ALIPHATIC CHEMISTRY OF FLUORENE

PART V. SPIRO-KETONES¹

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ABSTRACT

A novel synthesis is described of 1,2;3,4-dibenzophenanthrene, based on the spiro-ketone (IIIb), which was cleaved by strong base to the acid (VIIb). An example is described of acylation of aliphatic carbon.

The ease with which methyl fluorene-9-carboxylate anion reacts with a wide range of alkyl halides (1, 2, 3) together with the formation of phenanthrene derivatives from carbonium ions (I) prompted the investigations described in this paper.



It has been reported (4) that 9-benzylfluorene-9-carboxylic acid chloride (IIa) was cyclized by aluminum chloride to the spiro-ketone (IIIa), which may be converted via the alcohol (IVa) to 1,2;3,4-dibenzofluorene. This synthesis has been repeated and some yields improved. In particular, phosphorus pentoxide under boiling xylene rather than fused zinc chloride is the reagent of choice for dehydrating the alcohol (IVa).

The synthesis has been extended by the preparation and cyclization of 9-(2'-phenyl-ethyl)-fluorene-9-carboxylic acid (IIc), cyclization being effected by hydrogen fluoride. The homologous acid (IIb) was unaffected by this reagent, in accord with the known



(5, p. 116) easier formation of six-membered ketones. All attempts to cyclize 9-(3'-phenylpropyl)-fluorene-9-carboxylic acid (II*d*) or its chloride have failed.

The formation of cyclic ketones from the tertiary acids is surprising since Lewis acids would have been expected to bring about decarbonylation. This exceptional behavior may be attributed to instability of the fluorene cation, which would be formed in the decarbonylation process (6).

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The ketone (IIIb) was converted via the alcohol (IVb) to 1,2;3,4-dibenzo-9,10-dihydrophenanthrene (V). In agreement with earlier workers (7) the hydrocarbon could not be obtained crystalline but was dehydrogenated in good yield to 1,2;3,4-dibenzophenanthrene, completing a novel synthesis of this ring system. It was intended that this work should be extended to more complex ring systems, but lack of time has curtailed the work. Some 9-aralkyl derivatives of methyl fluorene-9-carboxylate, prepared as desirable starting compounds, are described in the Experimental section. In addition, methyl 9-(4'-cyanobutyl)-fluorene-9-carboxylate has been prepared, as a possible precursor of VI. During its preparation, dimethyl butane-1,4-di-9'-fluorenyldi-9'-carboxylate was isolated as a by-product and identified by synthesis.



The spiro-ketones (III*a* and III*b*) were cleaved by strong base, as expected for nonenolizeable ketones, giving the acids (VII*a* and VII*b*), isomeric with (II*a* and II*c*). The direction of cleavage is controlled by formation of the more stable anion, as previously noted for 9-methyl-9-benzoylfluorene (8).



The chloride of the acid (VIIa) reacted with aluminum chloride to reform the spiroketone (IIIa) and not, as had been hoped, the isomeric ketone (VIII). A few similar examples of acylation of aliphatic carbon are known, e.g. the acetylation and benzoylation of 9,10-dihydroanthracene (9).

The chloride prepared from the alcohol (IVa) closely resembled IX (8), decomposing at its melting point or in boiling formic acid with formation of 1,2;3,4-dibenzofluorene. Silver acetate in acetic acid gave unrearranged acetate. A similar stabilization of neopentyl-type carbonium ions by phenyl has been reported (10, and references quoted therein).

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Other examples of non-rearrangement of neopentyl carbonium ions probably involve neighboring group participation (11). In agreement with this, the reaction between 9-methyl-9-fluorenylmethyl chloride and silver acetate gave 9-methylphenanthrene.

EXPERIMENTAL

Methyl fluorene-9-carboxylate anion was alkylated in the usual way (2) to give the following:

9-Benzylfluorene-9-carboxylic acid, prepared by saponification of the methyl ester (2), formed well-defined prisms from benzene-hexane, m.p. $204-205^{\circ}$ (4). Found: C, 84.25; H, 5.24%. Calc. for C₂₁H₁₆O₂: C, 83.97; H, 5.37%.

Methyl 9-(2'-phenylethyl)-fluorene-9-carboxylate crystallized as long white needles (74%) from methanol, m.p. 67–68°. Found: C, 83.81; H, 5.99%. Calc. for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14%. The *acid* (81%) crystallized as colorless rhombic plates from benzene-hexane, m.p. 143–144°. Found: C, 83.76; H, 5.66%. Calc. for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77%.

