

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 dispersion<sup>5</sup> 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*<sup>6</sup>. 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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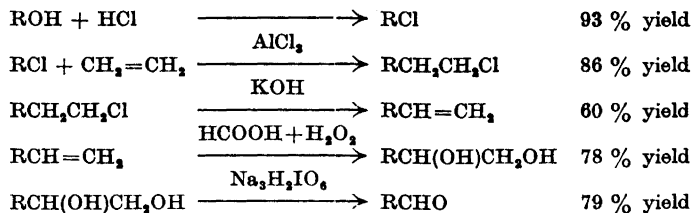
## A Method for the Preparation of Trialkylacetaldehydes

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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 trimethylacetaldehyde<sup>1</sup>). 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



from sodium chlorate and iodine<sup>2</sup> and can be recovered.

The method is demonstrated by the synthesis of trimethylacetaldehyde on a large laboratory scale.

*Experimental.* 1-Chloro-3,3-dimethylbutane<sup>3</sup>. In a 20 litre flask 3 kg of *tert*-butanol are shaken with 10 litres of concentrated hydrochloric acid for 20 min. The layers are separated, the upper layer washed with 1/2 litre of water and dried with 100 g of anhydrous sodium sulphate for 15 min at  $-20^\circ$ . The *tert*-butyl chloride which is quite pure is filtered into a 10 litre three-necked flask. The yield of *tert*-butyl chloride is 3.5 kg.

The flask is fitted with a stirrer, a gas inlet tube, a gas escape tube, and a thermometer, and is chilled in a dry ice-acetone bath to  $-20^\circ$ . 50 g of powdered anhydrous aluminium chloride are added and pure ethylene introduced as fast as it is consumed. The temperature is kept between  $-17^\circ$  and  $-20^\circ$  and regulated with the cooling and the rate of stirring (which determines the rate of absorption of ethylene). When the vigorous absorption of ethylene appears to cease (after about 2 h) the liquid is decanted into 200 ml of water, the mixture well shaken, the organic layer separated, dried with solid potassium hydroxide and distilled. The fraction boiling at  $115-122^\circ$  is taken as 1-chloro-3,3-dimethylbutane and weighs 3 900 g.

*tert-Butylethylene.* 2 100 g of potassium hydroxide are dissolved in 9 litres of polyethyleneglycol-300 and the solution is heated to  $130^\circ$  in a 20 litre three-necked flask placed in a heating mantle and fitted with a dropping funnel, a stirrer and a reflux condenser, the top of which is connected to a condenser arranged for distillation into a receiver chilled to  $-30^\circ$ . 3 600 g of 1-chloro-3,3-dimethylbutane are added at such a rate that the temperature in the flask is kept at  $120-190^\circ$ , and the temperature at the top of the reflux condenser is kept at  $40-60^\circ$  by regulating the cooling water in the mantle. When necessary, the flask

is heated by means of the heating mantle. When no more distillate is obtained, the organic layer is decanted from the ice in the receiver and distilled through a column into a receiver kept at  $-30^\circ$ . The fraction, b. p.  $40-50^\circ$ , is taken as *tert*-butylethylene and weighs 1 500 g.

*tert-Butylethylene glycol*<sup>4</sup>. 9 litres of formic acid (98-100 %) are mixed with 2.5 litres of hydrogen peroxide (30 %) and heated to  $37^\circ$  in a 20 litre three-necked flask fitted with a stirrer, a reflux condenser fed with ice-water, and a dropping funnel. 1.5 g of *tert*-butylethylene are added in 1 h with vigorous stirring and external cooling with ice-water so that the temperature is kept at  $37-40^\circ$ . When all the *tert*-butylethylene has been added, the mixture is stirred at the same temperature for another 1 1/2 h after which it is kept at room temperature over night.

The formic acid is removed under reduced pressure by means of a water-bath kept below  $55^\circ$ . When no more distillate is obtained (about 10 litres), the distillation condenser is replaced by a reflux condenser. 3.2 litres of a 33 % sodium hydroxide solution are added, and the mixture refluxed with rapid stirring for 15 min and then cooled to room temperature. 1.3 litres of benzene are added and the layers separated. The water layer is extracted with 1 litre of benzene and the combined organic layers are distilled under reduced pressure. 1.4 kg of *tert*-butylethylene glycol, b. p.  $95-115/8$  mm, are obtained. The residue in the distillation flask is refluxed with the aqueous layer from the separation for 15 min, the mixture extracted with 1 litre of benzene and then distilled. In this way another 250 g of *tert*-butylethylene glycol are obtained. The total yield is thus 1.65 kg. The product is completely solid at room temperature and pure enough for the next step.

*Trimethylacetaldehyde.* 4.15 kg of  $\text{Na}_2\text{H}_2\text{IO}_6$ , 1.65 kg of *tert*-butylethylene glycol and 11 litres of water are placed in a 20 litres three-necked flask fitted with a stirrer, a thermometer, a dropping funnel and a condenser