),[15] and 20 g. of pentaerythrityl dichlorohydrin b. p. 150–160° at 12 mm. The ether extract gave an additional 24 g. (4%) of pentaerythrityl trichlorohydrin and 42 g. of dichlorohydrin, b. p. 150–160° at 12 mm.

Anal. Calcd. for $C_5H_9OCl_3$: Cl, 55.55. Found: Cl, 55.71, 55.80.

Pentaerythrityl Dichlorohydrin (X).—The procedure used was identical with that employed in making the trichlorohydrin (VII) with the exception that the molar ratio of pyridine and thionyl chloride to pentaerythritol was two to one rather than three to one. In this case, most of the desired material was found in the ether solution obtained by continuous extraction. The mixed ether extract, benzene extract, and water insoluble layer was distilled giving from a one mole run 70 g. of pentaerythrityl dichlorohydrin (40%) b. p. 158.5–160° at 12 mm., m. p. 83° (cor.),[16] 28 g. of pentaerythrityl trichlorohydrin and a small amount of material of b. p. 183–188° at 16 mm., probably pentaerythrityl monochlorohydrin.

Anal. Calcd. for $C_5H_{10}O_2Cl_2$: Cl, 40.99. Found: Cl, 41.10, 41.12.

Pentaerythrityl Tetrachloride, Tetrakis-(chloromethyl)-methane (XI).—The procedure used for (XI) was the same as for (VII) and (X) with the exception that a molar ratio of four to one was used in this case. At the end of the period of heating, the dilution of the reaction mixture with water completely precipitated the product. The water layer was decanted and discarded and the insoluble portion distilled. The product from a one mole run amounted to 160 g. (76%) of pentaerythrityl tetrachlorohydrin. b. p. 100° at 12 mm., m. p. 97° (cor.).

Anal. Calcd. for $C_5H_8Cl_4$: Cl, 67.57. Found: Cl, 67.73, 67.80.

Tris-(chloromethyl)-acetic Acid (IV).—A weight of 0.75 mole (143.6 g.)[17] of pentaerythrityl trichlorohydrin was transferred to a three-liter, round-bottomed flask with ₮ joint, provided with a long Allihn condenser also with ₮ ground joint. The apparatus was set up in an efficient hood and 300 cc. of concentrated nitric acid was poured into the flask, after which the mixture was heated cautiously. At first the chlorohydrin dissolved and then two layers appeared. About this time the beginning of a reaction became apparent, whereupon the flask was rapidly lowered into a waiting bath of cold water and the operator withdrew. When the first violent reaction was over and the evolution of nitrogen oxides had practically ceased, the flask was heated carefully until no more brown fumes were evolved. At the end of this period, a clear almost colorless solution resulted. The dilution of this with water led to the precipitation of a quantitative yield of crude acid of m. p. 108–110°. The crystallization of this from petroleum ether gave a product of m. p. 112.8–113° (cor.).

Anal. Calcd. for $C_5H_7O_2Cl_3$: Cl, 51.78. Found: Cl, 51.87, 52.10.

The acid also may be crystallized from benzene, chloroform and carbon tetrachloride.

Amide of (IV).—The acid is readily converted to the amide by the use of thionyl chloride and aqua ammonia. After it was recrystallized from water, the amide melted at 121–122% (cor.).

Anal. Calcd. for $C_5H_8ONCl_3$: N, 6.85. Found: N, 7.00, 7.03.

3-Chloro-2-(chloromethyl)-1-propene (I).—Equimolar quantities of quinoline and crude tris-(chloromethyl)-acetic acid were mixed and heated under a reflux condenser until a reaction started. Half mole runs were found to be preferable. At this point heat was removed and the reaction allowed to proceed of its own accord. When the reaction subsided, a fractionating column was attached to the flask and all material distilling below 135° was distilled out of the reaction mixture as it was formed. The dried redistilled dichloro-isobutylene boiled quite sharply at 138–138.3°, melted from −15 to −13°, and was obtained in a yield of 75–85%; d^{20}_4 1.1782; n^{20}D 1.4754; *MR*D calcd., 29.94; *MR*D obsd., 29.90.

