Reactions of 1-Benzoylcycloheptatriene

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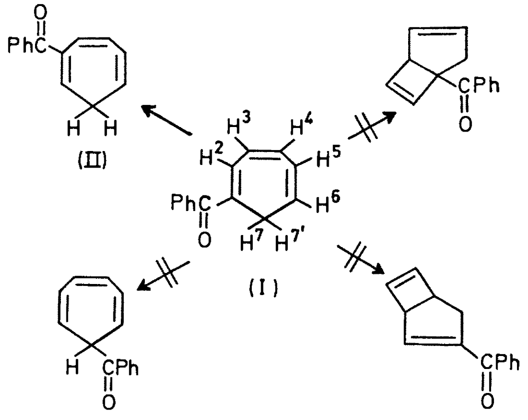
Summary Photolysis, thermolysis, and hydride-ion transfer of 1-benzoylcycloheptatriene are described.

Synthesis of 1-benzoylcycloheptatriene by cycloheptatriene acylation has been described.[1,2]

Photolysis of 1-benzoylcycloheptatriene (I), in benzene (30 h) using a Hanovia 125-w medium-pressure mercury lamp, gave 2-benzoylcycloheptatriene (II) as sole product, M^+ 196·0878, $C_{14}H_{12}O$ 196·0888, ν_{max} (thin film) 1680 cm^{-1} (C=O), τ (CCl_4, Me_4Si as standard) 1·9 (d, 3-H), 2·5 (m, C_6H_5CO, 5H), 3·3 (quartet, 4-H), 3·8 (quartet, 5-H), 4·15 (t, 1-H), 4·55 (m, 6-H), 7·75 (t, 7-H + 7′-H). Assignment of the position of substitution was from 1-H, τ 4·15, the triplet being due to coupling with the two methylene protons only.

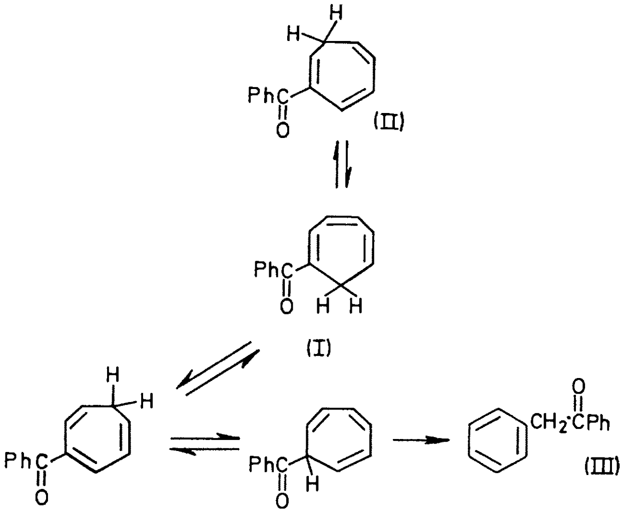


Scheme 1

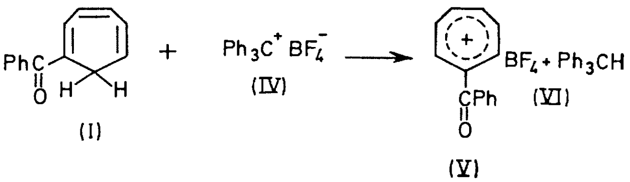
No valence tautomerism[3] was observed, and the direction of the 1,7 hydrogen shift[4] was specific (Scheme 1). 1-Cyanocycloheptatriene behaves similarly.[5] The specificity of the 1,7 hydrogen shift, and the percentage of valence tautomer formed, are related to the electron-withdrawing capacity of the substituent.[5]

Thermolysis of 1-benzoylcycloheptatriene (I) (184°, 24 h) gave deoxybenzoin (III) (n.m.r., i.r., identical with spectra of authentic material), as the only isolable product. Thermal rearrangements in the cycloheptatriene system, at these temperatures, proceed *via* 1,5 transannular hydrogen shifts.[6] This path for deoxybenzoin is given in Scheme 2. The n.m.r. spectra of samples taken at intermediate times showed small amounts of isomeric benzoylcycloheptatrienes, in agreement with the Scheme.

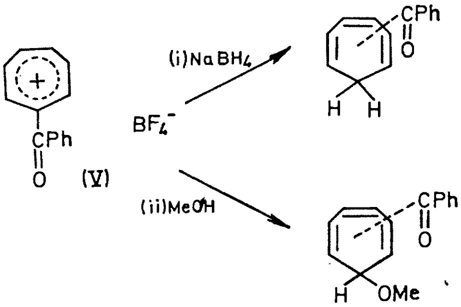
Hydride-ion transfer[7] with trityl fluoroborate gave benzoyltropylium fluoroborate (V) (Scheme 3). 1-Benzoylcycloheptatriene (1·2 g) in methylene chloride (5 ml) was added to a solution of trityl fluoroborate[8] (IV) (2·0 g) in methylene, chloride (10 ml). The heavy precipitate (20 min) was removed by filtration and washed (CH_2Cl_2) to give a pale yellow product (0·75 g) m.p. 150°, (decomp.), $(M + 1)^+$ 196·0862, $C_{14}H_{12}O$ 196·0888, ν_{max} (KBr disc) 1655 (C=O), 1050 cm^{-1} (BF_4), τ (trifluoroacetic acid, Me_4Si external reference) 0·9 (s, C_7H_6CO, 6H), 2·7 (m, C_6H_5CO, 5H). Removal of solvent followed by recrystallisation gave



Scheme 2



Scheme 3



Scheme 4

triphenylmethane (VI) (i.r. identical with spectrum of authentic material).

The fluoroborate (V) reacts with nucleophiles to form mixtures of isomeric cycloheptatrienes, *e.g.* (i) sodium borohydride and (ii) methanol (Scheme 4).

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[1] J. A. Blair and C. J. Tate, *Chem. Comm.*, 1969, 1506.
[2] J. A. Blair and C. J. Tate, *J. Chem. Soc.* (*C*), in the press.
[3] W. G. Dauben and R. L. Cargill, *Tetrahedron*, 1961, **12**, 186.
[4] W. von E. Doering and P. P. Gaspar, *J. Amer. Chem. Soc.*, 1963, **85**, 3043.
[5] A. P. Ter Borg, E. Razenberg, and H. Kloosterziel, *Chem. Comm.*, 1967, 1210.
[6] A. P. Ter Borg, H. Kloosterziel, and N. van Meurs, *Rec. Trav. chim.*, 1963, **82**, 717.
[7] H. J. Dauben, F. A. Gadecki, K. M. Harman, and D. L. Pearson, *J. Amer. Chem. Soc.*, 1957, **79**, 4557.
[8] H. J. Dauben, L. R. Honnen, and K. M. Harman, *J. Org. Chem.*, 1960, **25**, 1442.