Novel Aromatic Systems. Part VIII.[1] Attempts to make a Dibenzoanthrazulene

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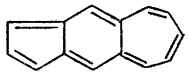
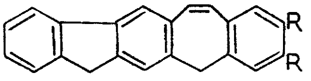
Fluorene has been acylated with phthalic anhydride and with homophthalic anhydride; the products have been briefly studied. Reaction of fluorenoyl chloride with methyl homoveratrate gave methyl-4,5-dimethoxy-2(2-fluorenoyl)phenylacetate which was converted, in several stages, into a dihydrodibenzanthrazulene. The latter underwent oxidation to carbonyl compounds rather than dehydrogenation.

SINCE all efforts to make anthrazulene(cyclohept[*f*]-indene) (I) derivatives have been unsuccessful,[2–6] we were interested to attempt a synthesis of a dibenzoanthrazulene. In practice this failed at the last step; we report briefly the details. By analogy with related work, our first objective was to find a route to fluorenobenzocycloheptatrienes [*e.g.* (II; R = H)] and the second objective was to remove two hydrogen atoms from (II) to obtain the fully conjugated molecule (III; R = H).

We could only conceive viable syntheses which started with fluorene. In one of these, we planned to bring



(I)



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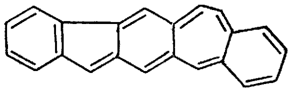

(III)

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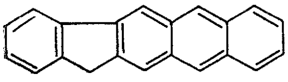
about ring expansion of the known[7] linear naphthofluorene (IV), or its derivatives. We found, in practice, that the oxo-acid (V; X = CO) was difficult to reduce (to V; X = CH_2) by the literature[7] method and that neither a Clemmensen nor Wolff–Kishner reduction was any better; indeed the latter reaction gave a pyridazine derivative. Direct cyclisation of *o*-aroylbenzoic acid can give anthraquinones:[8] in this case polyphosphoric acid converted (V; X = CO) into two isomeric quinones in poor yield, presumably by cyclisation to the 1- and 3-position of the fluorene nucleus. As these reactions were obviously not productive, we turned briefly to the reaction of homophthalic anhydride[9] with fluorene which gave the oxo-acid (*cf.* ref. 10) (VI; X = CO) in poor yield; reduction gave the acid (VI; X = $\cdot CH_2$) also in poor yield. Cyclisation of the latter yielded traces of the expected diaryl ketone in impure state: the whole process was unfruitful.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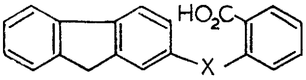

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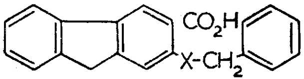

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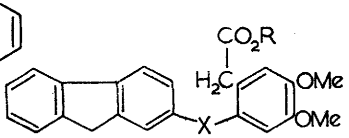
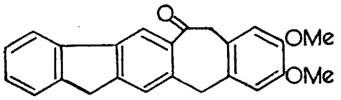


(VII)

The desired type of intermediate (II; R = OMe) was ultimately obtained by a series of reactions commencing with acylation of methyl homoveratrate[11] by 2-fluorenoyl chloride,[12] the product (VII; X = CO, R = Me) was hydrolysed to the corresponding acid which was reduced to the lactone of the intermediate hydroxy-acid (VII; X = CH·OH, R = H). Treatment of this with zinc dust in formic acid gave the acid (VII; X = CH_2, R = H) which was cyclised to a ketone, presumably (VIII): reduction of the latter and dehydration yielded the desired substituted cycloheptatriene (II; R = OMe). Oxidation of (II; R = OMe) with manganese dioxide proceeded with ease and gave the orange tropone (IX; X = O); DDQ reacted with (II; R = OMe) rapidly at 0° to yield, after chromatography, a yellow substance $C_{24}H_{20}O_3$ which we believe to be the tropone (IX; X = H_2), on the basis of its n.m.r. spectrum. The latter was strikingly similar to that of the tropone (IX; X = O) except that it contained a signal attributable to the two hydrogen atoms on C-13 of the fluorene nucleus: both spectra significantly showed a low-field singlet (τ 1·45) probably due to the hydrogen atom at C-1 of the fluorene nucleus which would be expected to be deshielded by the tropone carbonyl group.[13]



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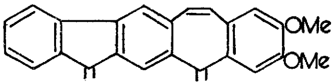

(IX)

Conversion of (II; R = OMe) to the corresponding tropylium salt followed by basification gave polymeric material as did reduction of the tropone with sodium borohydride in ethanol followed by acid treatment. We concluded that our objective was inaccessible.

