567. 1,2,3,4-*Tetrahydro*-8-*methylfluoren*-1-*one.*

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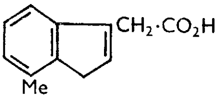
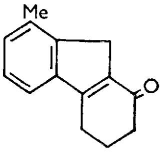
7-Methylindenyl-3-acetic acid has been synthesised by a Reformatsky reaction on 4-methylindan-1-one. Lengthening the side chain by two carbon atoms and cyclisation of the product with phosphorus pentachloride gives 1,2,3,4-tetrahydro-8-methylfluoren-1-one.

IN a recent paper Howell and Taylor[1] have described the synthesis of 1-methylfluorene from indene, but the method could not usefully be employed with *Bz*-substituted indenes because of the ambiguity between the 1- and the 3-position. A Reformatsky reaction has now been carried out on 4-methylindan-1-one.[2] In contrast to the results of von Braun *et al.* with indan-1-one the yield was rather low and the product was not completely separable from the original ketone by distillation. However, alkaline hydrolysis readily gave the expected acid. The side chain in this was lengthened twice by the sequence of reduction with lithium aluminium hydride, esterification with benzenesulphonyl chloride, reaction with potassium cyanide, and hydrolysis; in each case the reaction with cyanide gave a low yield.



(I)



(II)

All the compounds obtained had similar ultraviolet absorption spectra, and on this basis the Reformatsky product is formulated as 7-methyl-3-indenylacetic acid (I). β-3-Indenylpropionic acid[1,3] has a similar spectrum, $\lambda_{\text{max.}}$ (in cyclohexane) 252 mμ. The final product, γ-(7-methyl-3-indenyl)butyric acid cyclised readily with phosphorus pentachloride, to give the required 1,2,3,4-tetrahydro-8-methylfluoren-1-one (II); the overall yield was very small. Analogy with the unsubstituted series[1] suggests that a better yield would be obtained by the use of 3-(7-methyl-3-indenyl)propyl bromide in place of the sulphonic ester, but it is not likely to reach a useful level, for conversion of indenylethanol into indenylpropionitrile *via* the bromide[1,3] gives a very low yield indeed.

The Reformatsky reaction has been repeated on indan-1-one, and the results were very similar to those with the methylated derivative. The difficulty experienced by von Braun *et al.* in hydrolysing the ester was not found, and 3-indenylacetic acid was readily obtained.

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[1] Howell and Taylor, *J.*, 1957, 3011.

[2] von Braun, Danziger, and Koehler, *Ber.*, 1917, **50**, 56.

[3] Clemo, Groves, Munday, and Swan, *J.*, 1951, 863.

EXPERIMENTAL

7-*Methyl*-3-*indenylacetic Acid* (I).—4-Methylindan-1-one (120 g.), ethyl bromoacetate (96 g.), benzene (500 ml.), and granulated zinc (60 g.) were refluxed together for 2½ hr., then cooled. Dilute sulphuric acid was added, and the organic layer filtered from ketone dimer, washed with water, and evaporated. The residue was distilled and a fraction collected at 130—150°/0·5 mm. On cooling, crystals separated; filtration and crystallisation from cyclohexane gave 4-methylindan-1-one (25 g.), m. p. 95—97°. The residual oil, still containing much ketone, was refluxed for 5 min. with water (100 ml.), methanol (200 ml.), and potassium hydroxide (60 g.). The cooled solution was diluted with water (500 ml.), washed with chloroform, and acidified. Extraction with chloroform gave 7-*methyl*-3-*indenylacetic acid* (60 g.) which on crystallisation from benzene–cyclohexane formed laths, m. p. 118—120° (Found: C, 76·7; H, 6·45. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4%), $\lambda_{max.}$ (in cyclohexane) 253 mμ (log ε 4·0).

3-*Indenylacetic Acid.*—In the same way indan-1-one (16 g.) gave 3-indenylacetic acid (5·9 g.), m. p. 93—95° (Thiele and Rüdiger [4] give m. p. 95—96° for a specimen obtained in a different way) (Found: C, 75·8; H, 5·8. Calc. for $C_{11}H_{10}O_2$: C, 75·8; H, 5·8%), $\lambda_{max.}$ (in cyclohexane) 254 mμ (log ε 4·05).

