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THE REACTION OF CYANO-CARBALKOXY-PYRIDINIUM-METHYLIDS WITH DIMETHYL ACETYLENEDICARBOXYLATE

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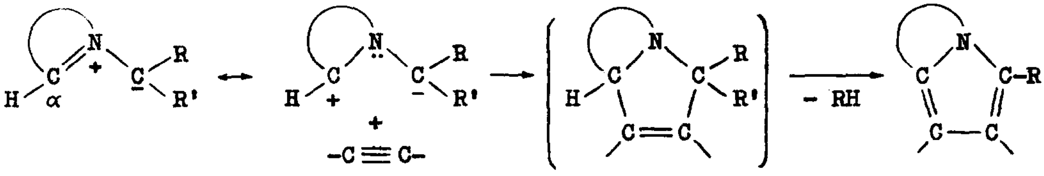
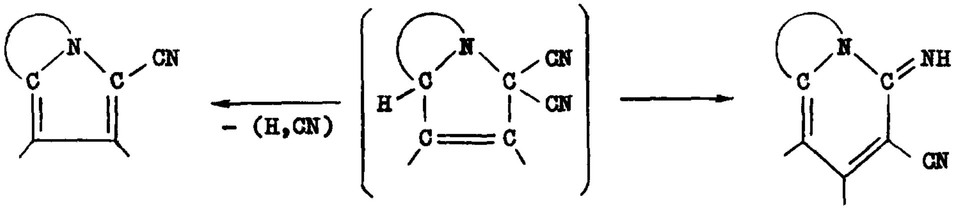
The heterocyclic nitrogen ylids react as 1,3 dipoles with acetylenic dipolarophiles, leading, via a hypothetical dihydroaromatic cycloadduct, to aromatic bicyclic derivatives, as follows (1,2):

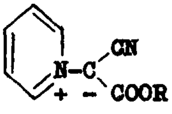


R = H, CO-C_6H_5, $COOC_2H_5$

On the other hand, in the case of heterocyclic dicyanomethylids (R = R' = CN), the intermediary cycloadduct undergoes either an 1,4 elimination as above (3) or a ring enlargement (4):



The present paper describes the course of the reaction between cyano-carbalkoxy-pyridinium-methylids (I) with dimethyl acetylenedicarboxylate (DMAD); this reaction was carried out with equimolecular amounts of the components, at ambient temperature, in several solvents of various polarities. Whereas in benzene or in dimethylformamide (DMF) solution, only common indolizinic derivatives were obtained, in acetonitrile solution the results were found to be wholly different from the known ones.

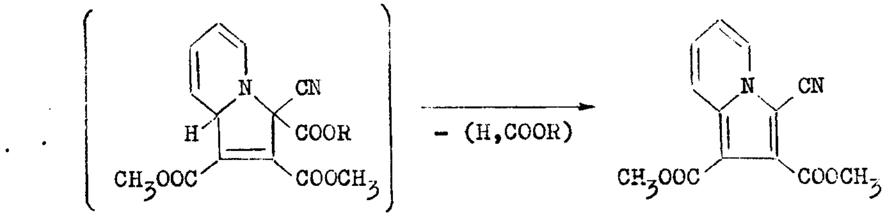


I

a) R = CH_3

b) R = C_2H_5

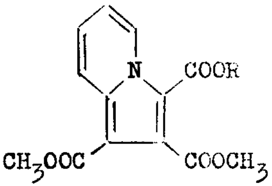
Thus, from I a,b with DMAD in benzene as solvent, the known III was obtained. The product, formally resulting by H,COOR loss from the presumable intermediary 1:1 cycloadduct II, was found to be identical with that obtained by Linn et al. (3) from $C_5H_5\overset{+}{N}-\overset{-}{C}(CN)_2$ and DMAD. The compound III also results from $C_5H_5\overset{+}{N}-CH_2CN\ Cl^-$ in the presence of $N(C_2H_5)_3$ (i.e. from the corresponding ylid) with DMAD in various aprotic solvents, by loss of H,H from the primary cycloadduct (II, H instead of COOR). In this case, the use of a dehydrogenating catalyst (Pd/C), as indicated in similar works, was not necessary, the rearomatization being ensured by the intervention of the air during the isolation of the product.



II III

a) R = CH_3
b) R = C_2H_5

In DMF solution the results were not always uniform. From Ia and DMAD only III was obtained, whereas the products isolated from Ib were III as well as the known IVb (2) (H,CN elimination from II). From the mixed triester IVb, by means of CH_3O^-/CH_3OH, the known IVa (5) was obtained. Both IVa and IVb also result from DMAD and the corresponding ylids formed "in situ" from $C_5H_5\overset{+}{N}-CH_2COOR\ X^-$ ($R = C_2H_5$, X = Br and $R = CH_3$, X = Cl) and $N(C_2H_5)_3$, in various aprotic solvents.



