542. *The Polymerizability of Methyl α-tert.-Butylacrylate. Part II.**

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The oxidation product dimethylmalonic acid, and the ultra-violet absorption spectrum of the ester prepared by dehydration of methyl tetramethyl-lactate, indicate that it is methyl 2 : 2 : 3-trimethylbut-3-enoate, formed by a *neo*pentyl rearrangement during the dehydration, and not methyl α-*tert.*-butylacrylate. α-*tert.*-Butylacrylic acid has been prepared by the Mannich synthesis from *tert.*-butylmalonic acid, and its structure confirmed. The methyl ester does not yield macromolecular polymers, but gives a considerable yield of dimer under the influence of sodium in liquid ammonia.

Crawford and Swift (Part I *) described unsuccessful attempts to induce ethenoid polymerization of methyl α-*tert.*-butylacrylate, obtained by dehydrating methyl tetramethyl-lactate with phosphoric oxide in presence of molar amounts of dimethylaniline. It was subsequently found that oxidation of the hydrolyzed ester with permanganate gave dimethylmalonic acid instead of the expected trimethylacetic acid. This led to the conclusion that during dehydration of the tetramethyl-lactate a *neo*pentyl rearrangement of the carbonium ion (I) occurred, with ultimate production of methyl 2 : 2 : 3-trimethylbut-3-enoate (II) instead of the expected methyl α-*tert.*-butylacrylate. This was supported by the resemblance of the ultra-violet absorption spectrum of the ester (*A*), to that of ethyl but-3-enoate (*B*), and its difference from that of methyl methacrylate (*C*) which has the form characteristic of αβ-unsaturated acid derivatives (Goodeve, *Trans. Faraday Soc.*, 1938, **34**, 1239) (see Fig.).

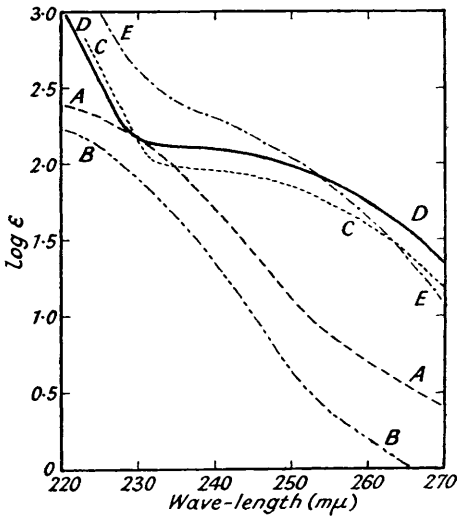
$Me_3C\cdot\overset{+}{C}Me\cdot CO_2Me$ (I) $\quad CH_2{:}CMe\cdot CMe_2\cdot CO_2Me$ (II) $\quad [Me_3C\cdot CH(CO_2Me)\cdot CH_2]_2$ (III)

α-*tert.*-Butylacrylic acid has been prepared by condensation of *tert.*-butylmalonic acid with formaldehyde and dimethylamine (cf. Mannich and Ganz, *Ber.*, 1922, **55**, 3486). The malonic acid has become readily available through Wideqvist's synthesis of the ester by condensation of *iso*propylidenemalonic ester with methylmagnesium iodide (*Arkiv Kemi, Min., Geol.*, 1946, **23**, *B*, No. 4). The Mannich reaction was incomplete, and led to small yields of α-*tert.*-butylacrylic acid, but much of the unchanged butylmalonic acid could be recovered and used again, with an acceptable overall yield of butylacrylic acid. The probable course of the Mannich reaction made it appear unlikely that rearrangement would occur during the synthesis; in any case, the structure of the butylacrylic acid was confirmed by formation of trimethylacetic acid in quantity on oxidation with permanganate. Methyl α-*tert.*-butylacrylate was prepared by direct esterification of the acid with methanol. Examination was made of the proposition that the butylacrylic structure could pass into the 2 : 2 : 3-trimethylbut-3-enoic structure during the esterification, through union with a proton to form the carbonium ion (I), followed by rearrangement, and proton elimination. However, when methyl butylacrylate was heated with the same methanol–sulphuric acid mixture as was used in the esterification, for 24 hours, there was no increase in refractive index or density: it was concluded that no significant rearrangement had occurred. Support for an αβ-unsaturated structure for the new ester and acid came from the resemblance of their ultra-violet spectra (*D*, *E* respectively) to that of methyl methacrylate (*C*). The ester, re-treated as above, gave the same spectrum as (*D*).