Anal. Calcd. for $C_4H_6Cl_2$: Cl, 56.73. Found: Cl, 56.73, 56.86.

The isomeric compound (III)[8] boils at 131–132.5° and is liquid at −65°.

3-Hydroxy-2-(hydroxymethyl)-1-propene (VI).—A weight of 28.5 g. (0.23 mole) of 3-chloro-2-(chlormethyl)-1-propene was mixed with 125 cc. of water and 46 g. (0.46 mole) of calcium carbonate and heated under reflux for seventy-two hours. The solid in the reaction mixture was collected on a filter and the water solution distilled giving 7.3 g. of material (36%) of b. p. 125–126° at 18 mm.; d^{20}_4 1.0791; n^{20}D 1.4758; *MR*D calcd., 23.25; *MR*D obsd., 23.02.

Anal. Calcd. for $C_4H_8O_2$: C, 54.53; H, 9.15. Found: C, 54.80; H, 9.00.

Bromine Absorptive Capacity of 3-Chloro-2-(chloromethyl)-1-propene.—Using McIlhiney's method as outlined in Meyer,[18] a quantitative study of the bromine absorptive capacity of 3-chloro-2-(chloromethyl)-1-propene was carried out. At the end of eighteen hours in carbon tetrachloride solution in the dark, no appreciable addition (2.9%) or substitution was observed.

Summary

1. The action of thionyl chloride on pentaerythritol in pyridine solution leads to the successive replacement of the four hydroxyl groups. However, only the di, tri and tetra chloro derivatives have been isolated.

2. The oxidation of pentaerythrityl trichlorohydrin with nitric acid gave a quantitative yield

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(13) Fecht, *Ber.*, **40**, 3888 (1907).

(14) A two-liter extraction apparatus, *e. g.*, Ace No. 6835; Scientific Glass Apparatus Co., No. J-1628B; Ashley and Murray, *Ind. Eng. Chem., Anal. Ed.*, **10**, 367 (1938).

(15) Fecht, *loc. cit.*, reported a m. p. of 80° and b. p. of 136° at 12 mm.

(16) Fecht reported a m. p. of 95° and b. p. of 160° at 12 mm.

(17) On account of the violence of the reaction, the use of a larger quantity is not recommended. Half-molar amounts are preferable.

(18) H. Meyer, "Lehrbuch der organisch-chemischen Methodik," Vol. I, p. 1126.

of tris-(chloromethyl)-acetic acid, presumably a new compound.

3. The action of hot quinoline on tris-(chloromethyl)-acetic acid gave a good yield of 3-chloro-2-(chloromethyl)-1-propene, whose structure is supported by its saponification to give the corresponding glycol.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BANTING INSTITUTE, UNIVERSITY OF TORONTO]

Conversion of D(+)-Acetone Glycerol into its Enantiomorph

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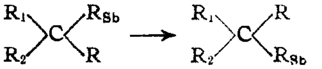
In principle any optically active substance whose asymmetry is due to substitution in one of two otherwise identical groups can be converted into its antipode by interchanging the position of the substituent (Scheme A).

E. Fischer and Brauns[1] succeeded in exchanging the position of the hydroxyl and amide group of the dextro-rotatory isopropylmalonamidic acid and obtained the levo-rotatory isomer with practically no loss in optical activity. This successful conversion is still regarded as an excellent experimental confirmation of the spatial concept of the asymmetric carbon atom as postulated by van't Hoff and Le Bel.

In 1937 the authors reported in a preliminary note, without giving experimental details,[2] the conversion of D(+)-acetone glycerol into L(−)-acetone glycerol. The levo-rotatory isomer was obtained by transposing the acetone group. The directing of this group into its new position and the maintenance of the optical activity of the molecule during the six steps of the conversion were accomplished by a series of asymmetric substitutions of the glycerol molecule as shown in Scheme B which also illustrates the steric relationships of the intermediary compounds.

