

SYNTHETIC EXPERIMENTS IN THE BENZO-PYRONE SERIES

Part V. Action of Aluminium Chloride on Karanjin

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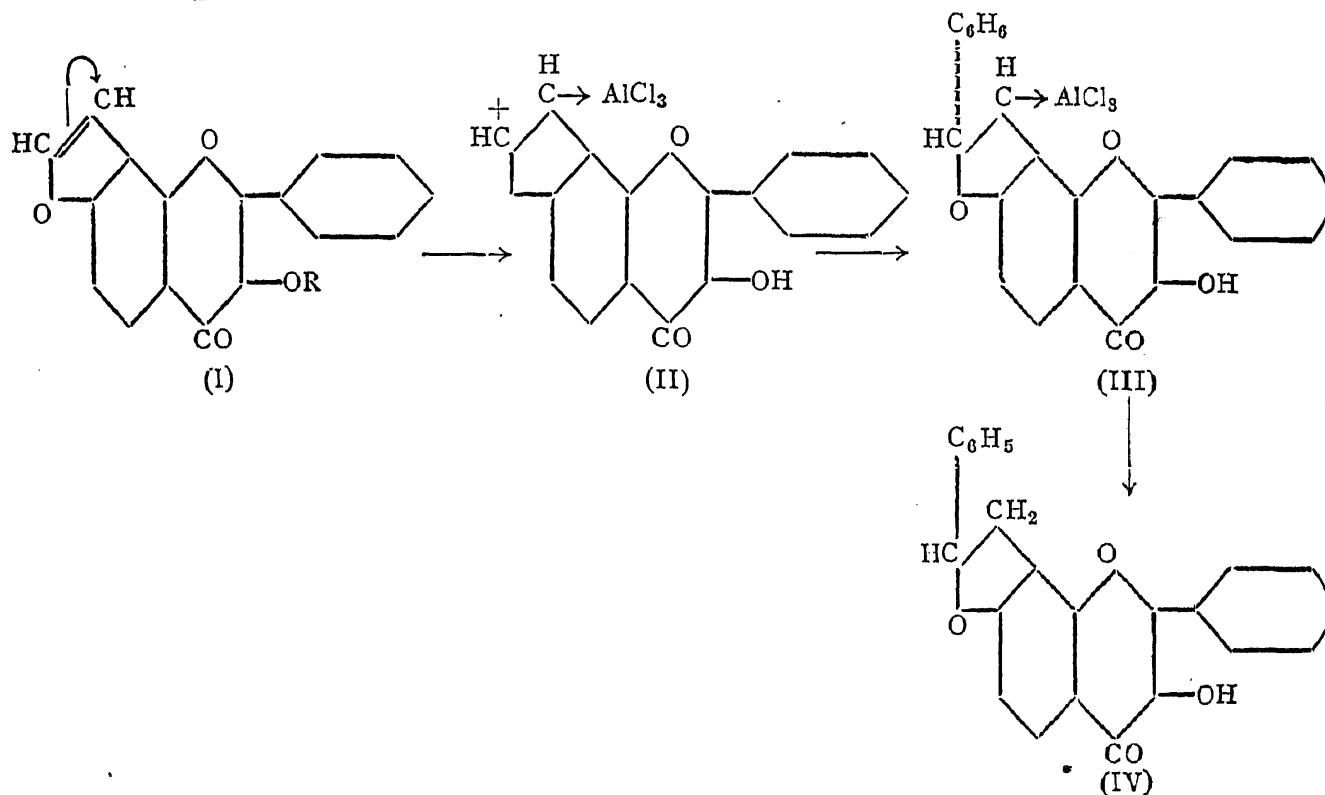
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THE constitution of karanjin which is one of the important crystalline compounds of pongamia oil has been established by a study of its reactions, an investigation of its decomposition products and by synthesis.¹ In the course of synthetic work on pyronofurans, the action of aluminium chloride on karanjin has been examined. If nitrobenzene is used as solvent, smooth demethylation takes place giving rise to a good yield of karanjonol (I, R = H). This hydroxy compound was originally obtained by Limaye from karanjin, by demethylation with hydrogen bromide.² Since benzene has been used by some investigators as solvent for demethylations and since it is much more convenient to work with, the reaction was studied in the presence of this solvent. In this case, however, instead of karanjonol an entirely new compound was obtained. From its properties and analysis, it was concluded that besides demethylation addition of benzene had taken place at the furan double-bond yielding α -phenyl- α : β -dihydro-karanjonol (IV). It forms a monoacetyl derivative. During methylation, the dihydrofuran ring seems to undergo partial opening, giving rise to a product which yields on analysis methoxyl values higher than that required for one methoxyl group.

