CCCXX.—*Di*iso*propylmalonic Acid and its Derivatives.*

By Frederick C. B. Marshall.

Attempts to improve the preparation of di*iso*propylmalonic acid from ethyl cyanoacetate (J., 1930, 2754) and also to prepare the acid from ethyl acetoacetate have been unsatisfactory, but further work has shown that a second *iso*propyl group can be introduced into ethyl sodio*iso*propylmalonate when the reaction is conducted in sealed tubes. The reaction does not appear to proceed if the pure (ether- and alcohol-free) sodio-derivative is used, and further, the ethyl ester gives a much better yield (40% yield) than the methyl ester (max., 10%).

Di*iso*propylmalonic acid, treated with thionyl chloride, yielded a liquid acid monochloride which, when heated under diminished pressure, lost, not hydrogen chloride to give the anhydride (Staudinger and Ott, *Ber.*, 1908, **41**, 2208; Staudinger, *ibid.*, p. 1356), but carbon dioxide to give *di*iso*propylacetyl chloride.*

EXPERIMENTAL.

*Ethyl di*iso*propylmalonamate*, which cannot be prepared from the acid and alcohol in the presence of either hydrochloric or sulphuric acid (Marshall, *loc. cit.*), was obtained from the silver salt and ethyl iodide. It is a solid, m. p. 62°, easily soluble in most organic solvents, but crystallisable from light petroleum (b. p. 40—60°), in which it is sparingly soluble (Found: C, 61·4; H, 10·1. $C_{11}H_{21}O_3N$ requires C, 61·5; H, 9·8%).

*Ethyl Di*iso*propylmalonate.*—Ethyl *iso*propylmalonate and the calculated amount of " molecularised " sodium were kept in ether for 1—2 days and the ether was then evaporated as completely as possible by 4—24 hours' heating on the steam-bath. The nearly ether-free ethyl sodio*iso*propylmalonate was heated with 2 equivalents (100% excess) of *iso*propyl iodide in a sealed tube at 250° for 12 hours. The product was poured into water, extracted with ether, and distilled, the fraction, b. p. 228—246°, being collected (42 g. from 51 g. of ethyl *iso*propylmalonate). It was contaminated with much monoalkylated ester, which was removed by boiling with excess of concentrated potassium hydroxide solution for 24—48 hours. The pure *ester* had b. p. 246·2°/751 mm., d^{20° 0·9774, $n_D^{20^\circ}$ 1·4356; whence $[R_L]_D$ 65·2 (calc., 65·3) (Found: C, 64·0; H, 10·1. $C_{13}H_{24}O_4$ requires C, 64·0; H, 9·8%).

*Ethyl Hydrogen Di*iso*propylmalonate.*—Ethyl di*iso*propylmalonate could not be hydrolysed with aqueous or aqueous-alcoholic caustic alkali solutions of any strength. Treatment of the ester with excess of concentrated potassium ethoxide solution at 95° for 30 hours gave a quantitative yield of *ethyl hydrogen di*iso*propylmalonate*, which could not be further hydrolysed with either potassium hydroxide or potassium ethoxide. Recrystallised from petrol (b. p. 60—80°), it was obtained as a solid, m. p. 66° (Found: C, 59·9; H, 9·45; *M*, by titration, 215. $C_{11}H_{20}O_4$ requires C, 61·1; H, 9·3%; *M*, 216).

*Methyl Di*iso*propylmalonate.*—Ethyl *iso*propylmalonate (100 g.) was hydrolysed to the acid, which was recrystallised from benzene till pure (m. p. 87°). The acid (58 g.) was kept in 400 c.c. of pure methyl alcohol and 40 c.c. of concentrated sulphuric acid for 48 hours. Methyl *iso*propylmalonate, isolated from the diluted mixture by extraction with ether and freed from traces of acid by shaking with sodium carbonate solution, was obtained boiling constantly at 198·2°/758 mm. (60 g.). Prepared in this way, whereby all possibility of the presence of ethyl malonate is excluded, it has a definitely higher b. p. than that recorded by Bishoff (*Ber.*, 1896, **29**, 977), *viz.*, 196°/770 mm.

The pure monoalkylated ester was converted into the di*iso*propylmalonate as described above for ethyl di*iso*propylmalonate. (Departure from the directions given, as, for example, when the quite pure sodio-derivative is used, invariably leads to failure.) Freed from methyl *iso*propylmalonate (usually more than 90% of the product) by prolonged refluxing with 30% potash solution, *methyl di*iso*propylmalonate* distilled at 228°/744 mm. and solidified to a mass of large hard prisms, m. p. 32°, which were too soluble in organic solvents to permit of recrystallisation (Found: C, 61·4; H, 9·15. $C_{11}H_{20}O_4$ requires C, 61·1; H, 9·3%). The supercooled liquid had $d^{20°}$ 1·017 and $n_D^{20°}$ 1·4417, whence $[R_L]_D$ 56·2 (calc., 56·1).

*Di*iso*propylmalonic Acid.*—The methyl ester, heated with excess of potassium ethoxide solution for 24 hours, gave a quantitative yield of methyl hydrogen di*iso*propylmalonate. Water was then added, and the mixture refluxed for a further 48 hours to effect hydrolysis to the acid. This was boiled in acetone solution with charcoal; the white crusts obtained on evaporation of the solvent crystallised from hot formic acid in large needles, m. p. 198° (not 197° as originally recorded) [Found : C, 57·5; H, 8·6; *M* (dibasic) by titration, 188. Calc. for $C_9H_{16}O_4$: C, 57·45; H, 8·5%; *M*, 188].

*Treatment of Di*iso*propylmalonic Acid with Thionyl Chloride.*—The acid (5 g.) in 20 c.c. of dry ether was heated for 3 hours with thionyl chloride (2½ mols.). The ether was then removed on a water-bath, the thionyl chloride in a vacuum, and the residual oil distilled, *di*iso*propylacetyl chloride* passing over at 63°/15 mm. This had $d^{20°}$ 0·9709 and $n_D^{20°}$ 1·4403, whence $[R_L]_D$ 44·1 (calc., 44·02) (Found: Cl, 22·4. $C_8H_{15}OCl$ requires Cl, 21·8%), and formed an *anilide*, fine silky needles, m. p. 148—149°, from ether–petroleum, identical with a specimen obtained from di*iso*propylacetic acid (J., 1930, 2760) by successive thionyl chloride and aniline treatment (Found : C, 76·5; H, 10·0. $C_{14}H_{21}ON$ requires C, 76·7; H, 9·6%).

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THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W.7.
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