

Some 1,3-Dipolar Addition Reactions of Isoquinolinium Ylides: Formation of 2,3-Dihydrobenzo[g]indolizines and Benzoindolizines

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Summary Isoquinolinium ylides react with dimethyl acetylenedicarboxylate to yield 2,3-dihydrobenzo[g]indolizines and the corresponding benzo[g]indolizines, whilst with methyl propiolate only the latter are obtained.

HETEROCYCLIC ylides of type (I) react with various activated acetylenes to give indolizines,¹ but in no case has the

acetylenedicarboxylate we have isolated 2,3-dihydrobenzo[g]indolizines (IIIa—d)† in addition to the expected benzo[g]indolizines (IVa—d).† The intermediate 3,10b-dihydrobenzo[g]indolizines (II) have not been obtained. The structures of (IIIa—d) are supported by the u.v. spectra which indicate a conjugated system and exclude structures of type (II). The n.m.r. spectra of (IIIb—d) show a one-proton singlet between 3.94 and 4.80 p.p.m., attributed to H². In (IIIa), H² and H³ are seen as doublets at 4.42 and 5.30 p.p.m. respectively and the coupling constant (*J* 13 Hz) suggests a *cis*-configuration. Further evidence for structures (IIIa—d) rests on chemical conversion into the corresponding indolizines; *e.g.*, oxidation (KMnO₄) of (IIIa) produces (IVa).

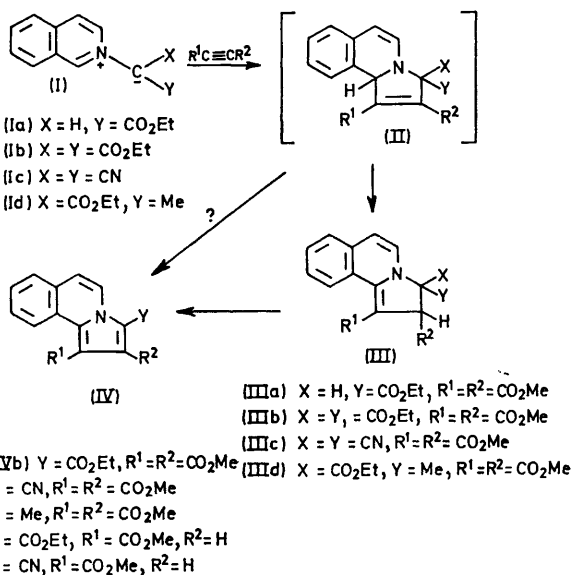
Reaction of dimethyl acetylenedicarboxylate with isoquinoline dicyanomethylide (Ic) gives the benzo[g]indolizine (IVc) and a second product, to which Linn and Webster³ assigned an iminoquinolizine structure. We have now shown this to be (IIIc), as its u.v. spectrum closely resembles that of the related diethoxycarbonyl compound (IIIb), and on treatment with sodium ethoxide it loses HCN to yield (IVc).

Ylides (Ia—c) react with methyl propiolate to give the expected indolizines (IVe) and (IVf), but no dihydroindolizines can be isolated. Structures (IVe) and (IVf) are assigned on the basis of their n.m.r. spectra, which show low-field multiplets (7.71—7.95 p.p.m.) for H¹⁰, owing to the deshielding effect of the ester group at C¹.

Further work on these adducts will be discussed in greater detail in a full paper.

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intermediate dihydroindolizine been isolated. Our own experiments with pyridinium ylides² give similar results, but with isoquinolinium ylides (Ia—d) and dimethyl

† All new compounds give satisfactory elemental analyses.

¹ T. Sasaki, K. Kanamatsu, Y. Yutimoto, and S. Ochiai, *J. Org. Chem.*, 1971, **36**, 813; T. Sasaki, K. Kanamatsu, and Y. Yutimoto, *J. Chem. Soc. (C)* 1970, 481; I. Zugravescu, E. Rucinschi, and G. Surpateanu, *Tetrahedron Letters*, 1970, 941.

² N. Basketter and A. O. Plunkett, unpublished results.

³ W. J. Linn, O. W. Webster and R. E. Benson, *J. Amer. Chem. Soc.*, 1965, **87**, 3651; V. Boekelheide and N. A. Fedoruk, *J. Amer. Chem. Soc.*, 1968, **90**, 3830.