That the furan double-bond is the one involved in the above condensation of karanjin was established by examining the behaviour of closely related flavones under the same conditions. For this purpose, 7-methoxy-flavone (V), 3-methoxy-7-hydroxy-flavone (VI) and 3:7-dimethoxy flavone (VII) were employed. In benzene solution smooth and complete demethylation took place in all the three cases and there was no addition of benzene. When, however, nitrobenzene was employed at about the same temperature, it was noticed that (V) was unaffected, (VI) underwent demethylation to yield 3:7-dihydroxy-flavone and (VII) suffered only partial demethylation yielding a monomethyl ether. The latter gave the reactions of a 3-hydroxy-flavone. Further, since 7-methoxy-flavone is unaffected in nitrobenzene solution, it is obvious that the new compound is 7-methoxy-3-hydroxyflavone. An easy method is thus available for the preparation of this compound which is otherwise not easily accessible. Our results further support the findings of Venkataraman and co-workers³ that besides the methoxyl groups in

5 and 4' positions, that present in 3 position of flavones is also susceptible to demethylation in nitrobenzene solution. The mild demethylating action of aluminium chloride in this solvent may be attributed to the formation of a co-ordination complex, $C_6H_5NO_2 \rightarrow AlCl_3$, which renders the reagent less easily available for the demethylation. This also explains the ready solubility of the reagent in the solvent.

In regard to the reaction of karanjin with benzene in the presence of aluminium chloride, the furan double-bond of the molecule obviously functions like an ethylenic double-bond and the addition is catalysed by aluminium chloride according to the following mechanism, the anionoid centre of benzene initiating the attack on the positive carbon atom of the aluminium chloride complex. Nitrobenzene is incapable of such nuclear activity owing to the existence of the nitro group.



Toluene, when employed as a solvent, behaves similarly giving rise to Toluyl-dihydro-karanjonol, which resembles very closely the phenyl derivative and yields similar acetoxy and methoxy derivatives.

Experimental

The general procedure adopted in regard to the demethylation of the methoxy flavones is described below with reference to 7-methoxy-flavone.

Action of aluminium chloride on 7-methoxy-flavone

(i) *In benzene solution.*—7-Methoxy-flavone (0.2 g.) was dissolved in benzene (10 c.c.), anhydrous aluminium chloride (Merck quality, 0.5 g.) added and the mixture refluxed on a water-bath ($80-85^\circ$) for about

45 minutes, after which the benzene solution was decanted into another flask and evaporated to dryness. 5 c.c. of 1:1-hydrochloric acid was then added to each of the containers to decompose the aluminium chloride complex. The contents of the two flasks were filtered using the same filter and the solid recrystallised from acetic acid. Needle-shaped crystals melting at 239–40° were thus obtained. Mixed melting point with 7-hydroxy-flavone was undepressed (yield 0.15 g.).

(ii) *In nitrobenzene solution*.—The above experiment was repeated using nitrobenzene in the place of benzene. The solvent was finally removed by steam-distillation and the product recrystallised from alcohol. The starting material was recovered quite unchanged, in the form of rectangular plates melting at 110°.

On 7-hydroxy-3-methoxy-flavone

In this case both when benzene and nitrobenzene were employed as solvents, the final product was found to be the same. On recrystallisation from acetic acid, it was obtained as long and narrow rectangular plates melting at 257–58° (*cf.* 3:7-dihydroxy-flavone^{4, 5} 258°).

