Tetrahedron Letters No. 6, pp 553 - 554. 0040-4039/79/0201-0553$02.00/0
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DECARBALKOXYLATION OF ALKYLIDENE CYANO-ESTERS

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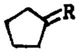
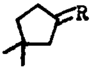
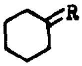
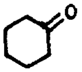
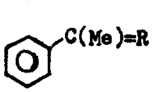
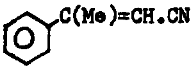
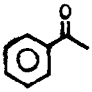
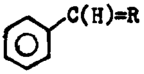
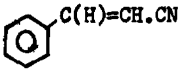
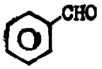
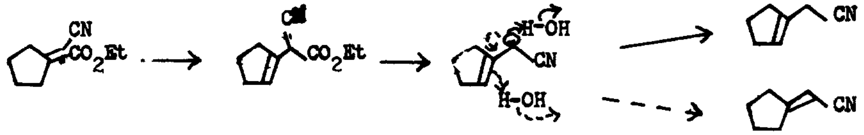
The Krapcho experimental condition involving DMSO, sodium chloride and water has since found wide-scale application as a facile means for decarbalkoxylation of geminal diesters, cyano-esters, β-keto-esters etc.[1] The logical extension of this method to alkylidene esters has not been reported so far. In this communication we report our preliminary findings on the application of this system to the decarbalkoxylation of a few representative alkylidene cyano-esters leading to fair yields of the unsaturated nitriles and probable mechanism of the reaction.

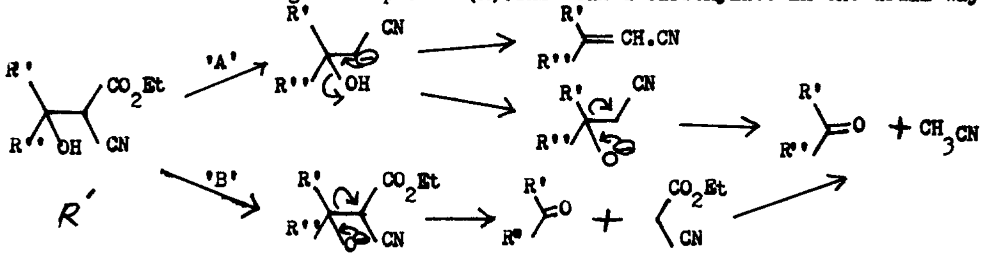
Table (condition: $NaCl/DMSO/H_2O$ 6hrs at 160°)

No	Substrate ($R= \overset{CN}{C}CO_2Et$)	Products	Proportion of αβ : βγ
1			3 : 1
2			4 : 1
3		 , 	1 : 2
4		, 	
5		, 	

As the Table reveals alkylidene cyano-esters undergo facile decarbalkoxylation with sodium chloride in wet DMSO and serves as a useful complementary procedure to the Wittig and Cope reactions for the conversion of carbonyl groups to unsaturated nitriles. Yields are in the range of 55-60% excluding the Ca 20% accounting for the starting ketones. No attempt has been made to optimise conditions or evaluate the proportions of DMSO, sodium chloride and water required, though the proportions suggested by Krapcho have been followed. The relative proportions of the products have been arrived at from NMR and GLC measurements[2].

Coming to mechanistic aspects, though the details of the reaction course have been lucidly worked out by Krapcho et al., a straight away enactment of the same situation appears improbable here since the generation of a vinylic carbanion is energetically unfavorable under these conditions. Searching for alternatives, an initial deconjugation, followed by decarboxylation and reconjugation appears a distinct possibility, particularly from the isolation of $\beta\gamma$-isomer(entries 1,2 & 3). But this assumption fails with benzaldehyde where no such possibility exists. A clue to the possible mechanism is suggested from the isolation of the starting carbonyl compound (cyclohexanone, acetophenone, benzaldehyde)[3], evidently arising out of a retro-aldol process. Hence it appears that the initial process is a conjugate addition of water leading to a species (R). This can decarboxylate in the usual way[1] (path 'A')





R′

followed by dehydration to afford the unsaturated nitrile or retro-aldolise to afford the carbonyl compound. Or some amount can collapse at this stage (path 'B'), though we are unable, at this stage to offer evidence in favor of either or speculate at what stage deconjugation occurs. One experiment carried out with (4) without sodium chloride afforded the same mixture of products suggesting halide has probably no role to play in the reaction.

We are currently conducting experiments to fully probe the mechanistic aspects as well as evaluate the implications of this interesting observation.

We thank Professor U.R.Ghatak for valuable discussions.

REFERENCES AND NOTES

1 A.P.Krapcho, J.F.Weimaster, J.M.Eldridge, E.G.E.Jahngen, Jr., and W.P.Stephens, J.Org.Chem., 43, 138 (1978) and references cited therein.

2 Entries 2,4 & 5 do not represent any particular geometrical isomer, but mixture. This aspect will be dealt with in detail in a subsequent full paper.

3 In the cases of entries 1 & 2, the starting ketones were not isolated largely because of their solubility in water which was added before work-up. Their presence was subsequently established by checking aliquots after reaction for spectral data and 2,4 DNPH formation.

(Received in UK 12 September 1978)