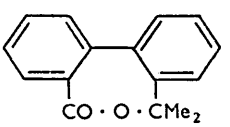
## 692. *The Isomerisation of the Lactone of 2′-(1-Hydroxy-1-methylethyl)-diphenyl-2-carboxylic Acid.*

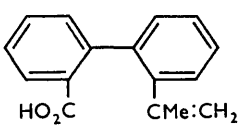
By Pauline M. Everitt and E. E. Turner.

When the lactone (I) is heated with anhydrous formic acid or with 50% sulphuric acid, 9 : 9-dimethylfluorene-4-carboxylic acid (III) is produced. When the lactone (I) is heated with alumina, 2′-(1-methylvinyl)diphenyl-2-carboxylic acid (II) is obtained.

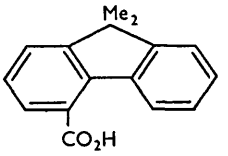
In an attempt to obtain 2′-(1-methylvinyl)diphenyl-2-carboxylic acid (II) by heating the lactone (I) with anhydrous formic acid or with 50% sulphuric acid, 9 : 9-dimethylfluorene-4-carboxylic acid (III) was isolated. This led us to find that 9 : 9-dialkylfluorenes had been obtained from dialkyl-2-diphenylylcarbinols, and 9 : 9-diphenylfluorene-4-carboxylic




(I)




(II)




(III)

acid from 2′-(α-hydroxydiphenylmethyl)diphenyl-2-carboxylic acid [1] in presence of acids. Decarboxylation of the acid (III) gave 9 : 9-dimethylfluorene, whilst treatment of its methyl ester with methylmagnesium iodide gave 4-(1-hydroxy-1-methylethyl)-9 : 9-dimethylfluorene, from which by dehydration, followed by hydrogenation, 9 : 9-dimethyl-4-*iso*propylfluorene was obtained.

The desired 2′-(1-methylvinyl)diphenyl-2-carboxylic acid (II) was later obtained by heating the lactone (I) with alumina. It was hydrogenated to 2′-*iso*propyldiphenyl-2-carboxylic acid, identical with the product of fusing 9 : 10-dihydro-9 : 9-dimethyl-10-oxophenanthrene with potassium hydroxide.[2] Decarboxylation of the *iso*propyl acid gave 2-*iso*propyldiphenyl [$\lambda_{max.}$ 233 mμ (ε 8800), $\lambda_{min.}$ 225 mμ (ε 8100) in 95% EtOH; cf. ref. 3].

[1] Anchel and Blatt, *J. Amer. Chem. Soc.*, 1941, **63**, 1948; Sergeev, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 1421.
[2] Meerwein, *Annalen*, 1913, **396**, 225.
[3] Braude and Forbes, *J.*, 1955, 3776; A.P.I. Research Project No. 44, no. 285.

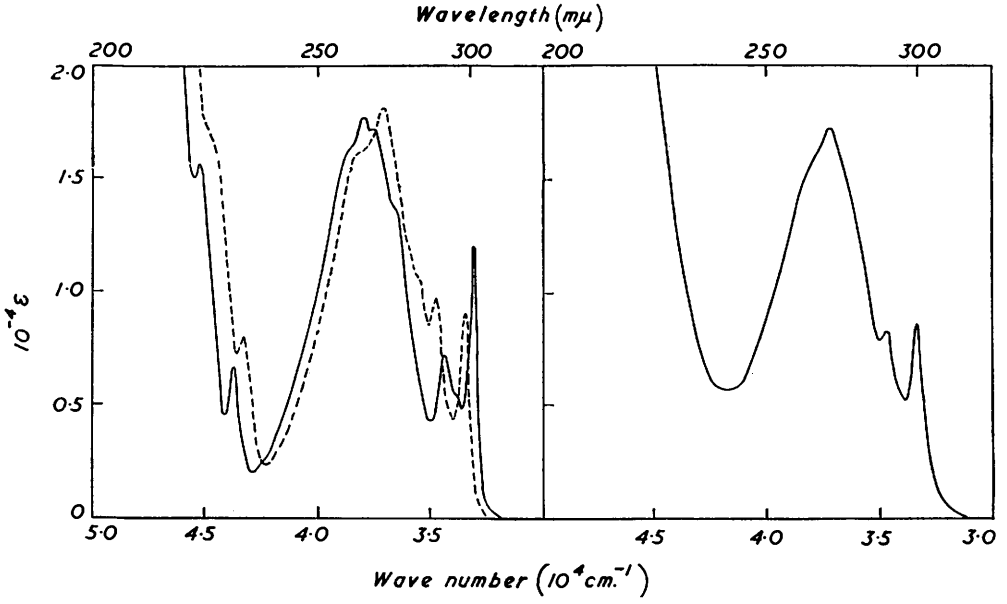
The ultraviolet absorption spectra (Figs. 1 and 2; Table) of the 9 : 9-dimethylfluorenes suggest that the steric effect of a substituent such as *iso*propyl in the 4-position is much

