The Reaction of Cycloheptatriene with Benzoylium Fluoroborate

By J. A. BLAIR, G. P. MCLAUGHLIN, and J. PASLAWSKI
(*University of Aston in Birmingham, Birmingham,* 4.)

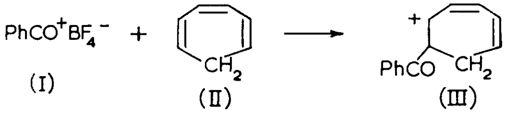
THE reaction of cycloheptatriene with triphenylmethyl perchlorate or fluoroborate to give excellent yields of cycloheptatrienylium perchlorate or fluoroborate and triphenylmethane is well established.[1] This reaction takes place without concurrent polymerisation of the cycloheptatriene. The reaction of cycloheptatriene with t-butyl chloride and allyl bromide in the presence of Lewis acids such as stannic chloride gives cycloheptatrienylium stannichloride and polymerised cycloheptatriene.[2] The formation of isobutane or propene was not reported. Apart from a reaction between acetylfluoroborate and cycloheptatrienecarboxylic acid,[3] no other examples have been recorded of the reaction between cycloheptatriene and acid halides and their derivatives. In the belief that the reaction between cycloheptatriene and an electrophilic species, such as the benzoylium cation, should proceed by a hydride-atom transfer yielding the cycloheptatrienylium cation and benzaldehyde a study was initiated of the reaction between benzoylium fluoroborate and cycloheptatriene. Previously it had been established that no reaction occurred between cycloheptatriene and benzoyl chloride.

A solution/suspension of benzoyl fluoroborate in methylene chloride at *ca.* $-30°$ was prepared by passing boron trifluoride gas into a solution of benzoyl fluoride in methylene chloride.[4] Cycloheptatriene (2 molar ratio) was quickly (5 min.) added to this solution at $-30°$ with stirring and the mixture was slowly allowed to come to room temperature. A crystalline solid was precipitated, filtered off, and identified as cycloheptatrienylium fluoroborate by its characteristic behaviour on heating, and by its u.v., i.r., and n.m.r. spectra. The yield of cycloheptatrienylium fluoroborate based on benzoyl fluoride used was 35%. No benzaldehyde could be isolated from the reaction mixture and the absence of benzaldehyde from the reaction products was confirmed by inspection of the n.m.r. spectrum of the methylene chloride filtrate which showed the absence of the characteristic absorption of benzaldehyde aldehydic proton in the region of τ 0·00. Removal of the methylene chloride followed by extraction with ether gave a brown polymeric solid. Work up of the ethereal solution gave a small yield (*ca.* 2%) of a low-melting solid identified as deoxybenzoin by mixed melting point, mixed melting point of the 2,4-dinitrophenylhydrazones of the unknown and synthesised deoxybenzoin, identity of the i.r. and n.m.r. spectrum.

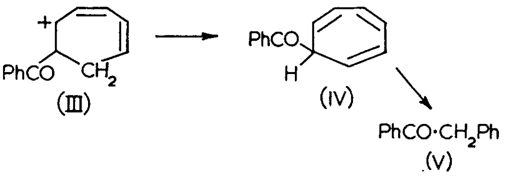
A repetition of this experiment but with the slow addition (75 min.) of cycloheptatriene in dilute methylene chloride solution gave a trace of cycloheptatrienylium fluoroborate, polymeric solid and an improved yield (*ca.* 9%) of deoxybenzoin.

It is clear from these experiments that in reacting with benzoylium fluoroborate, cycloheptatriene does not act as a hydride transfer agent. In an attempted synthesis of benzoyl cycloheptatriene, Doering and Knox found that deoxybenzoin was formed and suggested that the driving force of the ring contraction was the resonance energy of the benzene ring.[5] The deoxybenzoin formed in these experiments was probably derived from a similar rearrangement of benzoyl cycloheptatriene.

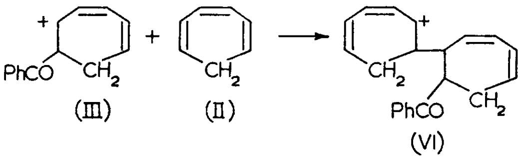
A reasonable explanation for the results obtained is that the first reaction of benzoylium fluoroborate (I) with cycloheptatriene (II) is addition to a double bond to yield a carbonium ion (III).



This carbonium ion can then lose a proton giving benzoyl cycloheptatriene (IV) which rearranges to deoxybenzoin (V).



An alternative reaction for the carbonium ion (III) is to attack a cycloheptatriene molecule giving another carbonium ion (VI).



Extension of this process would lead to the formation of a polymeric carbonium ion. This polymeric carbonium ion (VII) could revert to a neutral polymer either by loss of a proton or by hydride atom transfer from cycloheptatriene yielding the cycloheptatrienylium cation.

$$\underset{\text{(VII)}}{R^+} + BF_4^- \longrightarrow R + HBF_4$$

$$R^+ + C_7H_8 \longrightarrow C_7H_7^+ + RH$$

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