Direct Introduction of a Substituent in the Cycloheptatriene Nucleus: Acylation of Cycloheptatriene

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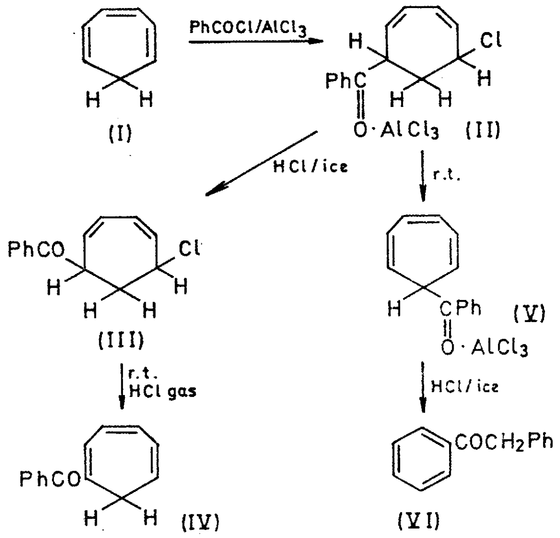
Summary Direct introduction of an acyl group into the cycloheptatriene nucleus to give 1-acyl cycloheptatrienes in good yield is described.

SUBSTITUTED cycloheptatriene derivatives are usually synthesised by ring expansion from six-membered rings[1] or nucleophilic attack upon the tropylium ion.[2] The phenyl group has been directly introduced into the cycloheptatriene nucleus.[3]

We report a convenient synthesis of 1-acyl-cycloheptatrienes in good yield by the direct introduction of an acyl group.

Cycloheptatriene is slowly added, while stirring, to a solution of benzoyl chloride (1 mole ratio) and aluminium chloride (1 mole ratio) in methylene chloride, at 0°. Pouring the solution into HCl–ice mixture gives an intermediate chloro-ketone (III), M^+ 232·0656, $C_{14}H_{13}ClO$, calc. 232·0655; i.r. (thin film), 1690 (s) (C=O of satd. ketone), and 675 cm.$^{-1}$ (s) (C–Cl stretch); n.m.r. (60 and 100 MHz; CCl_4) *ca.* τ 2·3 (m, ArH), 4·0 (m), 5·05 (m), 5·5 (m), 7·8 (m). Bubbling HCl gas through the methylene chloride solution (10 min.) gives 1-benzoylcycloheptatriene (IV) 42% yield; m.p. 45—47°; b.p. 108—135°/0·3 mm. M^+ 196·0894, $C_{14}H_{12}O$, calc. 196·0881; i.r. (KBr), 1640 cm.$^{-1}$ (C=O $\alpha\beta$ to C=C); n.m.r. (60 and 100 MHz; CCl_4) *ca.* τ 2·55 (m, 5H, ArH), 3·55 (m, 4H), 4·4 (m, 1H), and 7·25 (doublet, 2H).



The structure of (IV) is established by n.m.r. The 4H multiplet, τ 3·55 (3-H, 4-H, 2-H, 5-H of the cycloheptatriene ring), and the 1H multiplet, τ 4·4 (1-H or 6-H of the cycloheptatriene ring) place the acyl substituent in the 1-position. This is confirmed by the 2H doublet at τ 7·25 (7-H of the cycloheptatriene ring) instead of the characteristic triplet of the 7-methylene group.[4]

Compound (III) could not be isolated pure because of easy decomposition to (IV). The multiplet at τ 4·0 is characteristic of conjugated cyclohexadiene and cycloheptadiene rings.[5] Spin-decoupling experiments showed that the multiplets at τ 5·05 (C*H*Cl) and 5·5 (C*H*CO) are directly coupled to the 2H multiplet at τ 7·8 (methylene protons) and are not directly coupled themselves. This, together with the easy formation of a substituted cycloheptatriene, establishes the structure of the intermediate as (III).

Earlier work described the formation of deoxybenzoin from a similar reaction.[6] If the solution is allowed to warm to room temperature before decomposition of the $AlCl_3$ complex with HCl–ice, then only deoxybenzoin is obtained (43% yield, i.r. and n.m.r. identical with spectra of authentic material).

The probable reaction mechanism is:—(1) 1,6 addition of the $AlCl_3$–PhCOCl complex across the triene system of cycloheptatriene (I);[7] (ii) (II) decomposes at 0° in HCl–ice mixture to give the halogenoketone (III); (iii) (III) decomposes in the presence of HCl gas by elimination to give 1-benzoylcycloheptatriene (IV); (iv) deoxybenzoin (VI) is formed by the 1,2-elimination of HCl from intermediate (II) on warming to room temperature to give (V), which on acid decomposition rearranges to deoxybenzoin (VI).

1-Mesitoylcycloheptatriene (38% yield; m.p. 30—34°) and mesitoyl deoxybenzoin (13% yield; b.p. 167—180°/6 mm.) have also been prepared by these methods using mesitoyl chloride, with the difference that 1-mesitoylcycloheptatriene is obtained directly on acid treatment of the reaction solution at 0°. No mesitaldehyde could be isolated under either conditions.

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