467. *Gibberellic Acid. Part III.* Synthesis of Fluorenone-4 : 5-dicarboxylic Acid.*

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4 : 5-Dimethylfluorene, 4 : 5-dimethylfluorenone, and fluorenone-4 : 5-dicarboxylic acid have been synthesised.

Oxidation of gibberene (1 : 7-dimethylfluorene), the dehydrogenation product of gibberellic acid, was shown by Mulholland and Ward [1] to give fluorenone-1 : 7-dicarboxylic acid. Yabuta *et al.*[2] had suggested that an acid obtained from gibberene might be fluorenone-4 : 5-dicarboxylic acid, which we therefore prepared for comparison.

Kruber [3] obtained fluorenone-4 : 5-dicarboxylic acid by degradation of 4 : 5-methylenephenanthrene, isolated from the anthracene-oil fraction of coal tar. The present synthesis envisaged the ring closure of 6 : 6'-dimethyldiphenic anhydride [4, 5] to 4 : 5-dimethylfluorenone, followed by oxidation.

4 : 5-Dimethylfluorenone was formed in this way, but a better yield (77%) was obtained by heating 6 : 6'-dimethyldiphenic acid. Oxidation of the fluorenone in aqueous pyridine with potassium permanganate gave 4-methylfluorenone-5-carboxylic acid together with a small amount of fluorenone-4 : 5-dicarboxylic acid. Further oxidation of 4-methylfluorenone-5-carboxylic acid was difficult and fluorenone-4 : 5-dicarboxylic acid was only obtained in low yield. The melting points of the dicarboxylic acid and its anhydride correspond with those given by Kruber. The melting point of the dimethyl ester was depressed on admixture with methyl fluorenone-1 : 7-dicarboxylate. Wolff–Kishner reduction of 4 : 5-dimethylfluorenone gave 4 : 5-dimethylfluorene.

Experimental

M. p.s are corrected. The alumina used for chromatography was prepared as described by Mulholland and Ward.[1]

4 : 5-*Dimethylfluorenone*.—(*a*) 6 : 6'-Dimethyldiphenic acid [4] (5·00 g.) was heated at 360° for 1 hr. under nitrogen. 4 : 5-*Dimethylfluorenone* (3·08 g., 77%; m. p. 105—110°), obtained

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* Part II, *J.*, 1954, 4676.

[1] Mulholland and Ward, *J.*, 1954, 4676.

[2] Yabuta, Sumiki, Azabu, Tamura, Igarashi, and Tamari, *J. Agric. Chem. Soc. Japan*, 1940, **16**, 975.

[3] Kruber, *Ber.*, 1934, **67**, 1000.

[4] Bergmann and Pelchowicz, *J. Amer. Chem. Soc.*, 1953, **75**, 2663.

[5] Cf. Huntress, Hershberg, and Cliff, *ibid.*, 1931, **53**, 2720.

by extraction with benzene, recovery from the extract, and sublimation *in vacuo*, crystallised from benzene–light petroleum (b. p. 60—80°) in yellow needles and prisms (2·50 g.), m. p. 117—119°, raised to 119—120° by further crystallisation (Found: C, 86·5; H, 6·0. $C_{15}H_{12}O$ requires C, 86·5; H, 5·8%). The 2 : 4-*dinitrophenylhydrazone* crystallised from benzene in orange-red needles, m. p. 252—253° (Found: C, 64·9; H, 4·55; N, 14·65. $C_{21}H_{16}O_4N_4$ requires C, 64·9; H, 4·15; N, 14·4%). The *oxime*, prepared in pyridine, crystallised from benzene–light petroleum (b. p. 60—80°) in pale yellow needles, m. p. 218—219° (Found: C, 80·5; H, 5·8; N, 6·6. $C_{15}H_{13}ON$ requires C, 80·7; H, 5·9; N, 6·3%).

(*b*) 6 : 6′-Dimethyldiphenic acid (1·00 g.) was heated under reflux with acetic anhydride for 1 hr. The crude gummy anhydride recovered by evaporation was heated at 360° for 2 hr. under nitrogen. Carbon dioxide (0·98 mol.) was evolved and considerable charring took place. The neutral fraction of a benzene extract of the product was chromatographed in benzene (9 ml.) on alumina (5 × 0·8 cm.). Elution with benzene in ultraviolet light removed white bands and then a deep yellow band. On recovery, the last gave 4 : 5-dimethylfluorenone (166 mg.), m. p. 105—110°, raised to 117—119° (120 mg.) by recrystallisation.

