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AN UNUSUAL REACTION OF PARA-NITROPHENYL ALDEHYDES WITH ACETONE CYANOHYDRIN

S.K. Grover*, L.A. Yanovskaya, O.S. Chizhov and V.F. Kucherov
N.D. Zelinsky Institute of Organic Chemistry, U.S.S.R. Academy of Science,
Moscow

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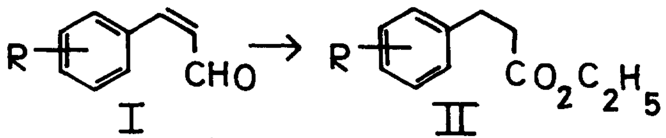
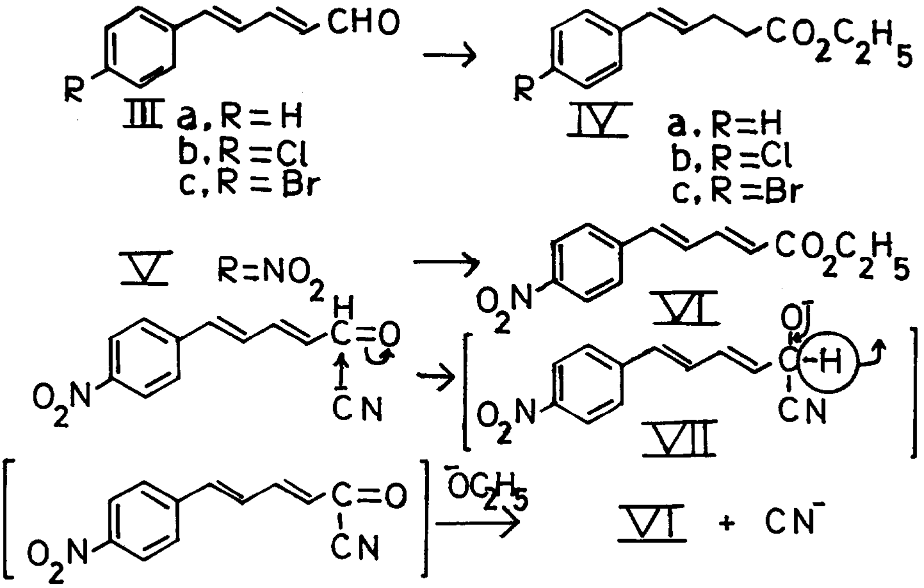
In an earlier publication from this Institute[1], an oxygen rearrangement was reported in the case of aromatic and unsaturated esters under electron impact. In the case of γ,δ-unsaturated esters the intensity of the oxygen rearrangement peak was found to be low. Synthesis of some more examples of γ,δ-unsaturated esters was undertaken in order to study their behaviour under electron impact. α,β-Unsaturated aldehydes (I) on reaction with acetone cyanohydrin in ethanolic solution in the presence of triethylamine are known to yield the corresponding saturated esters (II)[2].



For the synthesis of γ,δ-unsaturated esters, aldehydes having two conjugated double bonds (III) were subjected to this reaction and our results are presented below.

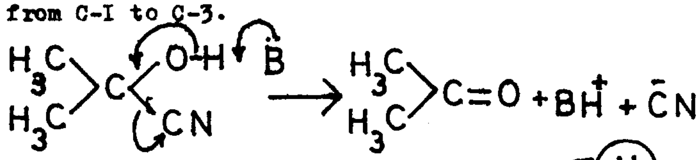
It was observed that aldehydes (IIIa,b,c), where R was either H, Cl or Br, reacted in the expected manner to yield the corresponding γ,δ-unsaturated esters (IV). However, when R was NO_2 (V), the product (A) m.p. 123-124° was found to be different. It showed a molecular ion peak at 247, carbonyl absorption in IR at 1720 cm^{-1} and had λ_{max}^{MeOH} at 246 (ϵ 11500) and 346mμ(ϵ 29300). These results could be explained on the basis of structure (VI) for product A. This structure was further proved by its NMR spectrum where it showed the expected peaks. The identity was finally confirmed by comparing product (A) with an authentic sample prepared from p-nitrocinnamaldehyde and (EtO)$_2$POCH$_2$COOEt involving a Wittig reaction when the two samples were found identical in all respects. Product (A) could have been formed from the original aldehyde according to the following mechanism involving the loss of a hydride ion from the intermediate VII.