IV

a) R = CH_3
b) R = C_2H_5

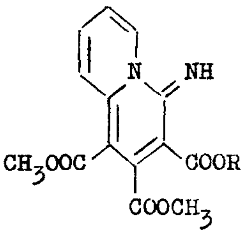
The further fate of the residues H,COOR and H,CN , eliminated in all the above reactions of the ylids Ia and Ib, has not been investigated.

The corresponding reaction products of Ia and Ib with DMAD in acetonitrile solution, were isolated as orange crystalline compounds, m.p. 245°C and 239°C respectively (mixed m.p. about 228°C). Although their ir spectra are not identical, these are, however, very similar. From the analytical data it was established that the two compounds are 1:1 adducts.

Ia + DMAD = 1:1 adduct, m.p. 245°C

Ib + DMAD = 1:1 adduct, m.p. 239°C

As possible structures of these very stable 1:1 adducts, those corresponding to the dihydroaromatic cycloadducts II, easily aromatizable, were out of question. Other structures, resulting from a ring enlargement (Boekelheide), (V), were invalidated by the presence of an ir absorption characteristic for a CN group (at 2240 and 2250 cm^{-1} respectively), as well as by the failure of any attempt to alkylate the compounds ($>C{=}NH \xrightarrow{RX} >C{=}\overset{+}{N}H{-}R\ X^{-} \xrightarrow{HO^{-}} >C{=}N{-}R$); moreover, the attempts at passing from one adduct to another by transesterification ($-COOC_2H_5 \rightarrow -COOCH_3$), were also unsuccessful.



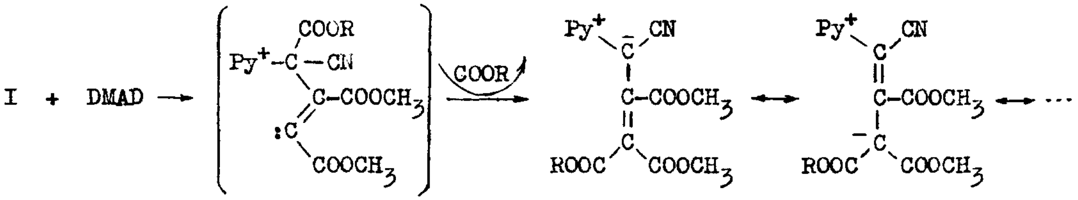
V

a) R = CH_3

b) R = C_2H_5

A good evidence against a bicyclic structure was obtained from the fact that, through treatment with the Zn-Cu couple, pyridine was detected among other unidentified reduction products.

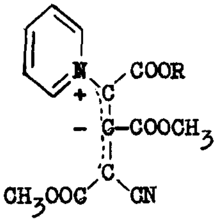
According to the above observations as well as to the nmr data, an ylidic structure VIa,b was assigned to the two products. Such a structure may be considered as a result of an uncommon cationotropic shift of the COOR group from the primitive ylidic carbon to the intermediate carbanion, formed in the initial step of a Michael type addition of the ylid I to the activated triple bond of the acetylenic compound. The driving force of the reaction is probably due to the formation of a highly stabilized ylidic system.



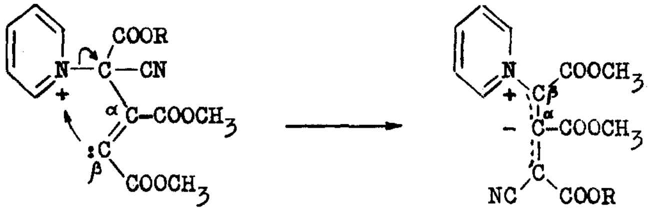
VI (Py = C_5H_5N)

a) R = CH_3; b) R = C_2H_5

In the nmr spectrum of VIa the protons of two $COOCH_3$ groups have an identical situation (δ = 3,7 ppm), those of the third $COOCH_3$ group being more deshielded (δ = 4,1 ppm). On this ground, other possible ylidic structures, as VII, formed by an analogous transfer of the cyano group, or VIII, resulting by the pyridinium ring transfer, were eliminated, since in the case of (Ia + DMAD) adduct the nmr spectrum should show three different $COOCH_3$ signals.



VII



VIII

The formation of such ylidic structures as VI in the reaction of an ylid with DMAD via COOR transfer is, to our knowledge, without precedent (see, however, ref. 6 for an analogous proton shift).

The easy scission of the COOR group has also been observed in some other reactions of the ylids I, as in the protonation of Ib (7),

$$C_5H_5\overset{+}{N}-\overset{-}{C}(CN)COOC_2H_5 + HClO_4 \longrightarrow C_5H_5\overset{+}{N}-CH_2-CN\ ClO_4^- + CO_2 + C_2H_5OH$$

as well as in the reaction, previously observed by us, with the bromocyanoacetic ester:

$$C_5H_5\overset{+}{N}-\overset{-}{C}(CN)COOR + BrCH(CN)COOR \longrightarrow C_5H_5\overset{+}{N}-\overset{-}{C}(CN)_2$$

It is clear that, in all the above cases, the COOR scission may occur only <u>after</u> the interruption of the conjugation between this group and the carbanion, i.e. after the disappearance of the anionic charge from the ylidic carbon atom.

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