STUDIES IN THE WAGNER–MEERWEIN REARRANGEMENT

PART IV. DERIVATIVES OF BENZ[b]FLUORENE[1]

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ABSTRACT

10-Methyl-10-benz[b]fluorenylmethyl tosylate[3] gave mainly 5-methylbenz[a]anthracene on formolysis, but the related alcohol gave a mixture of the 5- and 6-methyl isomers by reaction with phosphorus pentoxide. Reaction of benz[b]fluorenone with excess diazomethane gave 5-methoxybenz[a]anthracene as the only isolable product. The alkylation of methyl benz[b]fluorene-10-carboxylate was studied.

Collins and his co-workers have employed ^{14}C to study migratory aptitudes in Wagner–Meerwein rearrangements of polycyclic systems (1, 2, 3, 4). In particular, 10-benz[b]fluorenylmethanol-11-^{14}C (I) was dehydrated by phosphorus pentoxide in boiling xylene to benz[a]anthracene (II), in which ^{14}C was found at carbon atoms 5 and 6 in the ratio 48:52 (3).

It seemed to us that similar information could be obtained without the use of ^{14}C, by using 10-methyl-10-benz[b]fluorenylmethyl tosylate (III), in which the carbon is labelled with a methyl group. On formolysis III gave almost pure 5-methylbenz[a]anthracene in about 60% yield. Examination of infrared spectra suggested the presence of traces of 6-methylbenz[a]anthracene (V) in the mother liquors from IV. However, the infrared spectra of IV and V were not sufficiently different to enable an accurate analysis to be made.

The greater migrating power of the naphthelenic over the benzenic ring in the formolysis of III is in contrast to the reaction of I with phosphorus pentoxide, where the two rings have about equal migrating powers. This may be due to the different experimental conditions leading in the case of Collins' work to a transition state more nearly approximating to a free carbonium ion which should have a low selectivity. In the case of the tosylate (III), formation of the benzanthracene probably occurs with participation of the aromatic ring in the ionization step, as in simpler systems studied by Cram (5). However, the reaction of 10-methyl-10-benz[b]fluorenylmethanol with phosphorus pentoxide gave nearly equal proportions of IV and V, in agreement with the results of Collins.

By reaction of benz[b]fluorenone with excess diazomethane, 5-methoxybenz[a]anthracene (VI) was obtained as the only isolable product, but in only fair yield (38%). The intermediate involved is almost certainly VII or a close approximation to it (6), so that this reaction is similar mechanistically to the Wagner–Meerwein rearrangement. A similar ring-expansion of benz[a]fluorenone has been reported (7), the only product isolated being 6-methoxychrysene. Thus in both of these examples the naphthalenic ring appears to have the greater migratory power.

Methyl benz[b]fluorene-10-carboxylate was not alkylated as smoothly as the fluorene analogue (8), the reaction failing with *t*-butyl bromide, though the methyl and isopropyl derivatives were readily obtainable.

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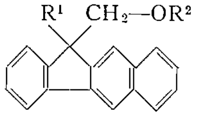
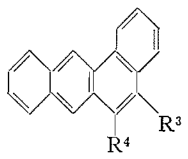
[3] *Ring Index nomenclature and numbering are used throughout.*



(I) $R^1 = R^2 = H$

(III) $R^1 = CH_3$
$R^2 = CH_3C_6H_4.SO_2$

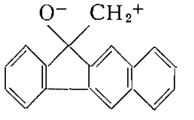


(II) $R^3 = R^4 = H$

(IV) $R^3 = CH_3$
$R^4 = H$

(V) $R^3 = H$
$R^4 = CH_3$

(VI) $R^3 = OCH_3$
$R^4 = H$



(VII)

EXPERIMENTAL

Methyl Benz[b]fluorene-10-carboxylate

Benz[b]fluorene (10 g) in warm benzene (150 ml) was added to a vigorously stirred solution of phenyl lithium (from 10.5 g bromobenzene and 1 g lithium) in ether (500 ml) under an atmosphere of dry nitrogen. The solution rapidly assumed a deep purple color. After half an hour it was poured onto powdered Dry Ice (500 g). Next day the mixture was acidified with dilute hydrochloric acid and steam-distilled to remove solvents. After cooling, the solid was collected, washed, and dissolved in hot 5% sodium carbonate solution (400 ml). Filtration with Norite and subsequent acidification gave the acid as a white solid. Esterification was effected by boiling for 4 hours with dry methanol previously saturated with hydrogen chloride. Concentration to 600 ml and cooling gave pale yellow prismatic needles of methyl benz[b]fluorene-10-carboxylate (8.7 g, 70%), m.p. 124–125°, raised to 126–126.5° by a further crystallization from acetone–methanol. (Lit. m.p. 117–118° (2).) Found: C, 83.23; H, 5.71. Calculated for $C_{19}H_{14}O_2$: C, 83.20; H, 5.15%.