The methods described in Part I were used for investigation of the polymerizability of methyl α-*tert.*-butylacrylate. Prolonged heating with benzoyl peroxide, or long exposure in borosilicate glass to ultra-violet radiation, failed to produce a macromolecular polymer. A considerable yield of nitrogen-free, saturated liquid dimer, $C_{16}H_{30}O_4$, was obtained by

* Part I, *J.*, 1952, 1220.

the action of a solution of sodium in liquid ammonia; this was in contrast to the behaviour of methyl 2 : 2 : 3-trimethylbut-3-enoate, which yielded under the same conditions a negligible amount (0·5%) of material approximating in molecular weight to dimer. The difference seems to result from the comparatively ready activation of the butylacrylate, because of the influence of the carbomethoxy-group adjacent to the ethylene bond. Failure of the butylacrylate to propagate macromolecular polymer appears, as was discussed in Part I, to be the result of the steric effect of the α-*tert.*-butyl groups. A head-to-head



Absorption spectra in n-*hexane.*
A, Methyl 2 : 2 : 3-*trimethylbut*-3-*enoate.*
B, Ethyl vinylacetate.
C, Methyl methacrylate.
D, Methyl α-tert.-*butylacrylate.*
E, α-tert.-*Butylacrylic acid.*

saturated dimer (III) (methyl αδ-di-*tert.*-butyladipate) could, however, be formed without serious interference of this kind. Formation of (III) under the influence of the sodium appears analogous to the formation of 1 : 1 : 4 : 4-tetraphenylbutane from the sterically hindered 1 : 1-diphenylethylene by treatment of the latter with sodium in liquid ammonia (Wooster and Ryan, *J. Amer. Chem. Soc.*, 1934, **56**, 1133).

Experimental

Hydrolysis and Oxidation of the Unsaturated Ester from Methyl Tetramethyl-lactate.—The ester (1·42 g., 0·01 mole) was hydrolyzed under reflux on the water-bath for 16 hr. with alcoholic 0·5N-potassium hydroxide (50 c.c.). The product was diluted with water, and alcohol boiled off. The residue, diluted to 300 c.c., was stirred at 20° with potassium permanganate (5·3 g. equiv. to 5 O). Decolorization was complete after 25 hr. A further 0·2 g. of permanganate was unreduced 25 hr. later. Excess of permanganate was reduced with sodium sulphite solution, the filtrate from manganese dioxide evaporated nearly to dryness on the water-bath, acidified with hydrochloric acid (*d* 1·18; 3·5 c.c.), and extracted five times with ether, and the combined extracts were neutralized with N-sodium hydroxide (phenolphthalein). The solution of sodium salt was concentrated, slightly acidified with hydrochloric acid, and heated under reflux for 2 hr. with *p*-bromophenacyl bromide (1·6 g.) and 95% alcohol (7 c.c.). The crystalline ester obtained was recrystallized from alcohol and had m. p. 128—128·5° (Found : Br, 30·4. Calc. for $C_{21}H_{18}O_6Br_2$: Br, 30·4%). Authentic *p*-bromophenacyl dimethylmalonate had m. p. 128·5—129°.

Synthesis of Methyl α-tert.-*Butylacrylate.*—*Ethyl* tert.-*butylmalonate.* Repetition on a five-fold scale of Wideqvist's synthesis (*loc. cit.*) gave the same yield (39%) of ester as recorded by the author. The side-reactions mentioned by Wideqvist were reduced by lowering the temperature of reaction of ethyl *iso*propylidenemalonate and methylmagnesium iodide to −20°, and by increasing the amount of solvent ether used, to prevent deposition at this temperature of viscous intermediate which interfered with stirring. To a Grignard solution (from methyl iodide, 600 g., magnesium, 102 g., and ether, 1050 c.c.), cooled to −15° to −20°,

with stirring, ethyl *iso*propylidenemalonate (750 g.) in ether (750 c.c.) was added during 65 min. The mixture was allowed to warm to −5° during 40 min., and decomposed on cracked ice (2 kg.). Magnesia was dissolved by addition of hydrochloric acid, the ethereal layer washed twice with water, once with dilute sodium sulphite solution, and twice again with water, and dried ($CaCl_2$), and solvent was removed. Fractionation of the crude ester through a 9″ Vigreux column gave ethyl *tert.*-butylmalonate, b. p. 102—105°/11 mm. (649 g., 80%).

tert.-*Butylmalonic acid.* Ethyl *tert.*-butylmalonate (600 g., 2·8 moles) was hydrolyzed with absolute alcoholic potash solution as directed by Wideqvist, boiling under reflux being for 23 hr. The deliquescent potassium salt which had deposited was filtered off and washed with absolute alcohol (2 × 600 c.c.), and the bulk of adhering solvent removed over sulphuric acid *in vacuo*. The dried salt was dissolved in water (3 l.) and treated during 45 min. at <30° with 98% sulphuric acid (333 g., 3·3 moles) with good stirring. Butylmalonic acid was extracted with ether (3 × 500 c.c.). Removal of solvent and desiccation of the crystalline residue to constant weight *in vacuo* over sulphuric acid gave *tert.*-butylmalonic acid (346 g.). A further 8 g. of the acid was obtained by extracting the mixture again with ether (500 c.c.). Titration with sodium hydroxide (phenolphthalein) indicated 99·8% purity (79% yield, calc. on ethyl *tert.*-butylmalonate).

