[CONTRIBUTION FROM GALAT CHEMICAL CORPORATION]

The Preparation of 2,4,5-Trichlorophenoxyacetic Acid (2,4,5-T)

BY ALEXANDER GALAT

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The preparation of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) by a new method is described. The mixture of α- and β-isomers of benzene hexachloride, available as a by-product in the manufacture of the γ isomer, is converted into 1,2,4-trichlorobenzene in the presence of a basic catalyst, sulfonated, the sulfonic acid treated with sodium hydroxide and the sulfonic group removed to yield 2,5-dichlorophenol. Chlorination and condensation with chloroacetic acid gives 2,4,5-T.

Phytotoxicological studies of the past several years have established the value of 2,4,5-trichlorophenoxyacetic acid as a non-selective general type herbicide. Species of plants such as ash, brambles, ground cherry, gum, hawthorne, maple, oak, poison ivy and others, which are resistant to 2,4-dichlorophenoxyacetic acid (2,4-D), are effectively controlled by 2,4,5-T. This plant hormone has also been successfully used in the dormant treatment of standing brush and stumps, the control of which could not be accomplished in the past with other phytotoxic agents. Unfortunately, the comparatively high cost of 2,4,5-T prevents its wider use at the present time.

2,4,5-T is prepared industrially from *o*-dichlorobenzene *via* 1,2,4,5-tetrachlorobenzene and 2,4,5-trichlorophenol, a costly and inconvenient method giving low conversions and involving the use of high pressures.

The new method for the preparation of 2,4,5-T which we wish to describe appears to provide a more economical route to this plant hormone.

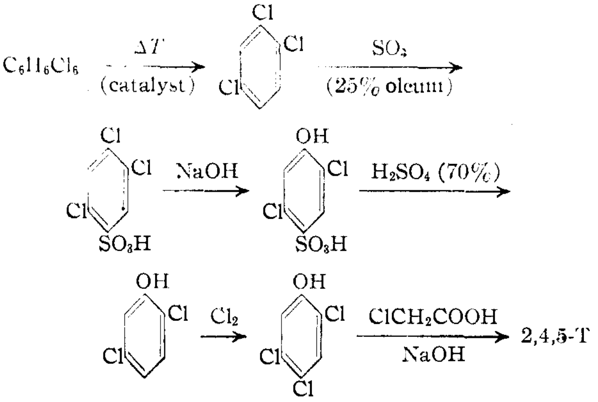
The starting material is a mixture of α- and β-isomers of benzene hexachloride (α,β-BHC). This mixture is insecticidally inactive and is available in very large quantities and at a low cost as a by-product of the industrial manufacture of the γ-isomer (BHC).[1] It was found that on heating this mixture in the presence of a basic ion-exchanger, which acts as a catalyst, three molecules of hydrogen chloride are split off giving 1,2,4-trichlorobenzene in an almost quantitative yield.

In order to activate the atom of chlorine in the desired position and facilitate its subsequent replacement with a hydroxyl group, 1,2,4-trichlorobenzene was sulfonated by the use of 25% oleum. The sulfonation proceeds smoothly and almost instantaneously and the product is easily isolated in the form of its sparingly soluble sodium salt by the addition of an equivalent amount of sodium chloride. The yield of the crude sodium salt is over 90%.

The sodium salt of 2,4,5-trichlorobenzenesulfonic acid readily reacted with two moles of aqueous sodium hydroxide at about 230° and under a moderate pressure to give 2,5-dichloro-4-phenolsulfonic acid in a yield of 85–90%. The sulfonic group was removed by boiling with dilute sulfuric acid and 2,5-dichlorophenol was thus obtained in a yield of 70–75%.

2,5-Dichlorophenol was converted into 2,4,5-trichlorophenol by chlorination (quantitative yield of the crude material) and the latter was condensed with chloroacetic acid by the usual procedure to give "2,4,5-T".

The new process is represented as



Experimental

1,2,4-Trichlorobenzene.—Two hundred and ninety-two grams (1 mole) of the mixture of α- and β-isomers of benzene hexachloride (commercial "Alpha–Beta Crystals") and 15 g. of IRA-400 Base (Rohm & Haas Company) was gradually heated with stirring under an air-condenser connected to a water-trap. About 20 g. of benzene distilled at 80–90°. When the temperature of the mixture reached 240° there began a copious evolution of hydrogen chloride which continued for 30 to 40 minutes.[2] The amount of hydrogen chloride, as determined by the increase in weight of the water-trap and by titration, was 85–86 g. which corresponds to about 85% of the theory. The mixture was distilled at atmospheric pressure and practically the entire amount passed over at 210–215° (lit.[3] 213°), as a colorless liquid. The yield of the crude product was 150 g. (88%). The material was washed with dilute sodium hydroxide and water and dried azeotropically with benzene. On redistillation at 15 mm. the product distilled at 90–95° and weighed 145 g. (85%). The freezing point was 8–10° (lit.[5] 17°) indicating the presence of impurities, probably isomers.