| | Diphenyl band | | Long-wave band | |
|---|---|---|---|---|
| Compound (in 95% EtOH) | $\lambda_{max.}$ (m$\mu$) | $\varepsilon$ | $\lambda_{max.}$ (m$\mu$) | $\varepsilon$ |
| 9 : 9-Dimethylfluorene ..... | 263 | 17,500 | 290, 302 | 7100, 12,000 |
| 9 : 9-Dimethyl-4-*iso*propylfluorene ..... | 269 | 18,000 | 287·5, 298·5 | 9600, 9000 |
| 9 : 9-Dimethyl-4-(1-methylvinyl)fluorene ... | 268·5 | 17,000 | 288, 299·5 | 8200, 8500 |

less than in the corresponding position in diphenyl; presumably this is due to the planar, non-collinear configuration of fluorene [4] which leaves more space for an *ortho*-substituent.

FIG. 1. *Absorption of* (——) 9 : 9-*dimethylfluorene and* (– – – –) 9 : 9-*dimethyl*-4-iso*propylfluorene.*

FIG. 2. *Absorption of* 9 : 9-*dimethyl*-4-(1-*methylvinyl*)*fluorene.*




## EXPERIMENTAL

9 : 9-*Dimethylfluorene*-4-*carboxylic Acid.*—(*a*) A solution of 2′-(1-hydroxy-1-methylethyl)diphenyl-2-carboxylic lactone (1 g.) in anhydrous formic acid (20 c.c.) was boiled under reflux for 4 hr. The cooled solution deposited crystals which were filtered off, dissolved in ether, washed with brine, and then extracted with 30% aqueous sodium hydroxide. The alkaline extract was acidified and the precipitate filtered off and dried (0·6 g.). After crystallisation from benzene the dimethylfluorenecarboxylic acid (0·4 g.) had m. p. 195—196°.

(*b*) A mixture of the lactone (25 g.) and 50% sulphuric acid (250 c.c.) was boiled under reflux for 1 hr., then cooled and poured into ice-water. Extraction with ether, etc., as in (*a*), gave 20 g. of dimethylfluorenecarboxylic acid.

*Methyl* 9 : 9-*dimethylfluorene*-4-*carboxylate*, obtained from the acid by treatment with thionyl chloride and then methanol, formed hexagonal prisms, m. p. 82—83°, from methanol (Found : C, 80·9; H, 6·4. $C_{17}H_{16}O_2$ requires C, 80·95; H, 6·4%). The *amide*, prepared from the acid by the successive use of thionyl chloride and aqueous ammonia, had m. p. 180·5—181·5° after crystallisation from aqueous ethanol (Found : N, 5·8. $C_{16}H_{15}ON$ requires N, 5·9%).

[4] Brown and Bortner, *Acta Cryst.*, 1954, **7**, 139; Burns and Iball, *Nature*, 1954, **173**, 635.

9 : 9-*Dimethylfluorene*.—A solution of the fluorene-acid (2 g.) in quinoline (20 c.c.), containing a little copper bronze in suspension, was boiled for 3 hr. and then poured into dilute hydrochloric acid. The solution was extracted with ether, and the ethereal solution suitably washed. Evaporation, followed by crystallisation from aqueous ethanol (charcoal), gave the dimethylfluorene (1·1 g.), m. p. 95—96° (Found : C, 92·7; H, 7·3. Calc. for $C_{15}H_{14}$ : C, 92·8; H, 7·2%).

