Formation of Diazepinones from Pyrazolidinones and Dimethyl Acetylenedicarboxylate

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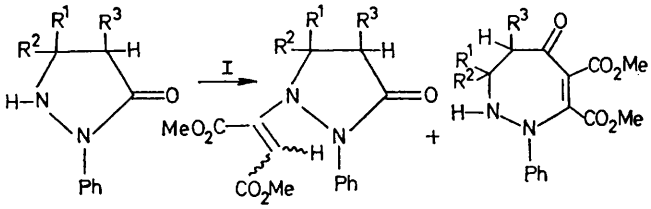
Summary The pyrazolidinones (IIa—c) react with dimethyl acetylenedicarboxylate (I) to give the tetrahydro-1,2-diazepin-5-ones (IVa—c) as well as the expected Michael addition products (IIIa—c).

THE varied reactions of dimethyl acetylenedicarboxylate (I) with heterocyclic compounds which give rise to new ring systems by the incorporation of one or two molecules of ester have been widely studied.[1] Recently indoles have

been reported to add the ester (I) to give benzazepines,[2] and pyrrole to react with it photochemically to give an azepine.[3] We have found that the ester (I) reacts with the 2-phenylpyrazolidin-3-ones (IIa—c) under conditions ranging from ether as solvent at room temperature to refluxing toluene, to give, besides the normal Michael addition[4] products (IIIa—c) (which have all the expected spectral properties), yellow crystals in *ca.* 40% yield, which were shown by elemental and mass spectral analysis to be 1:1 adducts of the pyrazolidinones and the ester. They are assigned structures (IVa), m.p. 162·5—163°; (IVb), m.p. 177·5—178·5°; and (IVc), m.p. 136—137·5°, on the bases of the following data.

All three compounds have two carbonyl bands in their i.r. spectra near 1750 and 1650 cm^{-1}. Their ^1H n.m.r. spectra are consistent with the structures, the most informative band being one corresponding to a single proton which is easily exchanged with D_2O, and the multiplicity of which varies with the substitution on C-5 of the parent pyrazolidinone: singlet for (IVa); doublet for (IVb); broad multiplet for (IVc). The significant resonances in their ^{13}C n.m.r. spectra occur near 194 p.p.m. (downfield from Me_4Si) which points to the presence of an $\alpha\beta$-unsaturated carbonyl group, and near 114 p.p.m. which indicates an olefinic carbon β to nitrogen and α to a carbonyl group.[5]

The compounds exhibit a lack of normal basicity. They do not dissolve in aqueous acid, and are recovered unchanged from such treatment. While models show the secondary nitrogen to be quite hindered, the unusual inertness to acid of a system which has an alkylhydrazine structure, as well



(II) (III) (IV)

a; $R^1 = R^2 = Me$; $R^3 = H$
b; $R^1 = Me$; $R^2 = R^3 = H$
c; $R^3 = Me$; $R^1 = R^2 = H$

as the novel insertion of the acetylenic ester into a non-aromatic five-membered ring led us to seek further confirmation of the structure through *X*-ray crystallography. Compound (IVa) crystallizes in the monoclinic space group $P2_1/n$, $a = 12·25$, $b = 22·51$, $c = 6·196$ Å, $\beta = 99·61°$. The solution of the structure (preliminary $R = 0·117$ for C, N, O atoms only) indeed shows the compound to be the diazepinone (IVa).

We thank Professor P. Yates and Dr. D. N. Reinhoudt for helpful discussions. National Science Foundation assistance in the purchase of a Syntex four-circle automated diffractometer is gratefully acknowledged.

(*Received, 7th January* 1974; *Com.* 007.)

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