α-tert.-*Butylacrylic acid.* *tert.*-Butylmalonic acid (320 g., 2·0 moles) was stirred and cooled below 30° whilst aqueous dimethylamine (25·4 g./100 c.c.; 350 c.c., 2 moles) was added. Formaldehyde solution (35·5%; 169 g., 2 moles) was stirred into the crystalline paste at <20°. The mixture, now liquid, was kept at 20° for 6½ hr. (no evolution of carbon dioxide), then boiled under reflux for 6½ hr. Gas evolution commenced at 60°, and diminished gradually. The cooled product was acidified at <30° with 98% sulphuric acid (110 g., 1·1 mole), and the clear homogeneous liquid treated with water (1 l.). Rapidly crystallizing oil was precipitated. The mixture was extracted with light petroleum (b. p. 40—60°; 2 × 500 c.c.). The dried (Na_2SO_4) extracts left crude butylacrylic acid (62 g.) after removal of solvent and desiccation *in vacuo* over calcium chloride and active charcoal. Further extraction with light petroleum gave an additional 1 g. of acid. The crude butylacrylic acid was contaminated with *tert.*-butylacetic acid derived by decarboxylation of *tert.*-butylmalonic acid which had not undergone the Mannich reaction. Pure α-tert.-*butylacrylic acid*, obtained by recrystallization from warm light petroleum (b. p. 40—60°) in which, however, it is very soluble, had m. p. 44—44·5° (Found: C, 65·2; H, 9·5%; acid value, 437. $C_7H_{12}O_2$ requires C, 65·6; H, 9·5%; acid value, 438).

tert.-Butylmalonic acid (206 g.; 97·2% pure) was recovered from the reaction mixture by extraction with ether (2 × 350 c.c.).

Oxidation of α-tert.-*Butylacrylic Acid.*—The acid (2·6 g., 0·02 mole) was warmed above its m. p. with potassium hydroxide (1·2 g.) in water (400 c.c.). After cooling to 21°, potassium permanganate (6·3 g., 3 O) was added in portions during 6 min., with stirring. Reduction was rapid. This stage of the oxidation corresponded to conversion of the butylacrylic acid into *tert.*-butyltartronic acid. Further permanganate (4·2 g., 2 O) was then added, and the mixture warmed at 90° for 18 hr. Slow reduction, presumably after decarboxylation of the tartronic acid, was by then complete. Manganese dioxide was filtered off, and washed with water. Filtrate and washings were evaporated to about 25 c.c. on the water-bath, cooled, and treated with hydrochloric acid (10 ml.; *d* 1·18). Trimethylacetic acid which appeared was extracted with light petroleum (b. p. 40—60°). The petroleum extract was neutralized (phenolphthalein) with N-sodium hydroxide (17·4 c.c.; 87% of theory). The solution of sodium salt was concentrated and converted into the *p*-bromo- and *p*-phenyl-phenacyl ester. The esters, recrystallized from 95% alcohol, had (*p*-bromo), m. p. 77·5—78° (Found: Br, 26·9. Calc. for $C_{13}H_{15}O_3Br$: Br, 26·8%), and (*p*-phenyl), m. p. 113—113·5°. Authentic samples of the trimethylacetic esters had m. p.s 77·5—78·5° and 113·5—114° respectively.

