60. *A Synthesis of Methacrylic Acid.*

By Theodore White.

The synthesis of methacrylic acid has been achieved by oxidation of methyl *iso*propenyl ketone with sodium hypochlorite. The preparation of two new esters is described.

The importance in plastics chemistry of polymeric materials formed from derivatives of methacrylic acid has led to the development of a number of syntheses of this αβ-unsaturated acid and its esters, some of which are described only in the patent literature. Frankland and Duppa (*Annalen*, 1865, **136**, 12) first prepared the esters by treating α-hydroxy*iso*butyric esters with phosphorus trichloride, and the related dehydrohalogenation of α- or β-halogenated *iso*butyric esters was used by Walden (*Z. physikal. Chem.*, 1896, **20**, 574) and has since been the subject of several patents, *e.g.*, Bauer (B.P., 1930, 316,547) and Barrett (U.S.P., 1935, 2,013,048). Ritchie, Jones, and Burns (J., 1935, 714) prepared methyl methacrylate by pyrolytic removal of acetic acid from methyl α-acetoxy*iso*butyrate, and an alternative method of preparation from acetone cyanohydrin by treatment with hot concentrated sulphuric acid and with methyl alcohol devised by Crawford (B.P., 1932, 405,699) and by Hill (B.P., 1938, 490,007) is now in extensive use. The latter method constitutes by far the most convenient way of obtaining the acid itself.

A further method, based on Einhorn's observation (*Annalen*, 1888, **243**, 362) that aromatic αβ-unsaturated ketones of the type $R{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_3$ can be oxidised by hypohalogenites to the corresponding unsaturated acid $R{\cdot}CH{:}CH{\cdot}CO_2H$, has now been devised. In the course of work on polymerisable αβ-unsaturated aliphatic ketones (cf. White and Haward, this vol., p. 25) it was observed that the combination of electronic effects present in these compounds rendered the carbon–carbon double bond remarkably inert to electrophilic reagents and caused it to react preferably with such nucleophilic reagents as would normally add on only to a carbonyl group. This enabled such unsaturated ketones to be satisfactorily oxidised by hypohalogenites similarly to the corresponding aromatic ketones or the saturated aliphatic ketones, the reaction proceeding thus:

$$CH_2{:}CR{\cdot}CO{\cdot}CH_3 + 3NaOCl = CH_2{:}CR{\cdot}CO_2Na + 2NaOH + CHCl_3.$$

Methyl vinyl ketone and methyl *iso*propenyl ketone were successfully oxidised in this manner to acrylic acid and methacrylic acid respectively, despite the tendency displayed by both ketones to resinification in the presence of aqueous alkali solutions and their tendency to add on hypochlorous acid to give the corresponding α-chloro-β-hydroxy-ketones. The oxidation of methyl vinyl ketone proceeded smoothly with bleaching powder or hypohalogenites in general, but the difficulty of extracting the resultant acrylic acid (owing to its great solubility in water and tendency to polymerise) made the preparation one of mainly theoretical interest.

The oxidation of methyl *iso*propyl ketone to methacrylic acid proved to be rather more difficult owing to the fact that the inductive effect of the α-methyl group tended to favour the addition of hypochlorous acid to the αβ-double bond, this tendency being so marked that in attempted oxidations with bleaching powder and solutions of calcium hypochlorite only the hypochlorous acid addition product was formed. However, by using strongly alkaline solutions of sodium hypochlorite, and by paying particular care to the conditions of the reaction, it was found that both resinification and the addition of hypochlorous acid were avoided and that the reaction proceeded smoothly to give equivalent amounts of sodium methacrylate and chloroform. The suppression of the addition of hypochlorous acid in these circumstances would appear to be related to the greater stability of the hypochlorite ion in the presence of sodium hydroxide than in the presence of calcium ions, where the tendency to formation of hypochlorous acid predominates. On neutralising such strongly alkaline solutions of sodium hypochlorite with sulphuric acid, saturated sodium sulphate solutions were produced, from which the methacrylic acid was salted out in a state of fairly high purity, and the pure acid was readily obtained by drying and redistillation of this product.

Some esters of methacrylic acid are preferably prepared, not by esterification of the acid, but by alcoholysis from monomeric methyl methacrylate along the lines laid down by Izard (B.P., 1937, 470,503). n-*Hexyl methacrylate* and *ethylene dimethacrylate* were thus prepared, and since the marked tendency of these products to polymerise gives rise to practical difficulties which are absent from similar reactions with non-polymerisable esters, the details of the methods are recorded.

Experimental.