EXPERIMENTAL

2-(2-*Fluorenoylmethyl*)*benzoic Acid* (VI; X = CO).—To a cooled (0°) stirred solution of fluorene (150 g.) in dry methylene dichloride (350 ml.) was added anhydrous aluminium chloride (60 g.) followed by homophthalic anhydride[9] slurried in dry methylene dichloride (400 ml.). After 1 hr. at 0°, the reaction mixture was set aside for 2 days and then poured into ice; the mixture was filtered and separated. The organic layer was washed with aqueous sodium hydroxide, dilute hydrochloric acid, and water; it was then dried and evaporated to leave an unidentified neutral product (4·5 g.) (lactone of enol form?) which crystallised from chloroform–ethanol as yellow flakes, m.p. 185° (Found: C, 84·9; H, 4·8. Calc. for $C_{22}H_{14}O_2$: C, 85·15; H, 4·55%), $\nu_{max.}$ (Nujol) 1712 cm.$^{-1}$. The sodium hydroxide extract was acidified to give the desired product (15 g.), m.p. 200° (from ethanol) (Found: C, 80·25; H, 5·1. $C_{22}H_{16}O_3$ requires C, 80·45; H, 4·9%), $\nu_{max.}$ (Nujol) 1682 cm.$^{-1}$ (arylcarboxyl and aryl lactone).

2-*Fluoren-2-ylethylbenzoic Acid* (VI; X = CH_2).—The above acid (7 g.) was treated with hydrazine hydrate (20·0%, 2·5 ml.), potassium hydroxide (3·5 g.), and ethylene glycol at 190° for 8 hr. The product (3·2 g.) chromatographed on silica MFC and crystallised from ethanol, had m.p. 186° (Found: C, 84·4; H, 6·0. $C_{22}H_{18}O_2$ requires C, 84·05; H, 5·75%), $\nu_{max.}$ (Nujol) 1680 cm.$^{-1}$ (aryl carboxyl).

Reaction of 2-(2-*Fluorenoyl*)*benzoic Acid* (V; X = CO) *with Polyphosphoric Acid*.[8]—To mechanically stirred polyphosphoric acid (250 g.) at 145° was added 2-(2-fluorenoyl)-benzoic acid[7] (16 g.) during 20 min. After a further 35 min. at 145°, the reaction mixture was cooled, poured into ice, filtered, and washed with dilute ammonia solution and with water. The dried product (13 g.) was chromatographed on alumina; benzene elution gave first a *quinone*, m.p. 225—226° (1·4 g. from benzene) (Found: C, 85·3; H, 4·1. $C_{21}H_{12}O_2$ requires C, 85·2; H, 4·1%), $\nu_{max.}$ ($CHCl_3$) 1667 cm.$^{-1}$ (C=O). Further elution yielded a *quinone*, m.p. 264° (2·8 g. from xylene) (Found: C, 85·1; H, 4·05. Calc. for $C_{21}H_{12}O_2$: C, 85·2; H, 4·1%), $\nu_{max.}$ ($CHCl_3$) 1670 cm.$^{-1}$ (C=O).

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1-*Fluoren-2-yl-4-hydroxybenzo*[e]*pyridazine*.— 2-(2-Fluorenoyl)benzoic acid (10 g.) was heated with hydrazine hydrate (100%, 5 ml.), potassium hydroxide (7 g.), and ethylene glycol at 190° for 3 hr. The nonacidic product (6 g.), isolated and crystallised from glacial acetic acid, had m.p. 310° (decomp.) (Found: C, 81·1; H, 4·75; N, 8·75. $C_{21}H_{14}N_2O$ requires C, 81·2; H, 4·55; N, 9·0%).

