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

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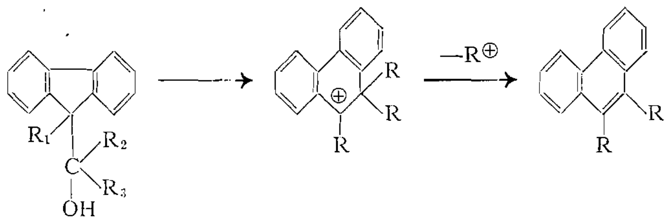
## ABSTRACT

2-(9-Methyl-9-fluorenyl)-propan-2-ol and 3-(9-ethyl-9-fluorenyl)-pentan-3-ol have been prepared and shown to give 9,10-dimethyl- and 9-10-diethylphenanthrene, respectively, when heated with polyphosphoric acid.

In Part I of this series (1), we reported that dehydration-rearrangement of 9-*t*-butyl-9-fluorenylmethanol (I, $R_1$ = *t*-butyl; $R_2 = R_3$ = hydrogen) by the action of polyphosphoric acid gave rise to a considerable amount of phenanthrene. Since 9-*t*-butylphenanthrene was stable under these conditions, loss of the alkyl group appeared to take place during the rearrangement process. Accordingly, we tried to prepare 2-(9-*t*-butyl-9-fluorenyl)-propan-2-ol (I, $R_1$ = *t*-butyl; $R_2 = R_3$ = methyl), which was expected to lead to 9,10-dimethylphenanthrene by expulsion of the *t*-butyl group and a double Wagner–Meerwein rearrangement. Our attempts to prepare this carbinol from methyl 9-*t*-butylfluorene-9-carboxylate have failed (see below), but we have made some related carbinols in which rearrangement and aromatization involved expulsion of an alkyl group.

Methyl magnesium iodide reacted with methyl 9-methylfluorene-9-carboxylate to give 2-(9-methyl-9-fluorenyl)-propan-2-ol (I, R = methyl) in 70–80% yield. Heating of this alcohol with polyphosphoric acid gave 9,10-dimethylphenanthrene. Similarly, ethyl magnesium iodide reacted with methyl 9-ethylfluorene-9-carboxylate to give 3-(9-ethyl-9-fluorenyl)-pentan-3-ol (I, R = ethyl), which gave by heating with polyphosphoric acid 9,10-diethylphenanthrene. In both reactions with polyphosphoric acid the yield of crude hydrocarbon was about 30–50%, but only about 4–10% was obtained completely pure.

These rearrangements may be represented as shown below. It is possible that a shuffling of the alkyl groups in II takes place, and this point could be examined by using suitably labelled alkyl groups.



I II

The increase in resonance energy on passing from II to the 9,10-dialkylphenanthrene probably supplies the driving force for the expulsion of the alkyl group (R).

It was shown previously (1) that methyl 9-*t*-butylfluorene-9-carboxylate was saponified much more slowly than the 9-methyl compound, the difference being attributed to steric hindrance in the former compound. In agreement with this we have found that the 9-*t*-

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butyl derivative was recovered unchanged after boiling for 1 hour with ethereal methyl magnesium iodide. Prolonged reaction with lithium methyl or the Grignard reagent gave a mixture which we were unable to resolve.

## EXPERIMENTAL

### *Preparation of the Tertiary Carbinols*

Methyl 9-methylfluorene-9-carboxylate (1) (3 g.) was boiled under reflux for 2 hours with ethereal methyl magnesium iodide (6 equivalents). The complex was decomposed with ice and ammonium chloride. Evaporation of chloroform extracts gave an oil which crystallized when left overnight in the ice chest under a little hexane. Recrystallization from hexane gave *2-(9-methyl-9-fluorenyl)-propan-2-ol* as long, colorless prismatic needles (2.1 g., 70%), m.p. 68°–69°. Found: C, 85.75; H, 7.52%. Calc. for $C_{17}H_{18}O$: C, 85.67; H, 7.61%.

Reaction of methyl 9-ethylfluorene-9-carboxylate (1) with ethyl magnesium iodide gave, in the same way, *3-(9-ethyl-9-fluorenyl)-pentan-3-ol* in 79% yield. It crystallized from hexane as short stout prisms, m.p. 103°–105°. Found: C, 85.55; H, 8.40%. Calc. for $C_{20}H_{24}O$: C, 85.66; H, 8.63%.

The infrared spectra of carbon disulphide solutions of the carbinols showed strong O–H stretching bands at 3615 $cm.^{-1}$. Solutions of the carbinols in cold concentrated sulphuric acid were carmine.

The crude carbinols melted over a wide range and 20°–30° below the pure compounds, although the infrared spectra did not show carbonyl absorption. It is likely that the carbinols have high molar depression constants, as have been found for other highly branched compounds (2).

### *Reaction of the Carbinols with Polyphosphoric Acid*

The methyl carbinol (1 g.) and polyphosphoric acid (150 ml.) were heated together with stirring at 160° for 1 hour and then at 180° for 15 minutes. The cooled mixture was poured onto ice and extracted with chloroform. Evaporation left an oil which was dissolved in hexane and purified by passage through a column of alumina. Further elution and subsequent evaporation gave a colorless oil. Crystallization from methanol–acetone gave white needles, m.p. 134°–137°, raised to 142°–144° by three more crystallizations. The melting point was not depressed when the compound was mixed with authentic 9,10-dimethylphenanthrene (3), m.p. 143°–144°. Alternatively the hydrocarbon was purified through its picrate or trinitrobenzene complex.

In a similar way the ethyl carbinol gave 9,10-diethylphenanthrene, which formed glistening plates, m.p. 103°–105°, after four crystallizations from methanol–acetone. The melting point was not depressed when the compound was mixed with authentic 9,10-diethylphenanthrene (4), m.p. 106°–107°. The identities were confirmed by comparison of infrared spectra.

### *Attempted Preparation of 2-(9-t-Butyl-9-fluorenyl)-propan-2-ol*

Methyl 9-*t*-butylfluorene-9-carboxylate (1) (12 g.) and ethereal methyl magnesium iodide (12 equivalents) were boiled under reflux for 24 hours. The product was isolated in the usual way, dissolved in hexane, and passed through a short column of activated alumina. When the product was concentrated to 15 ml. and left standing in the ice chest for 3 weeks it gave colorless prisms (7.4 g.). These were collected, washed with a little ice-cold pentane, and recrystallized from hexane (10 ml.) as before to give 4.2 g. of prisms, m.p. 70°–71°. The infrared spectrum of a chloroform solution did not show hydroxyl or carbonyl absorption. The yield of this compound was erratic. A solution of the crude product in carbon bisulphide showed an O–H stretching band at 3618 cm.$^{-1}$.

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