Reactions of Isoquinolium Ylides. Some Anomalous Products from Acetylenes and Olefins

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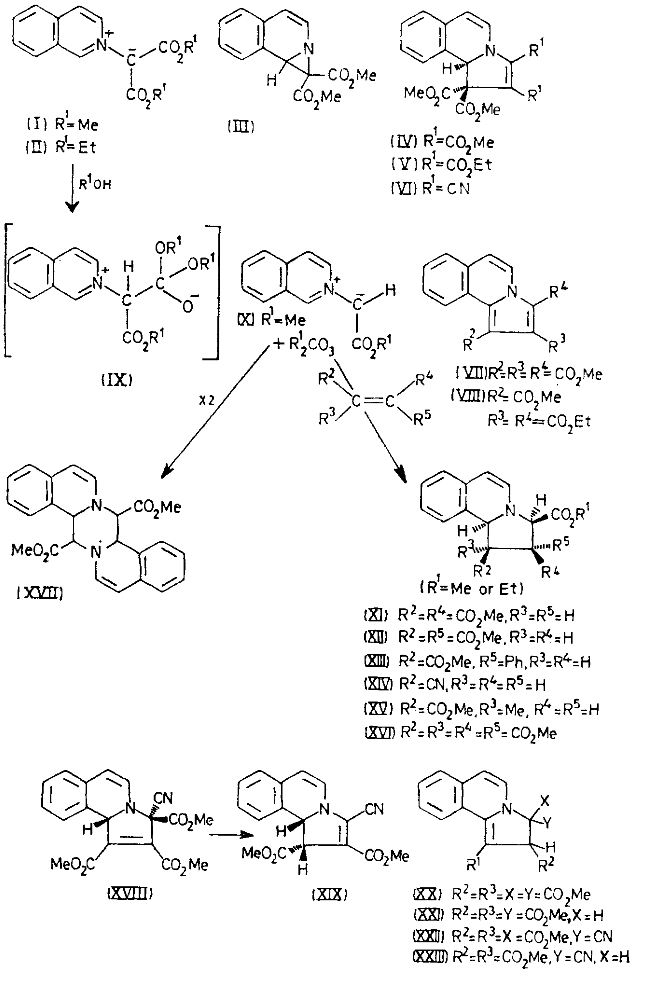
Summary Isoquinolinium dialkoxycarbonyl ylides (I) and (II) and dimethyl acetylenedicarboxylate react in methanol to give the 1,10b-dihydropyrrolo[2,1-*a*]isoquinolines (IV) and (V); (I) and (II) in methanol alone yield the more reactive monoalkoxycarbonyl ylides (X) and dialkyl carbonate, the former dimerises to (XVII) or reacts *in situ* with olefins to yield 1,2,3,10b-tetrahydropyrrolo[2,1-*a*]isoquinolines.

Isoquinolinium dialkoxycarbonylmethylides react with activated acetylenes in acetonitrile to give 3,10b- and 2,3-dihydropyrrolo[2,1-*a*]isoquinolines.[1] However, we find that the reaction of (I) and dimethyl acetylenedicarboxylate takes a very different course in methanol, yielding the 1,10b-dihydropyrrolo[2,1-*a*]isoquinoline 1,1,2,3-tetra-ester (IV) and a little of the pyrrolo[2,1-*a*]isoquinoline (VII). Chromatography of the crude reaction mixture gave (VII) and then (IV) (yellow prisms, m.p. 134—135 °C, $C_{20}H_{19}NO_8$; *m/e* 401 (22%), 370 (12), 342 (26), and 310 (100); λ_{max} 249 (14,100), 314 (5860) and 370 (12,710) nm; δ 7·0—7·5 (m, 7—10-H), 6·53 (d, 5-H, $J_{5,6}$ 8 Hz), 5·74 (d, 6-H, $J_{5,6}$ 8 Hz), 5·87 (s, 10b-H), and 3·97, 3·88, 3·73, and 3·55 (each 3H, s).



Structure (IV) is assigned on the basis of its u.v. and n.m.r. spectra which closely resemble those of other 1,10b-dihydropyrrolo[2,1-*a*]isoquinolines,[2] but differ markedly from that of the expected 2,3-dihydro-compound (XX).[3]

The formation of (IV) is analogous to that of the dicyano-compound (VI), obtained as a minor product from (I) and dicyanoacetylene,[4] and may involve the aziridine intermediate (III). Alternative mechanisms involving a shift of one methyl ester group can be excluded, as in (V), formed from (I) and diethyl acetylenedicarboxylate, both methyl ester groups are at C-1. This is deduced from its pyrolysis to (VIII) and methyl formate; the alternative products are not formed. Similarly in the mass spectrum of (V), the major fragmentation pathway involves aromatisation by loss of methyl formate. The n.m.r. spectra of both (IV) and (V) show a high field methyl ester (δ *ca.* 3·55), attributable to the shielding of the *endo* C-1 ester by the benzo ring.

We have also investigated the reactions of isoquinolinium ylides (I), (II), and (X) with olefins and report the formation of 1,2,3,10b-tetrahydropyrrolo[2,1-*a*]isoquinolines; similar adducts have also been obtained from enamines.[5] The alkoxycarbonylmethylides[6]† (X) react smoothly in methanol with a variety of olefins to yield the primary adducts (XI)—(XVI), R = Me, 34—81%). The same products (XI)—(XVI) were surprisingly obtained from the dialkoxycarbonylmethylides (I) and (II) and the corresponding olefin in comparable yield (41—83%). As dialkyl carbonate was also isolated, the reaction clearly involves *in situ* generation of the more reactive ylide (X) *via* the intermediate (IX); the formation of carbonates has also been reported to occur from the reaction of ylides and phenols.[7] In the absence of a dipolarophile, (I) in methanol gave the dimer (XVII) and dimethyl carbonate, whereas in boiling methyl cyanide (I) remains unchanged. (XVII) was also obtained directly from (X) (R^1 = Me). This novel elimination of an ester group was also observed to occur from 3,10b-[8] and 2,3-dihydropyrrolo[2,1-*a*]isoquinolines.[1,8] On treatment with sodium methoxide in methanol, (XVIII) gave the 1,10b-dihydro compound (XIX), whilst (XX) and (XXII) gave (XXI) and (XXIII) respectively.

The tetrahydropyrrolo[2,1-*a*]isoquinolines (XI)—(XVI) show the expected 1,2-dihydroisoquinoline type u.v. spectrum.[9] The geometry of the olefin is retained in the adducts, methyl maleate and fumarate giving the isomeric pair (XI) and (XII). The *endo* configuration of the C-1 ester group in adducts (XI)-(XIII), (XV), and (XVI) is

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† Generated *in situ* by the salt method (ref. 6).

deduced from their n.m.r. spectra, which show an abnormally high field C-1 methyl (or ethyl) ester resonance owing to shielding by the benzo ring. This signal is absent in the spectrum of (XIV).[1]

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