SCHEME A

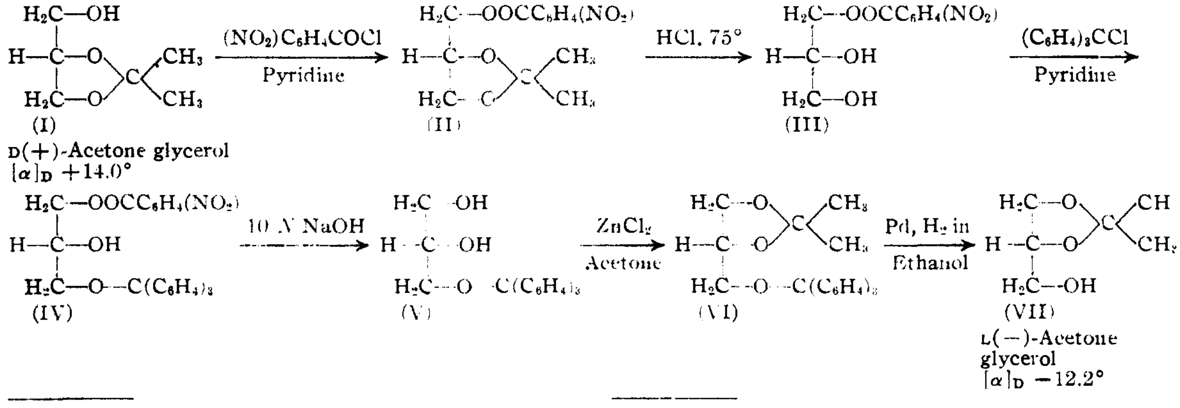


D(+)-Acetone glycerol (I) was nitrobenzoylated in pyridine and the resulting nitrobenzoate (II) was deacetonated in 0.5 N hydrochloric acid at 75 to 80°. The tritylation of L-(p-nitrobenzoyl) glycerol (III) in pyridine gave L-(p-nitrobenzoyl)-glycerol-trityl ether (IV). Saponification of IV with sodium hydroxide in ethanol yielded D-glycerol-trityl ether (V) which on acetonation with zinc chloride in acetone formed L-(−)-acetone glycerol-trityl ether (VI).[3] Catalytic removal of the trityl group in compound VI with hydrogen in the presence of palladium on charcoal resulted in the formation of L(−)-acetone glycerol (VII) which was identical with L(−)-acetone glycerol prepared from L-mannitol.[4]

Because of the numerous reactions involved, the L(−)-acetone glycerol was obtained in a yield of 6.6% only. Its optical activity was 12.5% less than that of D(+)-acetone glycerol. This small loss in optical activity must have occurred during detritylation, since the rotation of L(−)-acetone glycerol-trityl ether prepared by tritylation of L(−)-acetone glycerol is the same as that of L(−)-acetone glycerol-trityl ether obtained by conversion.

Early in our work dealing with the synthesis of optically active glycerides,[5] the need for L(−)-acetone glycerol as a starting material for the synthesis of the D-series of α-mono-glycerides arose and its preparation from D(+)-acetone glyc-

SCHEME B



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[1] E. Fischer and F. Brauns, *Ber.*, **47**, 3181 (1914); *cf.* Henry Gilman, "Organic Chemistry," second edition, John Wiley and Sons, Inc., New York, N. Y., 1943, Vol. I, p. 227.

[2] *Naturwissenschaften*, **25**, 588 (1937).

[3] Another method of preparation of this compound by tritylation of L(−)-acetone glycerol is also described in the experimental part.

[4] E. Baer and H. O. L. Fischer, THIS JOURNAL, **61**, 761 (1939).

[5] E. Baer and H. O. L. Fischer, *J. Biol. Chem.*, **128**, 475 (1939).