

ing at 130—133°/10 mm Hg is obtained in a yield of 40 %. The acid is solid at room temperature. The melting point is 44—46°.

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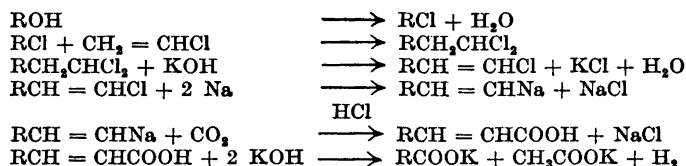
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A New Method to Prepare Trialkylacetic Acids

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There are many methods given for the preparation of trialkylacetic acids^{1,2} but no one is entirely convenient for a large scale preparation of these acids. They can, however, be prepared by the following satisfactory reactions, where R is a *tert*-alkyl group:



The yields in all these steps are excellent and the procedure very simple and rapid. Thus, great quantities of the acids are easily obtainable. As there are practically

no side reactions the acids obtained are easily purified.

The procedure is demonstrated by the synthesis of pivalic acid. Other acids can be prepared by exactly the same method.

*Experimental. tert-Butyl chloride*³. 1 kg of *tert*-butanol is shaken with 3.4 litres of conc. hydrochloric acid for 20 min in a 5-litre separatory funnel. The organic layer is separated, washed with 1 litre of water and dried with anhydrous magnesium sulphate at —20° for 10 min. The liquid is then transferred by filtration to a 5-litre three-necked flask. The yield is 1 160 g (93 %) of pure *tert*-butyl chloride.

*1,1-Dichloro-3,3-dimethylbutane*⁴. The 5-litre three-necked flask containing the *tert*-butyl chloride is chilled to —25° by means of a solid carbon dioxide-acetone bath and fitted with a stirrer, a gas inlet tube ending under the liquid, a thermometer, and a gas escape tube. 25 g of powdered anhydrous aluminium chloride is added, and the gas inlet tube connected to a 1-litre flask containing 860 ml of vinyl chloride. The vinyl chloride is distilled into the reaction mixture at such a rate that the reaction temperature can be kept at —25° to —30°. — *It is very important that the reaction starts before much vinyl chloride has been added.* This can be seen as a rapid rise in temperature if the cooling bath is temporarily removed. — After the reaction has started the vinyl chloride can usually be introduced in one hour. The reaction mixture is then kept at —25° to —30° for 15 min, and is then decanted into 500 ml of water. The mixture is thoroughly shaken, separated and dried with solid potassium hydroxide for 2 h. The yield is 1 870 g (96 %) of a nearly pure 1,1-dichloro-3,3-dimethylbutane.

1-chloro-3,3-dimethylbutene-1. 780 g of potassium hydroxide are dissolved in 3.6 litres of diethylene glycol in a 10-litre three-necked flask fitted with a dropping funnel, a reflux condenser, a thermometer, and a strong stirrer. The solution is heated to 140° and the dichlor

ide added. The mixture is refluxed with good stirring for 6 h, whereupon the product is distilled from the flask until the temperature in the liquid is 190°. The product is separated

from the water layer in the distillate, dried with anhydrous magnesium sulphate, and then distilled through a Widmer column. The yield is 1150 g of 1-chloro-3,3-dimethylbutene-1, b. p. 105–115°. 190 g of the dichloride, b. p. 148–153°, is recovered. This corresponds to a yield of 90 % calculated on the dichloride not recovered.

β-tert-Butylacrylic acid. A fine dispersion⁵ of 270 g of sodium in 270 ml of pure kerosene, free from sulphurous compounds and aromatics, is added to 4 litres of pure kerosene contained in a 10-litre three-necked flask fitted with a stirrer, a thermometer, a gas inlet tube, a gas escape tube, and a dropping funnel. A slow stream of dry nitrogen is passed through the flask, where the temperature is adjusted to 27°. A solid carbon dioxide acetone bath is kept ready for use and about 100 ml of a solution of 593 g of 1-chloro-3,3-dimethylbutene-1 in 1 litre of kerosene is added. If the reaction starts, which is indicated by a rapid darkening of the contents in the flask and a rapid rise in the temperature, the flask is cooled so that the temperature is kept within 25–30°, and the rest of the solution added as rapidly as possible without exceeding these temperature limits. — If the reaction will not begin, a few ml of *n*-butanol is added to help it to start. *Under no conditions more than 200 ml of the chloride solution should be added before the reaction starts or else the reaction may go beyond control.* — When all the chloride solution has been added (about 1 h) the reaction is completed by stirring at 25–30° for 1 h.

The flask is chilled to 0° and carbonated at 0–15° by a rapid stream of dry carbon dioxide, which is bubbled through the black reaction mixture. When the temperature does not rise, even if the cooling bath is removed, carbon dioxide is introduced for 15 min more. Water is then rapidly added through the dropping funnel to destroy the excess of sodium and dissolve the sodium salts. *This can be done without danger if the reaction between the chloride and sodium had started and a stream of carbon dioxide is passed through the flask.*

The layers are separated and the aqueous layer acidified with conc. hydrochloric acid. After cooling the solid acid cake is removed, transferred to a small beaker where it is melted and decanted from the resulting small water layer. The acid thus obtained weighs 550 g (86 %), and is pure enough for the next step.

*Pivalic acid*⁶. 1100 g of the acid above is carefully mixed with a solution of 1150 g of potassium hydroxide (85–87 %) in 1150 ml of water in a pan made of stainless steel. The pan is provided with a loose cover to avoid splashing and is heated electrically until the

temperature reaches 300°. The thermometer is protected from the caustic mixture by means of a copper tube.

The slightly coloured reaction mixture is allowed to cool, dissolved in water, acidified with conc. hydrochloric acid, the organic layer separated and the water layer extracted with benzene. The combined organic layers are dried with anhydrous magnesium sulphate and distilled through a 30 cm Widmer column. After a small forefraction at 150–162°, 760 g (87 %) of pivalic acid is obtained at 162–165°. The product is completely solidified at room temperature, and melts at 34–35°. The yield is 57 % calculated on the *tert*-butanol.

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A Method for the Preparation of Trialkylacetaldehydes

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In chemical literature there are given many methods to prepare trialkylacetaldehydes, but the starting materials are usually not readily available, and it is rather difficult to obtain even the most simple aldehyde of this kind (the trimethylacetaldehyde¹). The following method seems, however, quite satisfactory (p. 612).

From these formulas where R is a tertiary alkyl group it can be seen that there are only readily available starting materials except possibly the sodium periodate but this reagent is easily prepared