9-(3'-Phenylpropyl)-fluorene-9-carboxylic acid, obtained by saponifying the oily methyl ester, formed large pale yellow prisms (76%) from benzene-hexane, m.p. 125-127°. Found: C, 84.11; H, 6.13%. Calc. for C₂₃H₂₀O₂: C, 84.12; H, 6.14%.

Methyl 9-(2'-thienylmethyl)-fluorene-9-carboxylate crystallized as small white needles (71%) from hexane, m.p. 104–105°. Found: C, 75.13; H, 5.17%. Calc. for $C_{20}H_{16}O_2S$: C, 74.99; H, 5.03%.

Methyl 9-(3'-thienylmethyl)-fluorene-9-carboxylate formed clusters of white prisms (76%) from hexane, m.p. 119.5–120.5°. Found: C, 74.99; H, 5.22%. Calc. for $C_{20}H_{16}O_2S$: C, 74.99; H, 5.03%.

Methyl 9-(1'-naphthylmethyl)-fluorene-9-carboxylate* crystallized as small prisms (73%) from benzene-hexane, m.p. 154–156°. Found: C, 85.36; H, 5.48%. Calc. for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53%.

Methyl 9-(2'-naphthylmethyl)-fluorene-9-carboxylate^{*} formed small needles (79%) from benzene-hexane, m.p. 189–191°. Found: C, 85.82; H, 5.71%. Calc. for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53%.

Methyl 9-(4'-cyanobutyl)-fluorene-9-carboxylate

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1,4-Dibromobutane, b.p. 63–65° at 5 mm, $n_{\rm p}^{21}$ 1.5163, was prepared from tetrahydro-furan in 68% yield.

1,4-Dibromobutane (209 g, 0.84 mole) was stirred and boiled under reflux for 6 hours with potassium cyanide (55 g, 0.8 mole), water (65 ml), and ethanol (220 ml). After being diluted with water, the products were isolated with ether and separated by precise fractionation, giving δ -bromovaleronitrile (86 g), b.p. 102–103° at 8 mm, n_{23}^{23} 1.4776.

Prepared in the usual way, methyl 9-(4'-cyanobutyl)-fluorene-9-carboxylate crystallized as long white needles (93%) from methanol, m.p. 89-90°. The analytical sample was obtained after two further crystallizations and had a melting point of 90.5-91.0°. Found: C, 79.05; H, 6.74; N, 4.59%. Calc. for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59%. C=N stretching band, 2220 cm⁻¹; C=O stretching band, 1740 cm⁻¹.

Commercial δ -bromovaleronitrile (Sapon Laboratories) gave 63% of the cyano-ester and 31% of a substance insoluble in hot methanol. The latter crystallized from toluene as small colorless needles, m.p. 221.0–221.5°, after three crystallizations. Found: C, 80.64; H, 5.57%. Calc. for C₃₄H₃₀O₄: C, 81.25; H, 6.02%. It was identified as *dimethyl butane-1,4-di-9'-fluorenyldi-9'-carboxylate* by synthesis from 1,4-dibromobutane (0.56 g, 0.5 mole) and a solution of methyl fluorene-9-carboxylate (1.23 g, 2.2 moles) in methanol

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containing sodium methoxide (from sodium, 0.23 g, 2.1 atoms), identity being established by mixed melting point determination and comparison of infrared spectra.

Saponification of the diester in ethylene glycol gave 1,4-(di-9'-fluorenyl)-butane, which crystallized from acetone-methanol as small white needles, m.p. 161.0-161.5°. Found: C, 93.52; H, 6.49%. Calc. for C₃₀H₂₆: C, 93.22; H, 6.78%.

Spiro-compounds

Indan-1-one-2-spiro-9'-fluorene (IIIa) was prepared as described in the literature (4) in a maximum yield of 67%. Reduction with ethereal lithium aluminum hydride gave indan-1-ol-2-spiro-9'-fluorene (IVa) in almost quantitative yield. It formed prisms from cyclohexane, m.p. 159–160° (lit. m.p. 160° and 168° (dimorphic) (4)). Found: C, 88.27; H, 5.48\%. Calc. for C₂₁H₁₆O: C, 88.74; H, 5.67\%.

1-Chloroindane-2-spiro-9'-fluorene, prepared by the reaction between the alcohol and thionyl chloride, crystallized from heptane as elongated prisms (77%), m.p. 172–173° with decomposition to 1,2;3,4-dibenzofluorene. The chloride decomposed similarly in boiling 94% formic acid. Found: C, 83.20; H, 4.89%. Calc. for $C_{21}H_{15}Cl: C$, 83.30; H, 4.99%.

