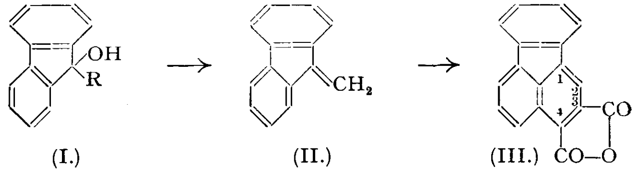
321. *Syntheses in the Fluoranthene Series.*

By Neil Campbell and H. Wang.

9-Hydroxy-9-alkylfluorenes in suitable solvents condense with dienophiles to give Diels–Alder adducts, and a number of fluoranthene derivatives have been thus synthesised. The substance considered by von Braun and Manz (*Annalen*, 1932, **496**, 170) to be naphtho-(2′ : 3′-3 : 4)fluoranthene-1′ : 4′-quinone has been shown to have some other structure and is probably 4 : 5-phthaloylfluoranthene.

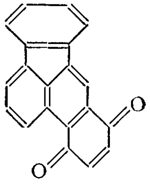
When 9-hydroxy-9-methylfluorene (I; R = Me) is treated with acetic anhydride and an excess of maleic anhydride, *fluoranthene*-3 : 4-*dicarboxylic anhydride* (III) is produced, presumably by Diels–Alder addition to the intermediate 9-methylenefluorene (II). Spontaneous dehydrogenation obviously occurs, and no hydrogenated intermediate was detected. The anhydride, when decarboxylated with calcium hydroxide, yielded fluoranthene, and with copper and quinoline gave an impure monocarboxylic acid which must be fluoranthene-3-carboxylic acid since the 4-carboxyl group is readily removed under the conditions used (Campbell and Easton, this vol., p. 340).



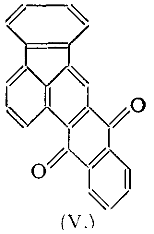
(I.) (II.) (III.)

The formation of fluoranthene-3 : 4-dicarboxylic anhydride is, so far as we know, the first example of an aromatic bond in fluorene participating in the Diels–Alder reaction (cf. Wagner-Jauregg, *Ber.*, 1930, **63**, 3213; *Annalen*, 1931, **491**, 1).

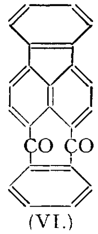
9-Hydroxy-9-ethylfluorene (I; R = Et) and excess of maleic anhydride in acetic anhydride yielded a non-crystalline product, m. p. 281—285°, probably a polymer, but in nitrobenzene 2-*methylfluoranthene*-3 : 4-*dicarboxylic anhydride* was obtained, condensation again being accompanied by dehydrogenation. Dehydrogenation in nitrobenzene is not unknown (*e.g.*, Clar, *Ber.*, 1932, **65**, 846; 1936, **69**, 1686), but the dehydrogenation in acetic anhydride was less easily anticipated. Decarboxylation of the anhydride gave 2-*methylfluoranthene.* No difficulty was encountered in preparing 9-*hydroxy*-9-*methyl*-2-*ethylfluorene,* the ether solution of which on evaporation on the water-bath yielded 2-*ethyl*-9-*methylenefluorene.* In contrast with 9-methylenefluorene (cf. Wieland *et al.*, *Ber.*, 1922, **55**, 3313; *Annalen*, 1937, **530**, 274), this compound is quite stable. Attempts to condense the hydroxy-compound with maleic anhydride in acetic anhydride or nitrobenzene were unsuccessful, only polymeric products being obtained.



(IV.)



(V.)



(VI.)

With *p*-benzoquinone and α-naphthaquinone as dienophiles 9-hydroxy-9-methylfluorene gave 3 : 4-*benzfluoranthene*-1′ : 4′-*quinone* (IV) and *naphtho*(2′ : 3′-3 : 4)*fluoranthene*-1′ : 4′-*quinone* (V), respectively. The constitution of the latter quinone (orange-red, m. p. 249—251°) follows unequivocally from its synthesis, and consequently the yellow quinone, m. p. 328—331°, obtained by von Braun and Manz (*loc. cit.*) by the cyclisation of 4-*o*-carboxybenzoylfluoranthene must have some constitution other than that of (V) assigned by these authors. It is suggested that their ring-closure occurred not at the 3-, but at the 5-, position to form 4 : 5-phthaloylfluoranthene (VI), and that the bluish-violet vat obtained by von Braun and Manz with sodium dithionite was due to an impurity. The formation of similar phthaloyl compounds has been noted in the naphthalene series (Rieche *et al.*, *Ber.*, 1932, **65**, 1371; B.P. 303,375), and preliminary ring-closure experiments with 3-*o*-carboxybenzoylacenaphthene indicate that one of the products is 3 : 4-phthaloylacenaphthene. Graebe and Perutz (*Annalen*, 1903, **327**, 99) effected ring-closure of 3-*o*-carboxybenzoylacenaphthene with phosphorus pentachloride and, without proof, assigned to the product the structure naphtho(2′ : 3′-2 : 3)acenaphthene-1′ : 4′-quinone. The matter is being further investigated.