On 3:7-dimethoxy-flavone

(i) *In benzene solution*.—0.3 g. of the dimethyl ether yielded finally 0.2 g. of 3:7-dihydroxy-flavone. The mixed melting point with the sample mentioned above was undepressed.

(ii) *In nitrobenzene solution*.—The procedure adopted was the same as for 7-methoxy-flavone. After removal of the solvent by steam-distillation, the precipitate in the flask was filtered and crystallised from glacial acetic acid. Yellow glistening plates melting at 177–78° were thus obtained in 75% yield. It gave a brown colour with ferric chloride and dissolved in sodium hydroxide to give a yellow solution (*cf.* 7-methoxy-flavonol⁴ 180°).

Action of aluminium chloride on karanjin

(i) *In nitrobenzene solution—preparation of karanjonol*.—The reaction was carried out starting with karanjin (1 g.), nitrobenzene (20 c.c.) and aluminium chloride (2 g.). The final product was obtained, on crystallisation from glacial acetic acid, as stout rhombic prisms melting at 192–93°.

(ii) *In benzene solution—preparation of α -phenyl- α : β -dihydro-karanjonol*.—Karanjin (1 g.), benzene (15 c.c.) and aluminium chloride (2 g.) were used for the reaction. The final product was crystallised repeatedly from hot glacial acetic acid. 0.6 g. of a pale yellow compound crystallising in the form of short rectangular plates and melting at 260–62° was obtained. It gave a brownish violet colour with ferric chloride. (Found : C, 77.1; H, 4.9 and there was no loss on drying at 120° for 2 hours. $C_{23}H_{16}O_4$ requires C, 77.5; H, 4.5%).

The above compound (0.2 g.) was acetylated with anhydrous sodium acetate and acetic anhydride. The acetyl derivative came down from alcohol as thin rectangular plates melting at 138-39°. (Found: C, 75.2; H, 4.8; $C_{25}H_{18}O_5$ (monoacetyl derivative) requires C, 75.5; H, 4.5%).

The methyl ether obtained by methylation with dimethyl sulphate and sodium hydroxide, crystallised out from alcohol in rectangular plates melting at 151-53°. (Found: OCH_3 , 13.5; $C_{23}H_{15}O_3$ (OCH_3) requires OCH_3 , 8.4; $C_{23}H_{14}O_2$ (OCH_3)₂ requires OCH_3 , 16.2%).

(iii) *In toluene solution—preparation of α -tolyl- α : β -dihydro-karanjonol.*—The method of preparation was just similar to the above except that in the place of benzene, toluene was used and finally the toluene was removed by steam-distillation. The product was crystallised from hot glacial acetic acid. Broad rectangular plates were thus obtained and the substance melted at 274-76°. The colour with ferric chloride was similar to that given by the benzene compound. (Found: C, 77.2; H, 5.2 and there was no loss on drying at 110-20° for 2 hours. $C_{24}H_{18}O_4$ requires C, 77.8; H, 4.9%).

The acetyl derivative was obtained in rectangular plates when crystallised from alcohol. It melted at 145-46°. (Found: C, 75.9; H, 5.4; $C_{26}H_{20}O_5$ (monoacetyl derivative) requires C, 75.7; H, 4.9%).

The methyl ether crystallised from alcohol as short plates melting at 157-59°. (Found: OCH_3 , 11.6; $C_{24}H_{17}O_3$ (OCH_3) requires OCH_3 , 8.1; $C_{24}H_{16}O_2$ (OCH_3)₂ requires OCH_3 , 15.6%).

Summary

By the action of aluminium chloride on karanjin using nitrobenzene as solvent, smooth conversion into karanjonol could be effected. When benzene is used instead, besides demethylation a molecule of benzene adds on to yield α -phenyl- α : β -dihydro-karanjonol. Similar addition takes place in the case of toluene also. That the double-bond of the furan ring is involved in this reaction has been established by studying the behaviour of a few similar flavone compounds under the same conditions. It has been incidentally shown that a methyl ether group in the 3-position is readily affected in nitrobenzene solution whereas in the 7-position it is stable and the preparation of 7-methoxy-flavonol is easily carried out by demethylation of 3:7-dimethoxy-flavone.

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