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THE REACTION BETWEEN CYANO-CARBALKOXY-PYRIDINIUM-METHYLIDS AND BROMOCYANO-ACETIC ESTER, A NEW ROUTE TO DICYANO-PYRIDINIUM-METHYLID

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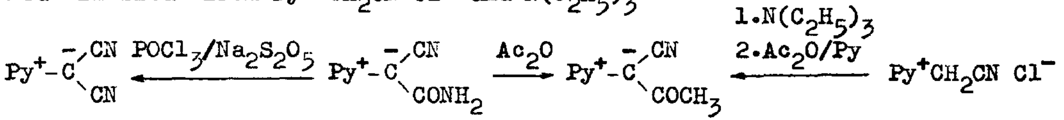
Dicyano-pyridinium-methylid (I, Py = C_5H_5N) was prepared by the action of pyridine on tetracyanoethylene oxide (TCNEO)(1,2). Several other dicyano derivatives of nitrogen and sulphur ylids have also been obtained in this way (3-5). Although very good yields are obtainable by this method, the dicyanomethylids remain scarcely available products, since the whole synthesis from common compounds includes six steps (cyanoacetic ester $\xrightarrow{1}$ cyanoacetamide $\xrightarrow{2}$ malononitrile $\xrightarrow{3}$ dibromomalononitrile $\xrightarrow{4}$ tetracyanoethylene $\xrightarrow{5}$ TCNEO $\xrightarrow{6}$ ylid).

Several of our attempts to obtain I by the salt method (from bromomalononitrile and pyridine) have been unsuccessful. We have found that this ylid may be obtained, but in very low yield, by heating cyano-carbamyl-pyridinium-methylid (II) with an excess of $POCl_3$ in the presence of a little amount of sodium pyrosulphite. When acetic anhydride was used as dehydrating agent, instead of $POCl_3$, cyano-acetyl-pyridinium-methylid (III) was isolated in small yield. III was also obtained by acetylation of the ylid $Py^+\text{-}\bar{C}H\text{-}CN$, formed "in situ" from $Py^+\text{-}CH_2CN\ Cl^-$ and $N(C_2H_5)_3$.



I II III

$$Py^+\text{-}\bar{C}(CN)_2 \xleftarrow{POCl_3/Na_2S_2O_5} Py^+\text{-}\bar{C}(CN)(CONH_2) \xrightarrow{Ac_2O} Py^+\text{-}\bar{C}(CN)(COCH_3) \xleftarrow{\substack{1.N(C_2H_5)_3\\ 2.Ac_2O/Py}} Py^+CH_2CN\ Cl^-$$

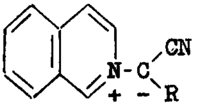
It was surprising to find out that the ylid I easily results from cyano-carbalkoxy-pyridinium-methylids (IV) by treatment with bromocyanoacetic ester:

$$Py^+\text{-}\bar{C}(CN)COOR + BrCH(CN)COOR \longrightarrow I$$

$$IV \quad R = CH_3,\ C_2H_5$$

When, one mole (or more) of bromocyanoacetic ester is added to an acetonitrile solution of IV, an exothermic reaction occurs and after a short time yellow crystals of I appear in the reaction mixture. The yields are moderate, but always higher than 25%. Other products of the reaction have not been identified and it seems that bromomalonic ester is not present in the residue.

The mechanism of this reaction is not yet elucidated, but the intervention of solvent (CH_3CN) is, without doubt, decisive in this process, since in other tested solvents, like benzene or chloroform, the change does not occur and the initial ylid is finally recovered.



V

a. R = $COOC_2H_5$
b. R = CN

Dicyano-isoquinolinium-methylid (Vb)(3) was similarly prepared in a 25% yield from Va and ethyl bromocyanoacetate. This result suggests that the reaction might also be used for the synthesis of the corresponding dicyano derivatives of other nitrogen ylids and, perhaps, of sulphur ylids.

The above procedure implies quite common experimental conditions; the starting ylids, especially the cyano-carbethoxy-methylids, are easily obtainable from bromocyanoacetic ester and the nitrogen base (2 moles), so that the whole reaction sequence involves only three steps (cyanoacetic ester $\xrightarrow{1}$ bromocyanoacetic ester $\xrightarrow{2}$ cyano-carbalkoxy-methylid $\xrightarrow{3}$ dicyanomethylid). The ylids II, IV ($R = CH_3$) and Va have been obtained as new compounds, according to the procedure described for IV ($R = C_2H_5$)(6). The melting points (uncorr.) of all new ylids described in the present paper are the following: II, 159°C (decomp.)(from ethanol); III, 143-144°C (from $CHCl_3$-pet. ether); IV ($R = CH_3$), 142-143°C (from acetone-pet.ether); Va, 146-147°C (from $CHCl_3$-pet.ether).

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