4 : 5-*Dimethylfluorene*.—A mixture of 4 : 5-dimethylfluorenone (2·54 g.), 100% hydrazine hydrate (3·60 ml.), and alcoholic sodium ethoxide, prepared from sodium (962 mg.) in ethanol (20 ml.), was heated at 185° for 5 hr. After dilution with water, the mixture was extracted with ether. The extract was washed with dilute sulphuric acid and with water, dried ($CaCl_2$), and evaporated. The residue (2·12 g.) in ether–light petroleum (b. p. 40—60°; 1 : 50) was chromatographed on alumina (15 × 1·2 cm.), and the column was eluted in ultraviolet light with the same solvent. A blue fluorescent band was collected and on recovery gave 4 : 5-*dimethylfluorene* (1·73 g.), m. p. 75—79°, which crystallised from methanol in needles, m. p. 81—82° (Found: C, 92·6; H, 7·4. $C_{15}H_{14}$ requires C, 92·7; H, 7·3%). The 1 : 3 : 5-*trinitrobenzene adduct* crystallised from ethanol in yellow prisms, m. p. 114° (Found: C, 61·9; H, 4·2; N, 10·6. $C_{15}H_{14},C_6H_3O_6N_3$ requires C, 61·9; H, 4·2; N, 10·3%).

Oxidation of 4 : 5-*Dimethylfluorenone*.—Potassium permanganate (2·50 g.) was added in portions during 30 min. to 4 : 5-dimethylfluorenone (500 mg.) in pyridine (4·5 ml.) and water (2·3 ml.) at 100°, more water and pyridine being added at intervals. When the reagent was consumed (20 min.), the mixture was cooled, diluted, and filtered, the precipitate being washed with water and acetone. The combined filtrate and washings, after evaporation of the acetone and most of the pyridine, were acidified. The precipitate was collected, washed with water, and extracted with cold dilute potassium hydroxide solution. Starting material (78 mg.) remained undissolved. Acidification of the alkaline extract gave a yellow solid (290 mg.) which was digested with cold acetone until the undissolved portion did not melt below 240°. This (30 mg.) consisted of crude fluorenone-4 : 5-dicarboxylic acid and was retained for further purification.

The acetone-soluble material crystallised from dilute acetone in needles (234 mg.), m. p. 192—195°. Further crystallisation gave 4-*methylfluorenone*-5-*carboxylic acid* as yellow needles, m. p. 191—192° (Found: C, 75·7; H, 4·3. $C_{15}H_{10}O_3$ requires C, 75·6; H, 4·2%). The *methyl ester* crystallised from methanol in yellow prisms, m. p. 112—113° (Found: C, 76·1; H, 4·9. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%).

A solution of crude 4-methylfluorenone-5-carboxylic acid (1·30 g.) in 3N-sodium carbonate (70 ml.) was stirred at 100° during the addition in 1 hr. of aqueous potassium permanganate (40 ml.; 5%). When the reagent was consumed, the mixture was cooled and filtered. The filtrate and water washings were acidified, giving a yellow precipitate (978 mg.), m. p. 195—220°, which was collected. This was separated with acetone as described above into crude fluorenone-4 : 5-dicarboxylic acid (111 mg.; m. p. $>$240°) and crude 4-methylfluorenone-5-carboxylic acid. The latter was reoxidised in the same way, and the acetone-soluble part from the second oxidation was oxidised again. The acetone-soluble part of the product from the third oxidation (216 mg.) crystallised from dilute acetone in needles of 4-methylfluorenone-5-carboxylic acid, m. p. 188—192°. The total yield of crude fluorenone-4 : 5-dicarboxylic acid was 205 mg.

Crude fluorenone-4 : 5-dicarboxylic acid (380 mg.) was fractionally crystallised from acetic acid, giving fluorenone-4 : 5-dicarboxylic acid as yellow prisms (198 mg.), m. p. 284—286° (decomp.; with sublimation, the decomp. point being lowered by powdering) (Found: C, 66·5; H, 3·25. Calc. for $C_{15}H_8O_5$: C, 67·2; H, 3·0%). Kruber[3] gave the m. p. as 285° (decomp.) and obtained a low figure for carbon. Similar difficulties in analysis have been encountered with fluorenone-1 : 7-dicarboxylic acid.[6]

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[6] Mulholland and Ward, unpublished results.

The anhydride, prepared as described by Kruber, crystallised from acetic anhydride in pale yellow needles, m. p. 258—259° (Found: C, 71·9; H, 2·5. Calc. for $C_{15}H_6O_4$: C, 72·0; H, 2·4%). Kruber gave the m. p. as 253°. The infrared absorption spectrum in a Nujol mull showed absorption in the carbonyl stretching region at 1767, 1733, and 1720 cm.$^{-1}$.

The *dimethyl ester* crystallised from methanol in pale yellow needles, m. p. 189—190°, depressed on admixture with methyl fluorenone-1 : 7-dicarboxylate (m. p. 189—191°) (Found: C, 68·75; H, 4·3; OMe, 20·5. $C_{17}H_{12}O_5$ requires C, 68·9; H, 4·1; 2 OMe, 21·0%).

The authors are indebted to Dr. L. A. Duncanson for the infrared absorption spectrum, and to Messrs. H. D. Preston and T. J. Ashman for technical assistance in part of the work.

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[*Received, January* 12*th*, 1956.]