

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

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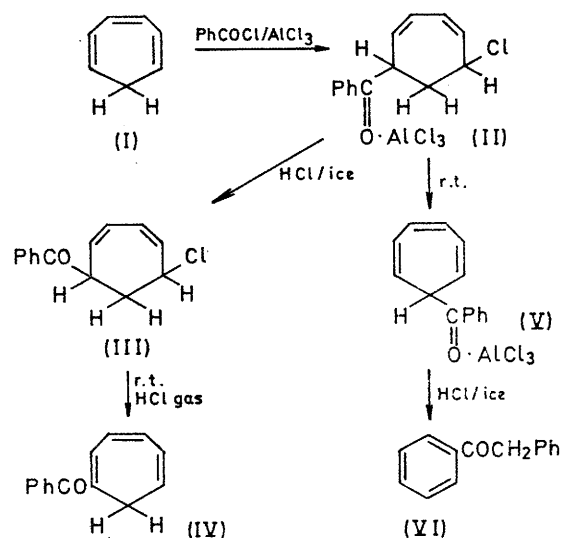
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Summary Direct introduction of an acyl group into the cycloheptatriene nucleus to give 1-acyl cycloheptatrienes in good yield is described.

SUBSTITUTED cycloheptatriene derivatives are usually synthesised by ring expansion from six-membered rings¹ 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 (CHCl) and 5.5 (CHCO) 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:—(i) 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-Mesitylcycloheptatriene (38% yield; m.p. 30–34°) and mesityl deoxybenzoin (13% yield; b.p. 167–180°/6 mm.) have also been prepared by these methods using mesityl chloride, with the difference that 1-mesitylcycloheptatriene is obtained directly on acid treatment of the reaction solution at 0°. No mesitaldehyde could be isolated under either conditions.

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¹ E. Vogel, W. Wiedemann, H. Kiefer, and V. F. Harrison, *Tetrahedron Letters*, 1963, 673; Eu. Müller, H. Fricke, and H. Kessler, *ibid.*, p. 1501; D. G. Lindsay and C. B. Reese, *Tetrahedron*, 1965, 21, 1673.

² G. D. Sargent and N. Lowry, *J. Amer. Chem. Soc.*, 1967, 89, 5985.

³ K. Weiss and Sister M. Lalande, *J. Amer. Chem. Soc.*, 1960, 82, 3117.

⁴ K. W. Egger and W. R. Moser, *J. Phys. Chem.*, 1967, 71, 3699.

⁵ E. Ciganek, *J. Amer. Chem. Soc.*, 1965, 87, 652; W. E. Parnam, *ibid.*, 1962, 84, 1755.

⁶ J. A. Blair, G. P. McLaughlin, and J. Paslawski, *Chem. Comm.*, 1967, 12.

⁷ J. Hutton and W. A. Waters, *Chem. Comm.*, 1966, 634.