STUDIES IN THE WAGNER–MEERWEIN REARRANGEMENT. PART II[1]

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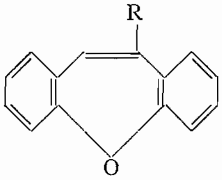
ABSTRACT

Dibenz[*b,f*]oxepin and its 10-methyl derivative have been prepared by ring expansion of suitable xanthene derivatives. 2-Fluorophenanthrene was synthesized from 2-fluorofluorene.

In Part I of this series (1) we described the Wagner–Meerwein rearrangement accompanying formolysis of 9-alkyl-9-fluorenylmethyl tosylates. We now report extension of these studies to other systems.

Reduction of xanthene-9-carboxylic acid with lithium aluminum hydride gave the alcohol, which was dehydrated with phosphorus pentoxide in xylene. Rearrangement took place and the product obtained was identified as dibenz[*b,f*]oxepin (I), which has been prepared recently by Manske and Ledingham (16) by an unambiguous method.



I, R = H
II, R = CH_3

9-Hydroxymethyl-9-methylxanthene was prepared by methylation of methylxanthene-9-carboxylate and subsequent reduction with lithium aluminum hydride. Tosylation followed by formolysis gave 10-methyldibenz[*b,f*]oxepin (II). This ring expansion is similar to that which occurs when 9,10-dihydro-9-anthranylmethyl tosylate undergoes acetolysis to dibenzocycloheptatriene (21). Apart from the parent compound already mentioned the only known derivatives of dibenz[*b.f*]oxepin are a compound related to the alkaloid cularine (15) and 3,4,6-trimethoxy[*b,f*]oxepin 10-carboxylic acid (19).

The ultraviolet spectra of I, II, and methyl 9-methylxanthene-9-carboxylate are shown in Fig. 1. It is interesting that there is a hypsochromic shift on methylation of the dibenzoxepin. Such hypsochromic shifts, except in cases of steric inhibition of resonance, occur only in certain non-alternant systems such as azulene, which has its longest wavelength absorption band at longer wavelength than either 1-methyl- or 5-methyl-azulene (18).

Dehydration of 9-ethylxanthydrol with formic acid did not give the oxepin but most probably 9-ethylidenexanthene, which was, however, not fully characterized (see Experimental).

Formylation of 2-fluorofluorene and reaction with alkaline formaldehyde gave 2-fluoro-9-hydroxymethylfluorene, which, with polyphosphoric acid at 160°, underwent a Wagner–Meerwein rearrangement to give 2-fluorophenanthrene.

It has been reported (20) that 2,2-diphenylpropanol gave *trans*-α-methylstilbene when distilled from phosphorus pentoxide. We prepared the tosylate of this alcohol, required for kinetic studies, and found that it gave the same stilbene on formolysis.

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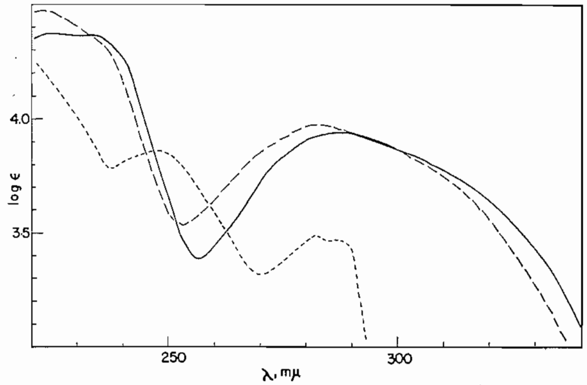

FIG. 1. Absorption spectrum of dibenz[*b,f*]oxepin ———, 10-methyldibenz[*b,f*]oxepin – – – –, methyl 9-methylxanthene-9-carboxylate - - - - -.

EXPERIMENTAL

The ultraviolet spectra were measured in methanol solution with a Beckman DK-2 Recording Spectrophotometer.