Methyl-2-(2-*fluorenoyl*)-4,5-*dimethoxyphenylacetate* (VII; X = CO, R = Me).—Fluorene-2-carbonyl chloride [12] (18 g. from 22 g. of the acid), dry methylene dichloride (200 ml.), and anhydrous aluminium chloride were stirred together at 1—3° while methylhomoveratrate [13] (16·5 g.) in dry methylene dichloride (100 ml.) was added during 15 min. After being stirred overnight at 20°, the reaction mixture was added to ice–concentrated hydrochloric acid and the whole was stirred for 2 hr. and filtered. The filtrate was separated, and the organic layer gave the product (15 g.) as prisms, m.p. 107° (from methanol) (Found: C, 74·2; H, 5·7. $C_{25}H_{22}O_5$ requires C, 74·6; H, 5·5%), $\nu_{max.}$ (Nujol) 1720 (ester), 1650 (diaryl ketone) cm.$^{-1}$. The n.m.r. spectrum (in $CDCl_3$) consisted of several multiplets from τ 1·9 to 3·2 (9 ArH) and several sharp signals not fully resolved from τ 6·0 to 6·4 (13 methyl and methylene H).

2-(2-*Fluorenoyl*)-4,5-*dimethoxyphenylacetic Acid* (VII; X = CO, R = H).—The above acid (10 g.) was hydrolysed with ethanolic-aqueous sodium hydroxide under nitrogen to yield the product (8·7 g.) as micro-crystals, m.p. 172° (from toluene) (Found: C, 74·15; H, 5·2. $C_{24}H_{20}O_5$ requires C, 74·2; H, 5·2%), $\nu_{max.}$ (Nujol) 1700 (carboxyl), 1655 (diaryl ketone) cm.$^{-1}$. The n.m.r. spectrum (in $CDCl_3$) consisted of a broad signal τ −0·8 (removed by D_2O) (1 acidic H), several multiplets from τ 2·0 to 3·05 (9 ArH) and two sharp singlets overlying other signals (total of 10 methyl and methylene H).

Lactone of 2-(*Fluoren-2-ylhydroxymethyl*)-4,5-*dimethoxyphenylacetic Acid* (VII; X = CH·OH; R = H).—The above acid (10 g.) in ethanol (200 ml.) and dilute aqueous sodium hydroxide (20 ml., 10%) was treated with sodium borohydride (15 g.). After 24 hr. at 20°, the reaction mixture was worked up to yield the product (8·8 g.), m.p. 178° (from methanol) (Found: C, 77·6; H, 5·8. $C_{24}H_{20}O_4$ requires C, 77·5; H, 5·4%), $\nu_{max.}$ (Nujol) 1740 cm.$^{-1}$ (lactone).

2-*Fluoren-2-ylmethyl*-4,5-*dimethoxyphenylacetic Acid* (VII; X = CH_2, R = H).—The above lactone (8·8 g.), formic acid (80 g., 98%), zinc dust (20 g.), and water (20 ml.) were stirred and heated under reflux for 14 hr. The reaction mixture was cooled and then stirred for 24 hr. with benzene and concentrated hydrochloric acid (excess) and finally filtered. The organic layer yielded the product (5·4 g.), m.p. 175° (from benzene) [Found: C, 77·2; H, 5·85; *M* (mass spectrum), 374·15161. $C_{24}H_{22}O_4$ requires C, 77·1; H, 5·9%; *M*, 374·15180], $\nu_{max.}$ (Nujol) 1695 cm.$^{-1}$ (carboxyl). The n.m.r. spectrum ($CDCl_3$) consisted of a broad signal around τ 0·5 (removed by D_2O) (1 carboxyl H), a multiplet from τ 2·2 to 3·3 (9 aryl H), several sharp overlapping signals from τ 6·0 to 6·2 (10 methyl and methylene H) and a singlet at τ 6·6 [2 methylene H, X in formula (VII)].