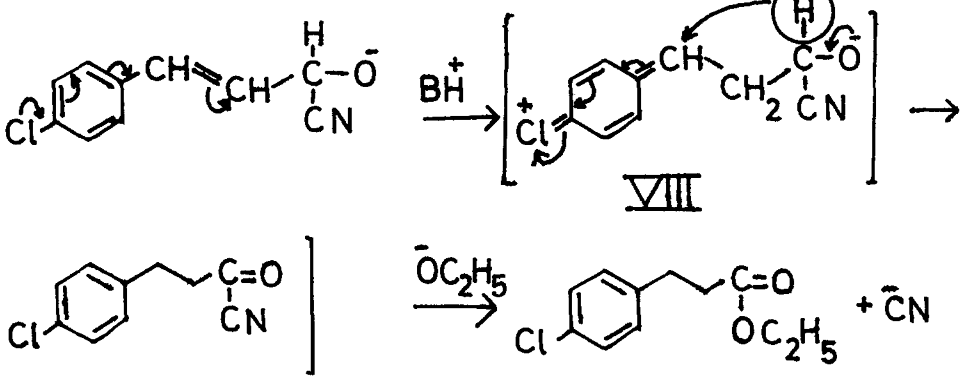


The hydride ion could have been taken up by the nitro group, or the carbonyl group in acetone or the starting aldehyde. Isopropanol was identified as one of the products of the reaction by gas chromatography. As the reaction was found to proceed with the formation of a large amount of intractable dark brown gum, it is likely the hydride ion could be very readily taken up by the nitro group leading to the formation of amino compound which could then condense with the aldehyde giving gum. All attempts to isolate or detect the alcohol corresponding to the starting aldehyde failed.

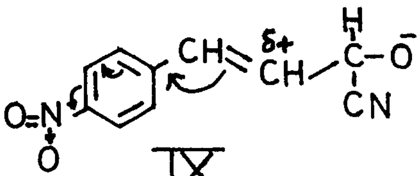
Next p-nitrocinnamaldehyde and p-nitrobenzaldehyde were subjected to this reaction and they were found to yield p-nitroethylcinnamate and p-nitroethylbenzoate respectively.

Cyanide ion seems to be necessary for this reaction, as it was observed when acetone cyanohydrin was excluded, product A could not be obtained. These results are difficult to be explained on the basis of the mechanism proposed earlier[3] for the production of saturated esters from α,β-unsaturated aldehydes. On the basis of the above mentioned results, it is necessary to take into consideration the substituent present in the phenyl ring. It is observed, when the phenyl ring has an electron donating substituent the reaction leads to the formation of saturated esters. This could be explained as follows: when the phenyl ring carries an electron donating group, there is a negative centre at the α-carbon which could be the seat of attack by the electrophile BH$^+$; when the intermediate VIII reverts back to aromatic system this would create a positive carbon at β-position which would lead to a hydride ion shift from C-I to C-3.





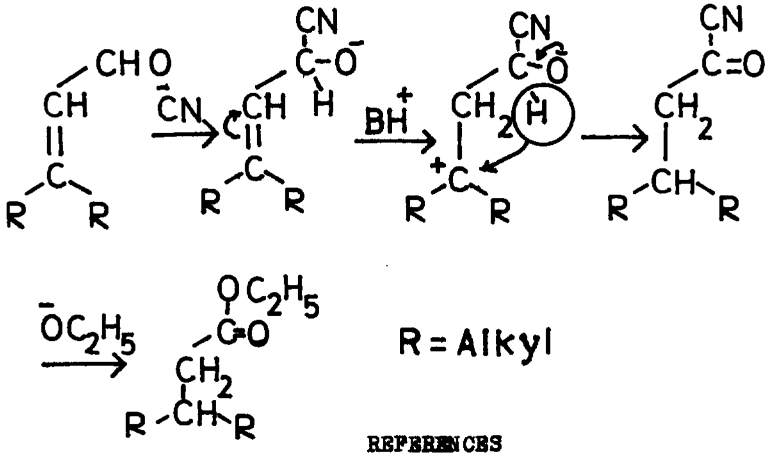
VIII



IX

This is supported by the fact that when acetonecyanohydrin labelled with deuterium on the hydroxylic hydrogen is used for the reaction, the deuterium is incorporated mainly at the α-position. However, when the phenyl ring has an electron withdrawing group (IX), this would create a positive centre at the α-carbon inhibiting the initial attack by BH^+ and in these cases, no saturated esters were obtained.

From what has been discussed above about the mechanism of the reaction with p-substituted phenyl aldehydes, it would follow that a general mechanism can be formulated about the reaction with α,β-unsaturated aldehydes which is given below.



R = Alkyl

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* Present address: Department of Chemistry, Delhi University, Delhi-7, India.