Methyl 10-Methylbenz[b]fluorene-10-carboxylate

The preceding ester (5 g) was dissolved in methanol (100 ml) containing sodium methoxide (from 1 g sodium) to give a deep orange solution. Addition of excess methyl iodide caused a rapid change of color to pale yellow. Isolation of the product in the usual way and crystallization from acetone–methanol gave pale yellow prisms (4.07 g) m.p. 141.5–142.5°, raised to 142–143° by a further crystallization. Found: C, 83.23; H, 5.23%. Calculated for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59%.

Concentration of the original mother liquors gave a second crop (9.4 g) of almost pure material, raising the yield to 87%.

10-Methyl-10-benz[b]fluorenylmethyl Tosylate

The preceding ester (3 g) was reduced with an excess of ethereal lithium aluminum hydride. 10-Methyl-10-benz[b]fluorenylmethanol was obtained as a difficultly crystallizable oil, slow evaporation of a benzene–hexane solution affording small well-defined rhombs, m.p. 108.5–110°. The bulk of the oil was esterified with tosyl chloride (2.6 g) in dry pyridine. The product crystallized from benzene–hexane as small white needles (2.95 g), m.p. 118–119°; concentration of the mother liquors afforded a further 0.16 g. An analytical sample was obtained after a further crystallization, m.p. 118.5–119.5°. Found: C, 75.33; H, 5.35%. Calculated for $C_{26}H_{22}O_3S$: C, 75.35; H, 5.35%.

5-Methylbenz[a]anthracene

(*a*) In the best of several experiments, the once-crystallized tosylate (0.82 g) and 95% formic acid (100 ml) were boiled under reflux for 1 hour. Isolation of the product with chloroform gave a yellow gum, which was dissolved in hexane containing a little benzene and the solution passed through a column of activated alumina. Further elution with hexane and evaporation of the combined eluants gave crude 5-methylbenz[a]anthracene which crystallized from methanol as small white needles (0.28 g, 64%), m.p. 152–153°. (Lit. m.p. 155.9–156.9°, corr. (9).) The identity was confirmed by a mixed melting point with a sample of m.p. 154° and by comparison of infrared spectra. The melting point was strongly depressed by adding 6-methylbenz[a]anthracene.

Evaporation of the mother liquors gave material of m.p. 92–100° (0.08 g). The infrared spectrum showed a weak peak at 11.85 μ indicating the presence of a small proportion of the 6-methyl isomer, but attempts to isolate this through the picrate or by careful chromatography were unsuccessful.

(*b*) 10-Methyl-10-benz[b]fluorenylmethanol (0.5 g) and phosphorus pentoxide (1 g) in xylene (10 ml) were boiled under reflux for 4 hours. Purification of the product and examination of the infrared spectrum showed that there was present a mixture of about equal amounts of 5- and 6-methylbenz[a]anthracene.

Methyl 10-Isopropylbenz[b]fluorene-10-carboxylate

Methyl benz[b]fluorene-10-carboxylate (0.5 g) was alkylated using 3 equivalents each of isopropyl bromide and methanolic sodium methoxide. The product was a yellow oil which failed to crystallize, but passage of a hexane solution through a column of activated alumina and crystallization of the colorless fractions from acetone–methanol gave prisms, (0.4 g), m.p. 150–151°. Found: C, 83.40; H, 6.37%. Calculated for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37%.

Further elution of the chromatogram gave a yellow oil (0.09 g) which formed a vermilion 2,4-dinitrophenylhydrazone. This was not characterized.

Attempts were made to *t*-butylate methyl benz[b]fluorene-10-carboxylate, as described for the fluorene analogue (8). The product was always contaminated with orange material which could not be removed by chromatography. Saponification to an acid followed by esterification with diazomethane also failed to yield a pure compound, so these experiments were discontinued.

5-Methoxybenz[a] anthracene

Benz[b]fluorene (1 g) was oxidized with sodium dichromate in acetic acid and a solution of the products in hexane passed through a column of activated alumina. Elution of the yellow band and crystallization from methanol gave yellow needles, m.p. 151–152° (0.7 g). (Lit. m.p. 152° (10).)

The pure ketone (0.5 g) was dissolved in methanol (100 ml) to which was added a large excess of ethereal diazomethane. Next morning the solvent was removed and the residue dissolved in hot heptane. The solution was passed through a column of activated alumina, elution being continued with the solvent until a fluorescent colorless band had been eluted. Evaporation and crystallization from benzene–hexane gave colorless needles (0.22 g) (38%), m.p. 165–166°. (Lit. m.p. 167–168° (11).) The melting point was not depressed on mixing with an authentic specimen, prepared by methylating 5-hydroxybenz[a]anthracene with diazomethane.

The only other material recovered from the chromatogram was unreacted ketone (0.11 g).

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