2-(7-*Methyl*-3-*indenyl*)*ethanol.*—7-Methyl-3-indenylacetic acid (45 g.) in ether was added to lithium aluminium hydride (10 g.) in ether. The mixture was worked up with aqueous tartaric acid, and the organic layer distilled. 2-(7-Methyl-3-indenyl)ethanol (27 g.) was collected at 140°/0·5 mm. Crystallisation from cyclohexane gave a sample, m. p. 48°, $\lambda_{max.}$ (in cyclohexane) 253 mμ (log ε 3·92). This substance soon became sticky, and a good analysis was not obtained.

β-(7-*Methyl*-3-*indenylpropionic Acid.*—2-(7-Methyl-3-indenyl)ethanol (25 g.) in ether (100 ml.) was treated with pyridine (25 ml.) and benzenesulphonyl chloride (18 ml.). After 2 hr. the mixture was diluted with water, washed with dilute hydrochloric acid, dilute sodium carbonate solution, and water, and evaporated. The residue was refluxed for 3 hr. with water (25 ml.), methanol (80 ml.), and potassium cyanide (15 g.). After cooling, the product was isolated with benzene as a yellow oil (18 g.), b. p. 150—180°/2 mm. This was refluxed for 12 hr. with sodium hydroxide (10 g.) in water (30 ml.). The acidic product crystallised from benzene, to give β-(7-*methyl*-3-*indenyl*)*propionic acid* (5·5 g.) as yellow needles, m. p. 159° (Found: C, 76·9; H, 6·9. $C_{13}H_{14}O_2$ requires C, 77·2; H, 7·0%), $\lambda_{max.}$ (in cyclohexane) 254 mμ (log ε 3·95). Reaction of the sulphonic ester with diethyl sodiomalonate gave none of the required product.

3-(7-*Methyl*-3-*indenyl*)*propan*-1-*ol.*—The foregoing propionic acid (5·3 g.) was reduced with lithium aluminium hydride (2 g.) in ether. After working up with aqueous tartaric acid, the organic layer was evaporated. The residue crystallised from n-pentane to give 3-(7-*methyl*-3-*indenyl*)*propan*-1-*ol* (4·85 g.) as yellow plates, m. p. 72—73° (Found: C, 83·1; H, 8·6. $C_{13}H_{16}O$ requires C, 83·0; H, 8·6%), $\lambda_{max.}$ (in cyclohexane) 253 mμ (log ε 3·98).

γ-(7-*Methyl*-3-*indenyl*)*butyric Acid.*—The above alcohol (4·2 g.) in ether (20 ml.) was treated with pyridine (5 ml.) and benzenesulphonyl chloride (4 ml.). After working up, the residue was refluxed for 12 hr. with methanol (10 ml.), water (4 ml.), and potassium cyanide (3 g.). The crude nitrile (3·1 g.) distilled at 134°/0·5 mm., and was then hydrolysed with sodium hydroxide (5 g.) in water (30 ml.). The acidic product was crystallised from cyclohexane, to give γ-(7-*methyl*-3-*indenyl*)*butyric acid* (900 mg.) as colourless plates, m. p. 107—108° (Found: C, 77·4; H, 7·4. $C_{14}H_{16}O_2$ requires C, 77·75; H, 7·4%), $\lambda_{max.}$ (in cyclohexane) 253 mμ (log ε 3·98).

1,2,3,4-*Tetrahydro*-8-*methylfluoren*-1-*one* (II).—The butyric acid (95 mg.) and phosphorus pentachloride (100 mg.) were refluxed in benzene (2 ml.) for 1 hr. The solution was washed with water and with potassium carbonate solution, dried, and evaporated. The residue crystallised from cyclohexane to give 1,2,3,4-*tetrahydro*-8-*methylfluoren*-1-*one* (43 mg.) as colourless needles, m. p. 156° (Found: C, 85·6; H, 7·1. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%), $\lambda_{max.}$ (in cyclohexane) 294 mμ (log ε 4·19). The dinitrophenylhydrazone formed very insoluble, dark red crystals, m. p. 300—302°.

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[4] Thiele and Rüdiger, *Annalen*, 1906, **347**, 275.