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TRAPPING OF INTERMEDIATE IONS IN A REACTION RELATED TO THE COPE REARRANGEMENT

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In the previous communication, a reaction (1 → 4)* was presented, closely related to the Cope Rearrangement, for which an ionic mechanism seemed the most probable. In order to substantiate this view we have made efforts to intercept the reaction and trap the intermediate ions.

The rearrangement of 1 to 4 was conducted in the presence of thiophenoxide ion, with a view to trapping the carbonium ion 3 as the thioether 5a (Scheme) with simultaneous formation of the dinitrile 6, by eventual protonation of the sequestered anion 3. Although we have not been able to obtain evidence of the formation of thioether 5a, there is no doubt that the dinitrile 6 is formed under these trapping conditions, identified by identical retention times on glc and superimposable mass spectrum with those of an authentic sample.

Before the formation of dinitrile 6 can be regarded as evidence of ionic intermediates, an alternative route to the formation of 6 must be considered. This possibility, illustrated in the Scheme, involves direct nucleophilic attack on diene 1, is independent of the Cope rearrangement, but gives identical products to the trapped putative ions. In view of the powerful nucleophilicity of the thiophenoxide ion[1] this possibility may not be disregarded. In order to throw more light on the mode of formation of 6, it seemed desirable to change

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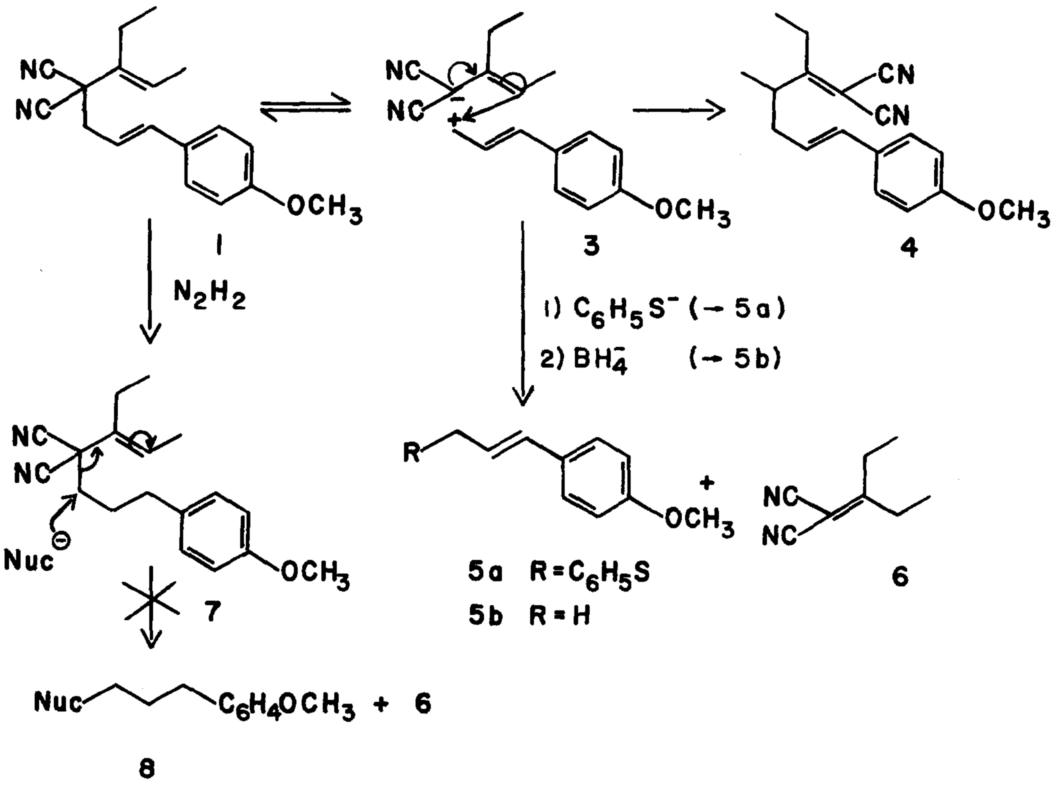
* The numbering scheme of compounds in the previous communication is used.



Scheme

the trapping agent to one with less force as a nucleophile, while retaining the ability to react with carbonium ions. The trapping agent selected for this purpose was borohydride ion, which, although not especially reactive in S_N2 type reactions, has been shown to be particularly effective in trapping carbonium ions[2]. The isomerization of diene 1 was therefore conducted in diglyme[2] at 88° for 16 hours in the presence of sodium borohydride. Under these conditions, a small amount of anethole 5b, identified by identical glc retention times and superimposable mass spectrum with those of an authentic sample, was indeed formed showing that formation of the "trapped ion products" was relatively independent of the nucleophilicity of the trapping reagent.

Although this evidence strongly indicated that formation of compounds 5 and 6 were formed as a result of the ions 3 being trapped rather than by direct nucleophilic attack on 1, an attempt was made to establish this point more rigidly by obtaining more quantitative evidence as to the feasibility of the direct nucleophilic attack of borohydride on 1. Removal of the styrene double bond of 1 by diimide reduction[3], which gives compound 7, is expected to completely inhibit ion formation but should only slow direct nucleophilic attack by the factor caused by the centre no longer being allylic. This factor, the ratio of rates at an ethyl as opposed to an allyl centre is generally considered to be approximately 40[1], on top of which is superimposed the factor due to the γ, trans aromatic ring which has been reported to be 6.8[4]. Thus direct nucleophilic attack on 7 will be expected to proceed approximately 270 times slower than on 1. Assuming an energy of activation of 19.0 $kcals.mole^{-1}$,[5] rate factor can be counteracted by a combination of an increase of reaction temperature from 88° to 167° (reflux) and an increase of reaction time from 16 hours to 38.6 hours. The formation of 8 from 7 under these conditions therefore provides a model for the feasibility of the formation of 5b from 1 by direct nucleophilic attack. Compound 7 was therefore heated at 167° for 46 hours in the presence of sodium borohydride. Under these conditions no trace of dihydroanethole 8 (Nuc = H) could be detected. This result strongly suggests that the isolation of anethole from reduction of diene 1 does not arise by direct nucleophilic attack on 1, and that the formation of anethole is a result of the carbonium ion 3 being trapped by borohydride.

These experiments are therefore consistent with the view that the conversion of 1 to 4 occurs by way of ionic intermediates.

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