607. *Gibberellic Acid. Part XIV.*[1] *1,7-Dimethylfluoren-2-ol.*

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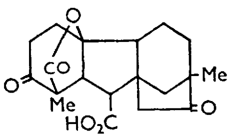
1,7-Dimethylfluoren-2-ol has been synthesised and is identical with a fluorenol, m. p. 202—204° (decomp.), obtained by degradation of gibberellic acid.

Conversion of gibberellic acid into a 4a-hydroxy-1,7-dimethyl-2,8-dioxo-7α-gibbane-1,10-dicarboxylic acid 1→4a-lactone (I), followed by selenium dehydrogenation, gave[1] a fluorenol, m. p. 202—204° (decomp.), which is now shown to be 1,7-dimethylfluoren-2-ol by its unambiguous synthesis.

3-Bromo-*o*-cresol (OH = 1) was prepared from 2-bromo-6-nitrotoluene[2] by way of the amine as described by Noelting,[3] and converted into its methyl ether. An attempt to prepare 3-bromo-*o*-toluidine by hydrogenating 2-bromo-6-nitrotoluene with a palladised charcoal catalyst gave a partly debrominated product.

The Grignard reagent from the bromo-ether reacted with 2,6-dimethyl-4-oxobenz-*m*-oxazine,[4] to give 2′-acetamido-3-methoxy-2,5′-dimethylbenzophenone.[5] Hydrolysis of the acetyl derivative to the amine followed by diazotisation and ring closure gave 2-methoxy-1,7-dimethylfluorenone which on demethylation yielded 2-hydroxy-1,7-dimethylfluorenone. Reductive demethylation of the methoxyfluorenone yielded 1,7-dimethylfluoren-2-ol but also, and in larger amount, 1,7-dimethylfluorene.[4] However, Wolff–Kishner reduction of the methoxyfluorenone gave 2-methoxy-1,7-dimethylfluorene, demethylation then affording 1,7-dimethylfluoren-2-ol in good yield. The latter was shown by its mixed melting point and ultraviolet and infrared absorption spectra to be identical with the fluorenol obtained by dehydrogenation of the diketone (I).



(I)

Experimental

M. p.s are corrected. The ultraviolet absorption spectra and alumina for chromatography were obtained as described previously.[1]

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[1] Part XIII, preceding paper.

[2] Gibson and Johnson, *J.*, 1929, 1229.

[3] Noelting, *Ber.*, 1904, **37**, 1015.

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

[5] Cf. Lothrop and Goodwin, *J. Amer. Chem. Soc.*, 1943, **65**, 363.

2-Bromo-6-nitrotoluene [2] (48% yield from 2,6-dinitrotoluene) had b. p. 136°/8 mm., m. p. 41—42° (lit.,[2] m. p. 42°).

3-Bromo-*o*-cresol prepared [3] from the nitro-compound had m. p. 95° (Found: C, 44·8; H, 3·8; Br, 42·7. Calc. for C_7H_7OBr: C, 45·0; H, 3·7; Br, 42·7%) (lit.,[3] m. p. 94·5°).

Hydrogenation of 2-*Bromo*-6-*nitrotoluene*.—The nitro-compound (5 g.) and 5% palladised charcoal (0·5 g.) in ethanol, shaken in hydrogen at room temperature and pressure until **3** mol. of hydrogen had been absorbed, gave a partially debrominated oil, b. p. 124°/7 mm. (Found: Br, 15·1. Calc. for C_7H_8NBr: Br, 43·0%). It gave an acetate, m. p. and mixed m. p. with *N*-acetyl-3-bromo-*o*-toluidine, 163° (lit.,[6] m. p. 164·5°).

2-*Bromo*-6-*methoxytoluene*.—3-Bromo-*o*-cresol (30 g.) in water (75 ml.) and 20% sodium hydroxide solution (48 ml., 1·5 mol.) was heated on a water-bath, and dimethyl sulphate (19·1 ml.) was added at a rate sufficient to keep the mixture boiling. After 35 minutes' further heating, more dimethyl sulphate (3·8 ml.) was added dropwise, the mixture was heated for 10 min., and more 20% sodium hydroxide solution (8 ml.) added. The last process was repeated four more times. An ethereal solution of the red oily product was washed with 20% potassium hydroxide solution and water and dried. Distillation gave the *methyl ether* (29·7 g.), b. p. 108°/9 mm. (Found: C, 47·6; H, 4·5; Br, 39·4; OMe, 15·3. C_8H_9OBr requires C, 47·8; H, 4·5; Br, 39·8; OMe, 15·4%).