9-Xanthylmethanol

Xanthene-9-carboxylic acid (0.2 g., Fluka A.G., m.p. 222–226°) was reduced with an excess of ethereal lithium aluminum hydride. After it had been allowed to stand for two hours the excess reagent was decomposed with wet ether and enough water added to coagulate the precipitate. The ether layer was decanted from the inorganic solids and evaporated to a small volume. Addition of pentane caused the alcohol (0.1 g.) to crystallize. It was recrystallized from ether–pentane, m.p. 68°. Found: C, 79.14; H, 5.74. Calc. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70%.

Dibenz[b,f]oxepin (I)

9-Xanthylmethanol (0.05 g.), phosphorus pentoxide (1 g.), and xylene (10 ml.) were boiled under reflux for 10 minutes. Water was added and the xylene solution separated, dried, and evaporated. When the residue was recrystallized several times from a small volume of methanol, colorless plates were obtained, m.p. 109–110°, undepressed by mixture with authentic dibenz[*b,f*]oxepin, kindly given by Dr. R. H. F. Manske.

Methyl 9-Methylxanthene-9-carboxylate

Xanthene-9-carboxylic acid was esterified with methanol saturated with dry hydrogen chloride. The product crystallized from methanol or hexane as prisms (91%), m.p. 85° (lit. m.p. 85–86° (10)).

The preceding ester (0.05 mole) was alkylated in ether – liquid ammonia, using sodamide (0.15 mole) and methyl iodide (0.2 mole). The product was crystallized twice from methanol or hexane to give colorless prisms (71%), m.p. 95–96° (lit. m.p. 96–97° (11)). Attempted methylation under the conditions used for methyl fluorene-9-carboxylate failed (cf. 1).

Hydrolysis of a portion of the product with potassium hydroxide in warm 50% aqueous ethanol and crystallization from heptane gave 9-methylxanthene-9-carboxylic acid as colorless needles, m.p. 204–206° (lit. m.p. 205–206° (11)). Neutralization equivalent: found, 238; calculated, 240.

9-Hydroxymethyl-9-methylxanthene Tosylate

The preceding 9-methyl ester was reduced with ethereal lithium aluminum hydride, giving 9-hydroxymethyl-9-methylxanthene in 94% yield. One crystallization from hexane gave colorless prisms, m.p. 77–78°. Esterification with tosyl chloride in pyridine gave the tosylate, which crystallized from benzene–hexane as rectangular tablets, m.p. 152–153° with decomposition, raised to 154° by a further crystallization. Yield: 81%. Found: C, 68.9; H, 5.5. Calc. for $C_{21}H_{20}O_4S$: C, 68.5; H, 5.5%.

10-Methyldibenz[b,f]oxepin (II)

The preceding tosylate (0.5 g.) was boiled for a few minutes with formic acid (10 ml.) and then poured into water. The product was isolated with chloroform and crystallized from methanol, giving clusters of needles (0.22 g.), m.p. 57–58.5°. Found: C, 86.35; H, 5.89%. Calc. for $C_{15}H_{12}O$: C, 86.51; H, 5.81%.

Oxidation of the product (0.1 g.) with sodium dichromate in acetic acid gave only a trace of an acidic product. Xanthone could not be isolated.

The product (0.02 g.) in acetone (20 ml.) containing potassium permanganate (0.1 g.) was heated under reflux for 2 hours. The solution was decolorized with sodium bisulphite solution and the acetone evaporated. The crystals (m.p. 150–180°) which separated were collected and dissolved in *N* NaOH (2 ml.). Iodine was added until no more iodoform precipitated and then the filtered solution was acidified. Colorless prisms separated, m.p. 225–228°, undepressed by admixture with an authentic sample of diphenyl ether 2,2-dicarboxylic acid, m.p. 229–230° (lit. m.p. 231° (16)).