12,14-*Dihydro*-9,10-*dimethoxybenzo*[5,6]*cyclohepta*[b]-*fluoren*-6(7*H*)-*one* (VIII).—The above acid (5·6 g.) was converted to the acid chloride with thionyl chloride (28 ml. freshly distilled) in dry benzene (50 ml.) and then added in dry methylene dichloride (100 ml.) to anhydrous aluminium chloride (2·6 g.) in dry methylene dichloride (50 ml.) at 0°. After 1 hr. at 0° and 16 hr. at 20°, the reaction mixture was worked up to yield the neutral product (4·2 g.), m.p. 218° (from benzene). Satisfactory analyses could not be obtained, carbon analyses were consistently 1·5% low; $\nu_{max.}$ (Nujol) 1670 cm.$^{-1}$ (aryl ketone).

12,14-*Dihydro*-9,10-*dimethoxybenzo*[5,6]*cyclohepta*[b]-*fluoren*-6(7H)-*one* (II; R = OMe).—The above ketone (1 g.), benzene (25 ml.), ethanol (25 ml.), and sodium borohydride (3·0 g.) were stirred together for 24 hr. After the customary work up, evaporation of the benzene left the hydroxy-compound (0·75 g.) as a crystalline solid which was not purified further. It was heated under reflux in dry benzene (50 ml.) with toluene-*p*-sulphonic acid (20 mg.) 4 hr. The solvent was washed with dilute aqueous sodium hydrogen carbonate solution and then dried and evaporated to leave the product (600 mg.) which crystallised as a fine powder, m.p. 225—226° (from benzene) (Found: C, 84·4; H, 6·15. $C_{24}H_{20}O_2$ requires C, 84·7; H, 5·9%). The n.m.r. spectrum ($CDCl_3$) consisted of a series of multiplets from τ 2·2 to 3·2 (10 aryl and olefinic H) and several sharp overlapping signals from τ 6·05 to 6·35 (10 methyl and methylene H). The mass spectrum showed that the parent ion 340·14598 (calc. 340·14632) was the base peak and that a strong, doubly charged parent-ion could be detected at *m*/*e* 170.

Reactions of 12,14-*Dihydro*-9,10-*dimethoxybenzo*[5,6]*cyclohepta*[b]*fluoren*-6(7H)-*one* (II; R = OMe).—(a) *With manganese dioxide*. The title compound (0·5 g.), active manganese dioxide (3 g.), and dry benzene (50 ml.) were heated under reflux for 12 hr. After filtration and concentration, a *yellow solid* (250 mg.) separated as clusters, m.p. 270° (decomp.) (from chloroform) (Found: C, 78·15; H, 4·35. $C_{24}H_{16}O_4$ requires C, 78·3; H, 4·4%), $\nu_{max.}$ (Nujol) 1722 cm.$^{-1}$ (fluorenone C=O).

The n.m.r. spectrum revealed the following signals: τ 1·45 (1H, s, ArH), τ 2·1 to 3·1 multiplets + quartet? (7 aryl and 2 olefinic H), τ 5·95 and 6·0 (both s, 6 methoxyl H).

(b) *With dichlorodicyano*-1,4-*benzoquinone* (DDQ). The title compound (164 mg.) in dry benzene (75 ml.) was treated with a solution of DDQ (125 mg.) in dry benzene (25 ml.) at 10° under nitrogen: a transient blue colour was followed by precipitation of brown material (150 mg.) the i.r. spectrum of which was almost identical with that of 2,3-dichloro-5,6-dicyanohydroquinone. Chromatography of the benzene solution on neutral alumina yielded a *product* (48 mg.) which crystallised as yellow needles, m.p. 218° (from benzene) [Found: C, 80·95; H, 5·25%; *M* (mass spectroscopy), 354·12674. $C_{24}H_{18}O_3$ requires C, 81·4; H, 5·15%; *M*, 354·12559].

The n.m.r. spectrum consisted of the following signals: τ 1·43 (s, 1H ArH), τ 2·0 to 3·2 (multiplets 9 aryl and olefinic H), τ 5·85 to 6·25 (2 sharp singlets overlapping a third signal, 8H in all).

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