1-Acetoxyindane-2-spiro-9'-fluorene, prepared either by acetylating the alcohol or by the reaction between the chloride and silver acetate in acetic acid, formed colorless prisms from benzene-hexane, m.p. 132–133°. Found: C, 84.66; H, 5.62%. Calc. for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56%.

Heating the alcohol (IVa) with twice its weight of phosphorus pentoxide under boiling xylene gave, after 1 hour, 1,2;3,4-dibenzofluorene (94%) which crystallized from heptane as slender white needles, m.p. 162–163°. Oxidation gave 1,2;3,4-dibenzofluorenone, identical with an authentic sample (8).

1,2,3,4-Tetrahydronaphthalene-1-one-2-spiro-9'-fluorene (IIIb) was prepared by cyclizing the acid (IIc) (3 g) in dry ether (50 ml) with hydrogen fluoride (150 ml). During 2 days at room temperature most of the solvents evaporated. The neutral product crystallized from cyclohexane as white needles (2.3 g), m.p. 201-202°. Found: C, 89.71; H, 5.32%. Calc. for C₂₂H₁₆O: C, 89.16; H, 5.44%.

1-Hydroxy-1,2,3,4-tetrahydronaphthalene-2-spiro-9'-fluorene (IVb), prepared by reducing the ketone with ethereal lithium aluminum hydride, crystallized from cyclohexane as small colorless blades (91%), m.p. 197.0–197.5°, depressed to 175–180° by the ketone. Found: C, 88.68; H, 6.11%. Calc. for $C_{22}H_{18}O$: C, 88.56; H, 6.08%.

1,2;3,4-Dibenzo-9,10-dihydrophenanthrene (V). Dehydration of the alcohol (IVb) (2 g) with phosphorus pentoxide under boiling xylene followed by purification over alumina gave a colorless oil (1.5 g) which has failed to crystallize. The 1,3,5-trinitrobenzene adduct separated from methanol as vermilion rods, m.p. 161–162°. Found: C, 67.98; H, 3.72%. Calc. for C₂₈H₁₉N₃O₆: C, 68.15; H, 3.88%.

Oxidation with chromic acid in acetic acid gave a trace of 1,2;3,4-dibenzophenanthrene-9,10-quinone.

1,2;3,4-Dibenzophenanthrene was prepared as follows. Dehydrogenation of the dihydro compound over 10% palladium-on-charcoal at 300° gave an almost quantitative yield of dibenzophenanthrene, which crystallized as white needles from heptane, m.p. 115- 116° . Identity was established by comparison with two authentic samples (12,* 13) and by preparation of the quinone and picrate. The 1,3,5-trinitrobenzene adduct crystallized as slender orange needles from methanol, m.p. 165- 166° . Found: C, 68.30; H, 3.64%.

*Provided by Dr. C. C. Barker.

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Calc. for C₂₈H₁₇N₃O₆: C, 68.43; H, 3.49%. (This derivative has been reported as forming bright yellow needles from benzene, m.p. 167° (13).)

Cleavage of the Spiro-ketones

The ketone (1 g) was warmed for 30 minutes with a solution of potassium hydroxide (1 g) in industrial alcohol (50 ml) and the acidic product isolated.

2-(9'-Fluorenylmethyl)-benzoic acid (VIIa) crystallized as slender needles (85%) from cyclohexane, m.p. 188-189°. Found: C, 83.72; H, 5.61%. Calc. for C21H16O2: C, 83.97; H, 5.37% (lit. m.p. 185-186° (14)). The acid chloride (SOCl₂) in benzene at 10° reacted with aluminum chloride to reform the spiro-ketone (57%), identified by mixed melting point determination and comparison of infrared spectra.

2-(2'-(9''-Fluorenyl)-ethyl)-benzoic acid (VIIb) crystallized from benzene-hexane as colorless blades (81%), m.p. 163-164°. Found: C, 84.21; H, 6.03%. Calc. for C₂₂H₁₈O₂: C, 84.05; H, 5.77%.

9-Methylphenanthrene

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The reaction between 9-methyl-9-fluorenylmethanol (2) and thionyl chloride gave a semisolid product which would not form a crystalline picrate from ethanol. The reaction with silver acetate in acetic acid was rapid, silver acetate separating. 9-Methylphenanthrene was isolated as its orange picrate (61%), from ethanol), identical with an authentic specimen (2).

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