2′-*Acetamido*-3-*methoxy*-2,5′-*dimethylbenzophenone*.—A Grignard reagent from 2-bromo-6-methoxytoluene (18·03 g.) and magnesium (2·33 g.) in ether (60 ml.) was filtered and added dropwise during 1 hr. to 2,6-dimethyl-4-oxobenz-*m*-oxazine [4] (15·71 g.) in ice-cold benzene (250 ml.) under nitrogen. The orange suspension was left for 1 hr. at room temperature, then heated at 30° for 1 hr., cooled, and poured on ice (400 g.) and 3N-sulphuric acid (280 ml.). The organic layer was combined with ether washings of the aqueous layer and washed with water, sodium hydrogen carbonate solution, and water. The ether was removed and the residue steam-distilled. The non-volatile product was washed in ether with water and dried, giving on recovery a brown gum (24·1 g.). This was chromatographed in ether–light petroleum (b. p. 40—60°) (1 : 1; 60 ml.) on alumina (40 × 4·5 cm.) in ultraviolet light. Elution with ether–light petroleum (b. p. 40—60°) (1 : 1), ether, and ether–methanol (20 : 1) of several fluorescent bands gave 8 fractions consisting of orange gums (total 20·8 g.) which failed to crystallise but all gave the amine on hydrolysis. One fraction was sublimed at 115°/10^{-4} mm., giving 2′-*acetamido*-3-*methoxy*-2,5′-*dimethylbenzophenone* as a yellow resin (Found: C, 72·6; H, 6·4; N, 5·5; OMe, 11·1. $C_{18}H_{19}O_3N$ requires C, 72·7; H, 6·4; N, 4·7; OMe, 10·4%) which crystallised when seeded with a specimen prepared by acetylating the free amine (see below).

2′-*Amino*-3-*methoxy*-2,5′-*dimethylbenzophenone*.—The above gummy amide (9·5 g.) was heated in ethanol (90 ml.) and concentrated hydrochloric acid (27 ml.) under reflux for 4 hr. The solution was basified with 7% aqueous ammonia (180 ml.), and the yellow precipitate (8·1 g.), m. p. 128—130°, was collected. Crystallisation from methanol gave the *amine* as yellow prisms, m. p. 131—132° (Found: C, 74·9; H, 6·95; N, 5·7; OMe, 12·4. $C_{16}H_{17}O_2N$ requires C, 75·3; H, 6·7; N, 5·5; OMe, 12·2%). The acetyl derivative formed yellow prisms from benzene–light petroleum (b. p. 60—80°), m. p. 93—94° (Found: C, 73·0; H, 6·85; N, 4·8%).

2-*Methoxy*-1,7-*dimethylfluorenone*.—A solution of the above amine (2·05 g.) in hydrochloric acid (160 ml.) and water (80 ml.) was diazotised at 0—4° with sodium nitrite (0·70 g.) in water (10 ml.) and allowed to warm to 11° during 1 hr. The solution was then heated on a water-bath for 2 hr. and finally under reflux for 30 min. The brownish-orange solid (1·66 g.), m. p. 140—155°, which separated was collected and washed with water. Crystallisation from benzene–light petroleum (b. p. 60—80°) (charcoal) gave the *fluorenone* as orange prisms (1·01 g.), m. p. 167—168° (Found: C, 80·9; H, 6·1; OMe, 13·3. $C_{16}H_{14}O_2$ requires C, 80·6; H, 5·9; OMe, 13·0%). The *oxime*, prepared in pyridine, formed yellow plates (from benzene), m. p. 207—208° (Found: C, 76·0; H, 6·1; N, 5·65. $C_{16}H_{15}O_2N$ requires C, 75·9; H, 6·0; N, 5·5%).