Methyl α-tert.-*Butylacrylate.*—Crude α-*tert.*-butylacrylic acid (49 g.), methanol (75 g.), and sulphuric acid (1 g.) were boiled under reflux for 18 hr. Excess of methanol was distilled off through an 18″ Vigreux column (10 : 1 reflux ratio), the residue treated with an equal volume of water, and made alkaline with sodium hydroxide solution, and ester extracted with ether. The dried (Na_2SO_4) extract left crude ester (21·4 g.) on removal of solvent. Butylacrylic acid (30 g.) was recovered by acidification of the alkaline wash-liquid, extraction with ether, drying (Na_2SO_4), and removal of solvent. This recovered acid, esterified as above, gave further crude ester (15·2 g.) and recovered acid (8·1 g.). Crude ester (35·4 g.) was twice fractionally distilled. through a 6″ Dixon column (*J. Soc. Chem. Ind.*, 1949, **68**, 299), with a 30 : 1 reflux ratio, and gave methyl *tert.*-butylacetate, b. p. 128—130°/759 mm. (3·6 g.), and *methyl* α-tert.-*butylacrylate*, b. p. 145—146°/757 mm. (10·6 g.). By use of a 50-cm. column (1·0-cm. bore), packed with

Podbielniak " Heli-pak " No. 2916 flattened metallic spirals, crude ester (52·0 g.) gave in one pass methyl α-*tert.*-butylacrylate (37 g.) with methyl *tert.*-butylacetate (4·0 g.).

Methyl α-*tert.*-butylacrylate had b. p. 146—146·5°, n_D^{20} 1·4272, d_4^{20} 0·9033, $[R_L]_D$ 40·41 (Calc. : 40·33) [Found : C, 67·6; H, 9·6% ; *M* (micro-vaporimetric), 140. $C_8H_{14}O_2$ requires C, 67·6; H, 9·9%; *M*, 142]. Methyl 2 : 2 : 3-trimethylbut-3-enoate obtained from methyl tetramethyllactate had n_D^{20} 1·4288, d_4^{20} 0·9126. Hydrogenation of the butylacrylate with Adams's catalyst (micro-method of Clauson-Kaas and Limborg, *Acta Chem. Scand.*, 1948, **1**, 884) showed 0·99 double bond.

Polymerizability of Methyl α-tert.-*Butylacrylate.*—(*a*) Ester (0·5 g.), containing benzoyl peroxide (5·6 mg.) in solution, was evacuated in a tube, cooled to −75°, and sealed. The tube was heated for 21 hr. at 85° without visible change. The product was evaporated at 15 mm. from a retort-shaped bulb of 25-c.c. capacity, immersed in a water-bath raised gradually to 100° and kept at 100° for 50 min. The wt. of residue, corrected for benzoyl peroxide, was 3% of the ester taken; it was a clear, colourless syrup, soluble immediately in cold light petroleum (b. p. 40—60°).

(*b*) Ester (6 c.c.) was irradiated for 213 hr. in a borosilicate tube with ultra-violet radiation, as described in Part I (*loc. cit.*). The appearance, viscosity, and refractive index (η_D^{20} 1·0 c. p.; n_D^{20} 1·4272) were unchanged. Evaporation of the irradiated ester as in (*a*) left 0·09% of residue after 60 min.' heating at 100°. Methyl methacrylate exposed simultaneously was converted into solid resin within 42 hr.

(*c*) Ester (4 g.) was treated with a solution of sodium (0·1 g.) in liquid ammonia (25 c.c.) at −75°, as described in Part I. The product was evaporated as in (*a*) (100°, 62 min., 9—10 mm.). The distillate had n_D^{20} 1·4272. A liquid residue of *methyl* αδ-*di*-tert.-*butyladipate*, readily soluble in cold light petroleum (b. p. 40—60°), amounted to 29·9% of the ester taken [Found : C, 67·4; H, 10·5%; *M* (cryoscopic in benzene), 283. $C_{16}H_{30}O_4$ requires C, 67·1; H, 10·6%; *M*, 286].

(*d*) Ester (20 g.) was added to a stirred solution of sodium (1·62 g.) in liquid ammonia (150 c.c.) at −75°. During the addition (4 min.) the blue colour of the sodium solution changed to green, which was not replaced by the yellow sodium amide colour until about 1 min. after the addition. Yellowish solid was formed. After 30 min. at −75°, ammonium chloride (5 g.) was added. The yellow colour disappeared at once. The mixture was allowed to warm to room temperature, and treated with water (25 c.c.). The solid dissolved and an upper oily layer (19·5 g.) separated. The oil was washed with water, dilute hydrochloric acid, and water, and dried ($CaCl_2$), and distilled on a water-bath for 1 hr. at 27 mm. The distillate, redistilled, boiled at 145—147° and had n_D^{20} 1·4270. Catalytic hydrogenation of this recovered methyl butylacrylate showed 0·98 double bond per molecule. The residual dimer (11·4 g.) had *M*, 259 (cryoscopic in benzene). It was distilled; after removal of some methyl butylacrylate, it passed over at 77°/0·04 mm. The colourless liquid had n_D^{20} 1·4530, and did not take up hydrogen in presence of Adams's catalyst [Found: C, 67·1; H, 10·5%; *M* (cryoscopic in benzene), 284].

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