2,4,5-Trichlorobenzenesulfonic Acid.—1,2,4-Trichlorobenzene (226 g., 1.25 moles of the crude product) was added with stirring within a period of 10 minutes to 25% oleum (500 g.). Several minutes after the addition of trichlorobenzene had been completed a sample of the mixture was completely soluble in water. The mixture was poured with stirring into a solution containing 80 g. (1.37 moles) of sodium chloride in 1.5 l. of water. The mixture was cooled to room temperature, the precipitate filtered, slurried in water, refiltered, washed free of acid and dried. The product, the sodium salt of 2,4,5-trichlorobenzenesulfonic acid, weighed

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(1) This mixture is available from The Pennsylvania Salt Manufacturing Company under the name of "Alpha–Beta Crystals." We wish to thank this Company for the generous samples of this product supplied to us.

(2) F. E. Matthews (*J. Chem. Soc.*, **59**, 165 (1891)) reported that benzene hexachloride decomposes into trichlorobenzene when heated above its melting point (about 150°). However, on heating α,β-BHC at 240–250°, or about 100° above the melting point, we could not detect any appreciable decomposition or change. When a small amount of IRA-400 Base was added to the melt, there began immediately a copious evolution of hydrogen chloride.

(3) A. Dadieu, A. Pongratz and K. W. F. Kohlrausch, *Monatsh.*, **61**, 433 (1932).

335 g. (93–95%).[4] An analytical sample was prepared by recrystallization from water and drying at 110°.

Anal. Calcd. for $C_6H_2O_3SCl_3Na$: C, 25.5; S, 11.3; H, 0.70; Cl, 37.7; Na, 8.13. Found: C, 25.1; H, 0.67; S, 11.1; Cl, 38.0; Na, 8.20.

2,5-Dichloro-4-phenolsulfonic Acid.—A mixture of 141.5 g. (0.5 mole) of the crude sodium salt of 2,4,5-trichlorobenzenesulfonic acid, 43.0 g. (1.07 moles) of sodium hydroxide and 225 ml. of water was heated for two hours at 230° in a stainless-steel autoclave at 150–160 lb. pressure. A sample withdrawn and analyzed for ionic chlorine showed that one atom of chlorine was split off under these conditions. The mixture was removed from the autoclave and treated with 30 ml. of glacial acetic acid. Upon cooling, the precipitate was filtered, washed with ice-cold water and dried; yield 114–115 g. (86–87%). The product is the sodium salt of 2,5-dichloro-4-phenolsulfonic acid. An analytical sample was prepared by recrystallization from water and drying at 110°.

Anal. Calcd. for $C_6H_3O_4Cl_2SNa$: C, 27.2; H, 1.13; S, 12.1; Cl, 26.8; Na, 8.7. Found: C, 27.0; H, 1.02; S, 12.3; Cl, 27.1; Na, 8.6.

2,5-Dichlorophenol.—A mixture of 132 g. (0.5 mole) of the sodium salt of 2,5-dichloro-4-phenolsulfonic acid above and 660 ml. of 70% sulfuric acid was boiled gently for two hours. 2,5-Dichlorophenol was then steam distilled out of the reaction mixture. The product solidified in the receiver in the form of white hard crystalline aggregates, which were filtered and dried at room temperature; yield 58–60 g. (71–73.5%), m.p. 53–55° (lit.[5] 58–59°). The crude product was used without purification in the next step. A sample recrystallized from petroleum ether melted at 58–59°.

2,4,5-Trichlorophenol.—Chlorine was introduced into a solution of 163 g. (1.0 mole) of 2,5-dichlorophenol in 650 ml. of glacial acetic acid at 10–15° until the increase in weight of the reaction mixture was 70–72 g. (corresponding to the combined weights of one atom of chlorine and one mole of hydrogen chloride). The mixture was poured onto 2 kg. of cracked ice and the precipitate washed by decantation with cold water, dilute solution of sodium bisulfite and again with water. The product was then filtered and air-dried; yield 195–200 g. (theory, 197.5 g.), m.p. 56–59°. The crude was used without further purification in the condensation with chloroacetic acid. A sample recrystallized from petroleum ether melted at 65–67° (lit.[6] 68°) and did not depress the melting point of an authentic sample.