EXPERIMENTAL.

All analyses were done by Drs. Weiler and Strauss, Oxford. Fluorescence observations were made under a Hanovia ultra-violet lamp.

Fluoranthene-3 : 4-*dicarboxylic Anhydride.*—9-Hydroxy-9-methylfluorene (12·0 g.), maleic anhydride (30 g.), and acetic anhydride (80 c.c.) were heated under reflux for 2 hours. *Fluoranthene*-3 : 4-*dicarboxylic anhydride* separated on cooling and crystallised from acetic anhydride in yellow needles, m. p. 267—268°, with an orange fluorescence (yield, 1·60 g.; 10%) (Found : C, 79·2; H, 3·3. $C_{18}H_8O_3$ requires C, 79·4; H, 3·0%). The *dimethyl* ester formed colourless needles (from methanol), m. p. 118—119° (Found : C, 75·0; H, 4·3. $C_{20}H_{14}O_4$ requires C, 75·4; H, 4·4%). The anhydride dissolved in warm aqueous sodium carbonate or sodium hydroxide, and the alkaline solution on acidification yielded a precipitate with a pale blue fluorescence, probably fluoranthene-3 : 4-dicarboxylic acid, but crystallisation from organic solvents yielded only the anhydride. The anhydride (0·5 g.) was heated to red heat with calcium hydroxide (5 g.) in a Pyrex tube; fluoranthene (50% yield) sublimed up the tube and was identified by its m. p., mixed m. p., and picrate. The anhydride (0·4 g.) was heated in an oil-bath at 180° with quinoline (20 c.c.) and copper bronze (0·1 g.) for ¾ hour; the mixture was filtered and treated with 10% sodium hydroxide (10 c.c.), and the quinoline removed by steam-distillation. The solution was acidified, and the gelatinous precipitate crystallised from benzene and light petroleum (b. p. 60—80°), to give impure fluoranthene-3-carboxylic acid, m. p. 240—243°, subliming in yellow needles with a pale blue fluorescence (Found : C, 81·1; H, 3·8. Calc. for $C_{17}H_{10}O_2$: C, 82·9; H, 4·1%).

Synthesis of 2-*Methylfluoranthene.*—9-Hydroxy-9-ethylfluorene (0·5 g.), nitrobenzene (20 c.c.), and maleic anhydride (1·5 g.) were boiled under reflux for 2½ hours, the solution on cooling deposited 2-*methylfluoranthene*-3 : 4-*dicarboxylic anhydride*, which was washed with ethanol and crystallised from tetralin in long yellow needles, m. p. 275—280° (decomp.), with a yellow fluorescence (yield, 0·28 g.; 41%) (Found : C, 78·65; H, 3·6. $C_{19}H_{10}O_3$ requires C, 79·7; H, 3·5%). The anhydride (0·2 g.) was heated with calcium hydroxide; 2-*methylfluoranthene* sublimed along the tube and after purification on a short column of alumina crystallised from light petroleum (b. p. 60—80°) in pale yellow needles, m. p. 72—73°, with a vivid blue fluorescence (yield, 0·10 g.; 66%) (Found : C, 94·4; H, 5·75. $C_{17}H_{12}$ requires C, 94·4; H, 5·6%). The *picrate* formed orange needles, m. p. 207—208° (Found : N, 9·35. $C_{23}H_{15}O_7N_3$ requires N, 9·4%).