4-(1-*Hydroxy*-1-*methylethyl*)-9 : 9-*dimethylfluorene*.—Methyl 9 : 9-dimethylfluorene-4-carboxylate (11·5 g., 1·0 mol.) was added to a Grignard reagent prepared from 5 g. (4·5 atom-equiv.) of magnesium and methyl iodide. The mixture was boiled for 5 hr., cooled, decomposed, and worked up in the usual way. The *hydroxy-compound* (6 g., 52%) crystallised from dilute ethanol in prisms, m. p. 118—119° after vacuum-drying (Found : C, 85·2; H, 8·1. $C_{18}H_{20}O$ requires C, 85·7; H, 7·9%).

9 : 9-*Dimethyl*-4-(1-*methylvinyl*)*fluorene*.—A mixture of the above hydroxy-compound (3 g.) and 50% sulphuric acid (75 c.c.) was boiled under reflux for 2 hr. and then poured into ice-water. Extraction with ether and normal working up gave the *hydrocarbon* (2·1 g., 75%) which crystallised from light petroleum (b. p. 40—60°) in prisms, m. p. 67—68° (Found : C, 92·4; H, 7·7. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%).

9 : 9-*Dimethyl*-4-iso*propylfluorene*.—A solution of the 1-methylvinylfluorene (1·5 g.) in ethanol (50 c.c.) and platinum oxide (0·5 g.) was shaken in hydrogen (95 lb./sq. in.) for 5 hr. After normal procedure the *hydrocarbon* crystallised from dilute ethanol (charcoal) as plates, m. p. 48—49° (1·2 g.) (Found : C, 91·4; H, 8·7. $C_{18}H_{20}$ requires C, 91·5; H, 8·5%).

2′-iso*Propyldiphenyl*-2-*carboxylic Acid*.—It was found advantageous to carry out the fusion of 9 : 10-dihydro-9 : 9-dimethyl-10-oxophenanthrene with less potassium hydroxide than Meerwein [2] used and at 185—190° instead of at 220—240°. The yield was 61% and the m. p. 110—111° (Meerwein gave m. p. 104—106°) (Found : C, 80·4; H, 6·9. Calc. for $C_{16}H_{16}O_2$ : C, 80·0; H, 6·7%).

The *amide*, prepared *via* the acid chloride, after being crystallised from light petroleum (b. p. 100—120°) had m. p. 115·5—116·5° (Found : N, 5·8. $C_{16}H_{17}ON$ requires N, 5·9%).

2-iso*Propyldiphenyl*.—A solution of the preceding carboxylic acid (2·4 g.) in quinoline (15 c.c.) containing a little copper bronze was boiled for 4 hr., then cooled and poured into dilute hydrochloric acid. Extraction with ether, followed by removal of the ether and distillation over sodium, gave 2-*iso*propyldiphenyl, needles m. p. 25—26° (from ethanol). Goodman and Wise [5] found m. p. 24·46°.

*Isomerisation of* 2′-(1-*Hydroxy*-1-*methylethyl*)*diphenyl*-2-*carboxylic Lactone*.—A mixture of the lactone (3 g.) and alumina (1 g.) was heated from 150° to 260° during 20 min. After cooling, the product was extracted with ether and the extract washed and extracted with alkali. Acidification of the alkaline extracts gave 2′-(1-*methylvinyl*)*diphenyl*-2-*carboxylic acid*, which after crystallisation from dilute ethanol and then light petroleum (b. p. 100—120°) formed prisms, m. p. 122° (Found : C, 80·6; H, 5·4. $C_{16}H_{14}O_2$ requires C, 80·7; H, 5·9%).

*Reduction of* 2′-(1-*Methylvinyl*)*diphenyl*-2-*carboxylic Acid*.—The unsaturated acid (0·5 g.) in ethanol (20 c.c.) with platinum oxide catalyst (0·05 g.) was shaken in hydrogen for 6 hr. at 95 lb./sq. in. Normal working up, followed by crystallisation from dilute ethanol, gave 2′-*iso*propyldiphenyl-2-carboxylic acid, m. p. and mixed m. p. with above acid 110—111°.

The authors thank Imperial Chemical Industries Limited for a grant and the Department of Scientific and Industrial Research for a maintenance grant (to P. M. E.).

Bedford College, University of London. [*Received, April 9th*, 1957.]

[5] Goodman and Wise, *J. Amer. Chem. Soc.*, 1950, **72**, 3076.