2,3,4,6-Tetrachlorophenol was obtained in a nearly quantitative yield by the same procedure as trichlorophenol, using the double amount of chlorine. A recrystallized sample melted at 67–69° (lit.[7] 70°) and did not depress the melting point of an authentic sample.

2,4,5-Trichlorophenoxyacetic acid (2,4,5-T) was obtained by the usual procedure by the condensation of 2,4,5-trichlorophenol with chloroacetic acid in the presence of sodium hydroxide.[7] The product is best isolated in the form of its sparingly soluble sodium salt which is readily purified and obtained colorless by recrystallization from water. The free acid, obtained from the sodium salt purified in this manner, melted at 153° (lit.[9] 153°) and did not depress the melting point of an authentic sample.

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(4) The barium and lead salts of 2,4,5-trichlorobenzenesulfonic acid were prepared by F. Beilstein and A. Kurbatow (*Ann.*, **192**, 231 (1878)). However, the amounts of reagents, the experimental conditions and the yields are not given. The barium salt is isolated by neutralizing the reaction mixture with barium hydroxide, removing barium sulfate by filtration and evaporating of the filtrate to dryness.

(5) G. J. Tiessens, *Rec. trav. chim.*, **50**, 112 (1931).

(6) L. G. Groves, E. E. Turner and G. I. Sharp, *J. Chem. Soc.*, 517 (1929).

(7) R. Pokorny, THIS JOURNAL, **63**, 1768 (1941).

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The Stereochemical Relationship between 2-Butanol and Lactic Acid

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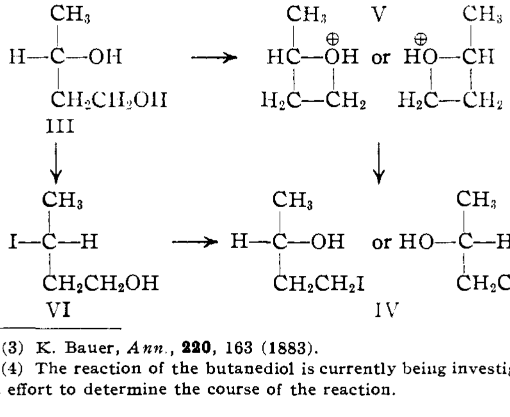
A series of conversions have been effected for redetermining the stereochemical relationship between 2-butanol and lactic acid. As a result, the previously determined relationship has been confirmed.

The relative configuration of 2-butanol (I) with respect to lactic acid (II) is particularly important in the scheme of stereochemical relationships since a large number of compounds have been related to lactic acid (and, thereby, glyceraldehyde) through I and its derivatives. Much of the available evidence[1] concerning the relative configurations of I and II is not entirely satisfactory for several reasons, the most cogent of which is the uncertainty associated with one reaction of the series employed.[1a]

This reaction, the conversion of 1,3-butanediol (III) to 4-iodo-2-butanol (IV) by treatment with hydrogen iodide, is unusual in that the primary, rather than the secondary hydroxyl is replaced. The reaction may proceed through a four-membered oxide intermediate (V)[2] leading to inversion or retention of configuration depending on which hydroxyl forms the oxide, or may involve the initial formation of 3-iodo-1-butanol (VI) followed by an exchange reaction of unknown stereochemistry such as that of *t*-butyl iodide and methanol giving *t*-butyl alcohol and methyl iodide.[3,4] In any case, the stereochemistry of the reaction is uncertain and it would be desirable to redetermine the relative configurations of I and II.



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(1) (a) P. A. Levene, A. Walti and H. L. Haller, *J. Biol. Chem.*, **71**, 465 (1927). (b) This relationship has also, in effect, been confirmed by the recently reported conversion of D-mannitol to D(−)-2,3-butanediol (L. J. Rubin, H. A. Lardy and H. O. L. Fischer, THIS JOURNAL, **74**, 425 (1952)). The configurational relationship between D mannitol and L(+)-lactic acid has been well established, and recently P. J. Leroux and H. J. Lucas, *ibid.*, **73**, 41 (1951), converted D(−)-2,3-butanediol to L(−)-2-butanol with effective inversion of configuration.

(2) W. E. Doering and R. W. Young, *ibid.*, **74**, 2997 (1952).

(3) K. Bauer, *Ann.*, **220**, 163 (1883).

(4) The reaction of the butanediol is currently being investigated in an effort to determine the course of the reaction.