Attempted Synthesis of 4-*Ethylfluoranthene.*—2-Acetylfluorene (25 g.), toluene (100 c.c.), water (35 c.c.), and concentrated hydrochloric acid (50 c.c.) were added to zinc dust (60 g.) which had been amalgamated with 5 g. of mercuric chloride in water (75 c.c.) and concentrated hydrochloric acid (2½ c.c.); the mixture was heated under reflux for 24 hours with the addition of concentrated hydrochloric acid (25 c.c.) every 6 hours. The cold solution was extracted with ether, and the dried ethereal extract evaporated. A brown semi-solid oil was obtained and gave a fraction, b. p. 170—175°/15 mm., which solidified and, when crystallised from light petroleum (b. p. 40—60°), gave colourless plates of 2-*ethylfluorene*, m. p. 81—82° (yield, 10·4 g.; 45%). This sublimed readily and had a bright blue fluorescence in solution (Found : C, 92·8; H, 6·9. $C_{15}H_{14}$ requires C, 92·7; H, 7·3%). Sodium dichromate (12·5 g.) in acetic acid (25 c.c.) was slowly added to a boiling solution of 2-ethylfluorene (12·0 g.) in acetic acid (25 c.c.), and the solution heated under reflux for 2 hours. The cold solution was extracted with ether, and the ethereal layer washed with water, dried ($CaCl_2$), and evaporated. The residue, after three crystallisations from light petroleum (b. p. 60—80°), yielded 5·5 g. of yellow prisms, m. p. 115—119°, consisting mainly of 2-ethylfluorenone. This gave a 2 : 4-*dinitrophenylhydrazone*, red needles, m. p. 267—268° (Found : N, 13·8. $C_{21}H_{16}O_4N_4$ requires N, 14·4%). The pure ketone was obtained by chromatographic separation on alumina with benzene as solvent and a 1 : 3 benzene–light petroleum mixture as developer. Two yellow zones separated, the lower of which on elution gave 2-*ethylfluorenone* as yellow plates (from light petroleum), m. p. 127—128° (Found : C, 85·9; H, 5·9. $C_{15}H_{12}O$ requires C, 86·5; H, 5·8%). The upper band gave 2-acetylfluorenone, yellow prisms (from light petroleum), m. p. 156—157° (lit., 154—155°) (Found : C, 80·4; H, 4·95. Calc. for $C_{15}H_{10}O_2$: C, 81·1; H, 4·5%). 2-Ethylfluorenone (6 g.) in anhydrous ether (300 c.c.) was added slowly with stirring to the Grignard reagent prepared from magnesium (2·0 g.), methyl iodide (16 g.), and anhydrous ether (50 c.c.); the solution was heated under reflux for ½ hour and then decomposed on ice, and the solution acidified. The ethereal layer was washed with aqueous sodium hydrogen sulphite and then with water, and dried. On evaporation at room temperature it yielded 9-*hydroxy*-9-*methyl*-2-*ethylfluorene*, which crystallised from benzene in needles, m. p. 124—125° (yield, 2·8 g.; 43%) (Found : C, 85·7; H, 6·8. $C_{16}H_{16}O$ requires C, 85·7; H, 7·2%). Evaporation of the solution on the water-bath, however, gave 2-*ethyl*-9-*methylene*-*fluorene*, plates (from benzene), m. p. 156—157° (Found : C, 93·0; H, 6·75; *M*, 220. $C_{16}H_{14}$ requires C, 93·2; H, 6·8; *M*, 206).

3 : 4-*Benzfluoranthene*-1′ : 4′-*quinone.*—9-Hydroxy-9-methylfluorene (2·5 g.), *p*-benzoquinone (10 g.), and acetic anhydride (50 c.c.) were heated under reflux for 2 hours. When the solution cooled, orange-red needles of the *quinone* separated and were crystallised from glacial acetic acid; m. p. 245—246°; yield, 0·90 g. (25%) (Found : C, 84·1; H, 3·65. $C_{20}H_{10}O_2$ requires C, 85·1; H, 3·6%). The quinone gives a purple colour in concentrated sulphuric acid and a wine-red vat with sodium dithionite.

Naphtho(2′ : 3′-3 : 4)*fluoranthene*-1′ : 4′-*quinone.*—9-Hydroxy-9-methylfluorene (2·5 g.), α-naphthaquinone (10 g.), and acetic anhydride (50 c.c.) were heated under reflux for 2 hours; on cooling, the mixture deposited orange-red needles of the *quinone* which was crystallised from nitrobenzene and light petroleum (b. p. 100—120°); m. p. 249—251°; yield 0·50 g. (12%) (Found: C, 86·35; H, 3·7. $C_{24}H_{12}O_2$ requires C, 86·7; H, 3·6%). The quinone gives a bluish-green colour with concentrated sulphuric acid and a bluish-violet vat with sodium dithionite.

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