Methyl iso*Propenyl Ketone*.—A mixture of methyl ethyl ketone (4 l.) and paraformaldehyde (600 g.) was stirred with 2N-methyl-alcoholic potash (20 ml.) (*ca.* 3 hours) until a test portion no longer reduced boiling ammoniacal silver nitrate solution. The mixture was then brought to pH 6·9 with 2N-acetic acid in methyl ethyl ketone, and the excess of ketone distilled off up to 100°. The remaining product was fractionally distilled under reduced pressure with a Fenske column of the type used by White and Haward (*loc. cit.*), giving ketomethylbutanol (1 kg.), b. p. 84°/19 mm. This distillate was treated with concentrated sulphuric acid (20 g.), and gave, on heating to distillation point, a water–methyl *iso*propenyl ketone mixture which distilled at 94—96°. The aqueous layer was separated. The methyl *iso*propenyl ketone was dried by shaking twice with anhydrous sodium sulphate and keeping overnight over anhydrous copper sulphate; on redistillation through a Fenske column, it gave pure methyl *iso*propenyl ketone (700 g.), b. p. 97·5—98°/760 mm.

Methacrylic Acid by Oxidation of Methyl iso*Propenyl Ketone*.—Since concentrated sodium hypochlorite solution tends to decompose during its preparation from chlorine and concentrated sodium hydroxide solution, the following method was normally adopted: "Maxochlor" (I.C.I. high chlorine content soluble dry bleach) (400 g.) was gradually added, with stirring and external cooling, to sodium hydroxide (360 g.) in water (1 l.), the temperature being maintained below 15°. The mixture was then stirred for 30 minutes and filtered, giving 3N-sodium hypochlorite in 6N-sodium hydroxide.

This solution was stirred in a flask cooled in water, and methyl *iso*propenyl ketone (84 g.) added at such a rate that the temperature remained below 20°. The mixture was stirred and cooled for a further hour, and the chloroform (50 g.) then allowed to settle and separated. The aqueous solution was acidified with 50% sulphuric acid, the temperature being maintained below 30°, and an upper layer of methacrylic acid salted out. This was separated, dried with anhydrous sodium sulphate, and redistilled under reduced pressure in the presence of 1% of quinol in an atmosphere of oxygen-free nitrogen, giving a colourless pungent acid, b. p. 63°/10 mm., $n_D^{20^\circ}$ 1·429 (Found : equiv., 86). Yield, 32 g.; *i.e.*, 41% (methacrylic acid has b. p. 65°/12 mm., $n_D^{20^\circ}$ 1·431, equiv., 86). The product added on the theoretical amount of bromine and polymerised readily to a hard white mass with peroxides or in the presence of light.

Ethylene Dimethacrylate.—A mixture of monomeric methyl methacrylate (750 g.), ethylene glycol (100 g.), concentrated sulphuric acid (5 g.), and quinol (50 g.) was heated at 150° for 5 hours in a current of oxygen-free nitrogen. The distillate was fractionated through a Fenske column with the reflux ratio so adjusted as to maintain the temperature of distillation at 64—65° (that of the methyl alcohol–methyl methacrylate binary mixture). After 5 hours the temperature rose steadily and the heating was then discontinued, 170 ml. of distillate having been collected containing 125 ml. of methyl alcohol (corresponding to 100% alcoholysis). The reaction mixture was then cooled, neutralised with solid sodium bicarbonate, washed with water, dried over calcium chloride overnight, and fractionated through a Fenske column under reduced pressure; the fraction, b. p. 80—140°/15 mm., was refractionated to give a small amount of product boiling up to 120°/15 mm. and a major portion, b. p. 122—126°/15 mm., $n_D^{20^\circ}$ 1·4558 (Found : C, 60·4; H, 7·3; equiv., by saponification. 200. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%; equiv., 198). Yield, 90 g.; *i.e.*, 46%. This product was *ethylene dimethacrylate*, which, in the presence of benzoyl peroxide, polymerised to a hard, colourless, insoluble, cross-linked resin.

n-*Hexyl Methacrylate.*—A mixture of monomeric methyl methacrylate (2850 g.), *n*-hexyl alcohol (656 g.), precipitated sulphur (20 g.), and concentrated sulphuric acid (20 ml.) was refluxed in an atmosphere of oxygen-free nitrogen until the temperature at the head of a Fenske column was 64—65°, the distillate being then taken off as rapidly as possible without rise of the distillation temperature. 285 Ml. of distillate (containing 220 ml. of methyl alcohol) were obtained at 65°, 65 ml. (containing 20 ml. of methyl alcohol) at 65—100°, and 1500 ml. of methyl methacrylate at 100°. The residual mixture was treated with 36 g. of powdered calcium carbonate to neutralise the acid present. A further 400 ml. of methyl methacrylate were then distilled off at 100° and the remaining product was fractionated through a Fenske column under reduced pressure to give methyl methacrylate (170 ml.), b. p. 20°/17 mm., *n*-hexyl alcohol (125 g.), b. p. 67°/17 mm., and n-*hexyl methacrylate*, b. p. 86—88°/17 mm., $n_D^{20^\circ}$ 1·4300 (Found : C, 70·3; H, 10·8; equiv., by saponification, 169. $C_{10}H_{18}O_2$ requires C, 70·6; H, 10·6%; equiv., 170). The yield was 735 g., *i.e.*, 83%, calculated on the *n*-hexyl alcohol. The product polymerised readily to a highly extensible, tacky polymer.

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