9-Ethylidenexanthene

9-Ethylxanthydrol was prepared as described in the literature (12) except that most of the ether was replaced by benzene to increase the solubility of the xanthone. The product (3 g.) was boiled with formic acid (20 ml.) for half an hour. The neutral fraction was isolated and purified by passage of a hexane solution through a column of activated alumina. Evaporation of the eluant gave 9-ethylidenexanthene as a slightly yellow oil with a green fluorescence. It failed to crystallize and did not form crystalline adducts with picric acid or trinitrobenzene. That it was 9-ethylidenexanthene was shown by the following: it was very rapidly oxidized by sodium dichromate in hot acetic acid, giving xanthone in almost quantitative yield, identified by melting point and mixed melting point. The ultraviolet spectrum was very similar to that of xanthone. It rapidly adsorbed 1.1 moles of hydrogen when reduced in ethanol with 10% palladium on charcoal as catalyst. The reduction product was a colorless non-fluorescent oil having a typical xanthene ultraviolet spectrum and, as expected for 9-ethylxanthene, it was oxidized by sodium dichromate in hot acetic acid very slowly.

1,1-Diphenylpropionic Acid

A solution of sodamide (0.1 mole) in liquid ammonia was added to a well-stirred solution of methyl diphenylacetate (0.1 mole) in a mixture of ether and liquid ammonia. After half an hour, methyl iodide (0.11 mole) was added dropwise and stirring continued for half an hour more. These additions were repeated twice more with 0.05 mole quantities. The product was isolated in the usual way to give an oil (methyl 1,1-diphenylpropionate has not been reported crystalline (14)) which was hydrolyzed as described for methyl 9-*t*-butylfluorene-9-carboxylate (1). Crystallization from benzene–hexane gave 1,1-diphenylpropionic acid as prisms (55%), m.p. 172–174° (lit. m.p. 172–174° (4)). Neutralization equivalent: found, 224; calculated, 226.

The anilide was prepared from the acid chloride and aniline. It crystallized from toluene–heptane as fine white needles, m.p. 117°.

2,2-Diphenylpropyl Tosylate

The preceding acid was reduced by boiling with ethereal lithium aluminum hydride for 24 hours. The product, isolated in the usual way, failed to crystallize. (2,2-Diphenylpropanol has not been reported crystalline (20).) Esterification with tosyl chloride in pyridine gave the crystalline tosylate, which formed small needles from benzene–hexane, m.p. 74°. Yield: 89% based on the acid. Found: C, 72.6; H, 6.3. Calc. for $C_{22}H_{22}O_3S$: C, 72.2; H, 6.1%.

Trans-α-methylstilbene

The preceding tosylate was boiled for a few minutes with formic acid. Crystallization of the neutral product from methanol gave lustrous plates, m.p. 81–82° (77%) (lit. m.p. 81–82° (13)). The ultraviolet spectrum was identical with the reported (13).

2-Fluorophenanthrene

2-Nitrofluorene (8) was reduced with ethanolic hydrazine and Raney nickel,[3] giving 2-aminofluorene in almost quantitative yield. This procedure is very much more convenient than that reported in Organic Syntheses (8). The preparation of 2-fluorofluorene has been described previously (7). 2-Fluorofluorene-trinitrobenzene adduct formed yellow needles from methanol, m.p. 95°. Found: C, 57.58; H, 3.17; N, 10.63. Calc. for $C_{19}H_{12}N_3O_6F$: C, 57.43; H, 3.05; N, 10.58%. 2-Fluoro-9-fluorenylmethanol was prepared from 2-fluorofluorene as described for the parent compound, 9-fluorenylmethanol (9). It crystallized from heptane as colorless microprisms, m.p. 94° (57%). Found: C, 78.55; H, 5.29. Calc. for $C_{14}H_{11}OF$: C, 78.49; H, 5.18%.

Dehydration of the carbinol by method A of Part I (1) gave 2-fluorophenanthrene in 64% yield, lustrous plates from methanol, m.p. and mixed m.p. 101–103° (see (5)). 1,3,5-Trinitrobenzene adduct: yellow needles from methanol, m.p. 132°.

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[3] *This method of reduction was first reported by Balcom and Furst (3). It is readily applicable to 1 mole or larger quantities by adding the hydrazine slowly to moderate an otherwise violent reaction. Compounds reduced on this scale include o- and p-bromonitrobenzene, p-nitrophenol, and 2-nitrofluorene (2, 6). Similar reduction of 2,2′-dinitrodiphenyl gave 3,4-benzcinnoline in 94% yield, providing the best preparation of this and similar compounds (2). Palladium on charcoal may replace the Raney nickel (14, 17).*