2-*Methoxy*-1,7-*dimethylfluorene*.—2-Methoxy-1,7-dimethylfluorenone (1·035 g.), 100% hydrazine hydrate (1·5 ml.), and sodium (0·40 g.) in ethanol (8 ml.) were heated in a sealed tube at 185° for 6·5 hr. The crystalline product (759 mg.; m. p. 168—169°) was collected, washed with water, and crystallised from methanol, giving 2-*methoxy*-1,7-*dimethylfluorene* as prisms, m. p. 168—169° (Found: C, 85·7; H, 7·15; OMe, 13·85. $C_{16}H_{16}O$ requires C, 85·7; H, 7·2; OMe, 13·8%), $\lambda_{\text{max.}}$ (in EtOH) 274—275, ~284, 303, and 313—314 mμ (log ε 4·35, 4·25, 3·78, and 3·74 respectively).

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[6] Coffey, *J.*, 1926, 637.

1,7-*Dimethylfluoren*-2-*ol*.—(*a*) 2-Methoxy-1,7-dimethylfluorenone (937 mg.), red phosphorus (117 mg.), acetic acid (12 ml.), and hydriodic acid (6 ml.; *d* 1·70) were refluxed for 96 hr. The solids were collected, washed with water, extracted with ether–light petroleum (b. p. 40—60°) (2 : 1; 15 ml.), and filtered from red phosphorus. The extract was chromatographed on alumina (15 × 1·3 cm.) in ultraviolet light. Elution with ether–light petroleum (b. p. 40—60°) (2 : 1) gave (i) a blue fluorescent eluate followed by (ii) a dark grey band the tail of which was eluted with ether.

Fraction (i) crystallised from methanol in curved needles (233 mg.), m. p. 105—107°, raised to 107—107·5° on recrystallisation (Found: C, 92·4; H, 7·3. Calc. for $C_{15}H_{14}$: C, 92·7; H, 7·3%), identical with 1,7-dimethylfluorene (infrared spectrum).

Fraction (ii) (272 mg.), m. p. 184—194°, crystallised from benzene in needles; it was 1,7-*dimethylfluoren*-2-*ol* (186 mg.), m. p. 198—199° (decomp.), raised to 202—204° (decomp.) (varied with the rate of heating) by recrystallisation (Found: C, 85·55; H, 6·8. $C_{15}H_{14}O$ requires C, 85·7; H, 6·7%), $\lambda_{max.}$ (in EtOH) 275, ~283, 305, and 313 mμ (log ε 4·33, 4·28, 3·75, and 3·71 respectively), $\lambda_{max.}$ (in 0·10N-NaOH) 294—296 and ~318 mμ (log ε 4·29 and 4·01 respectively): the *acetate* crystallised from methanol and from benzene–light petroleum (b. p., 60—80°) in needles, m. p. 153—155° (Found: C, 81·2; H, 6·5. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%). The methyl ether crystallised from methanol in prisms, m. p. 168—169°, not depressed on admixture with the specimen prepared as above.

(*b*) 2-Methoxy-1,7-dimethylfluorene (505 mg.), acetic acid (25 ml.), and 48% hydrobromic acid (20 ml.) were heated under reflux for 4 hr. The crystalline product [337 mg.; m. p. 196—198° (decomp.)] which separated on cooling was washed with water and combined with more material [90 mg.; m. p. 180—196° (decomp.)] obtained by diluting the filtrate with water. It was chromatographed in ether–light petroleum (b. p. 40—60°) (2 : 1) on alumina. The fractions eluted with ether–light petroleum (b. p. 40—60°) (2 : 1) and with ether crystallised from benzene–light petroleum (b. p. 60—80°) in needles of the fluorenol, m. p. and mixed m. p. 202—204° (decomp.).

2-*Hydroxy*-1,7-*dimethylfluorenone*.—2-Methoxy-1,7-dimethylfluorenone (500 mg.) was demethylated as described for 2-methoxy-1,7-dimethylfluorene. The product, red needles (438 mg.), m. p. 210—211°, in ether (70 ml.) was chromatographed on alumina (19 × 2·5 cm.) Elution with ether and with ether–methanol (99 : 1) afforded a red solid (420 mg.), m. p. 213—218°, which crystallised from acetic acid in red needles of 2-*hydroxy*-1,7-*dimethylfluorenone*, m. p. 225—226°. Good analyses were only obtained after sublimation *in vacuo* (Found: C, 79·9; H, 5·4. $C_{15}H_{12}O_2$ requires C, 80·3; H, 5·4%).

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