Reaction of Pyridinium Dicyanomethylide with Diphenylcyclopropenone and Diphenylcyclopropenethione

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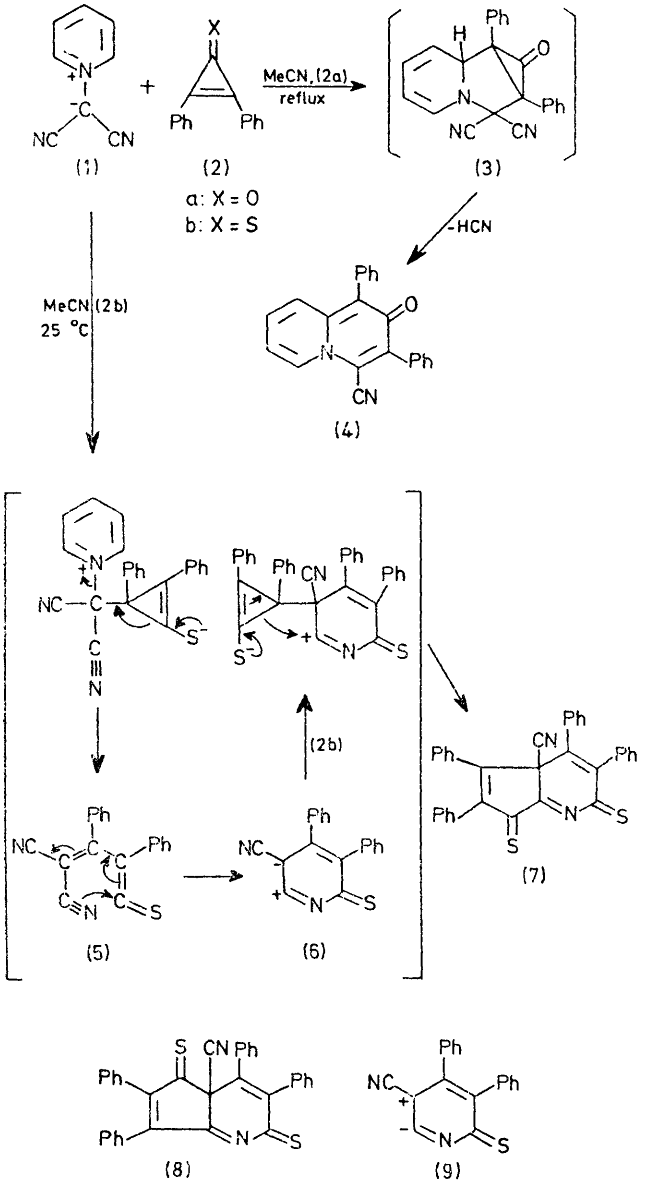
Summary Pyridinium dicyanomethylide (**1**) undergoes 1,3-dipolar cycloaddition to diphenylcyclopropenone producing the 2*H*-quinolizin-2-one (**4**), while, with diphenylcyclopropenethione, (**1**) reacts as a nucleophile to afford the indenopyridine-2-thione derivative (**7**).

Pyridinium *N*-methylides and iminopyridinium *N*-ylides react, in general, as nucleophiles with diphenylcyclopropenone and diphenylcyclopropenethione to give the 2-pyrone and 1,3-oxazine derivatives, respectively.[1,2] However, the first example of a possible 1,3-dipolar addition of iminopyridinium ylide to methylphenylcyclopropenone has been reported recently.[3] Moreover, the reaction of a pyridinium *N*-disubstituted methylide with cyclopropenone in which the usual cyclization to the 2-pyrone system is impossible, has not been reported.



Scheme

In the course of our studies on indolizine syntheses,[4] we have independently found an analogous 1,3-dipolar cycloaddition of pyridinium dicyanomethylide (**1**) to diphenylcyclopropenone (**2a**); refluxing of (**1**) with an equimolar amount of (**2a**) in acetonitrile produces, with elimination of hydrogen cyanide, the 2*H*-quinolizin-2-one (**4**)† [dark green prisms; 58%; m.p. 160—162 °C; ν_{max} 2210 (C≡N) and 1660 (C=O) cm^{-1}, λ_{max} (EtOH) 604 (log ε 4·03), 408sh (3·80), 298sh (4·23), and 234 (4·34); *m/e* 322 (M^+), 294 (M^+—CO), and 267 (M^+—CO—HCN), ^{1}H n.m.r. spectrum shows only aromatic protons].‡ No intermediate leading to (**4**) was isolated under these conditions (see ref. 3).

In contrast to its reaction with (**2a**), (**1**) reacts smoothly at room temperature with diphenylcyclopropenethione (**2b**) to give the indenopyridine-2-thione derivative (**7**)† [yellow crystals; 70%; m.p. 164—166 °C; *m/e* 508 (M^+), 476 (M^+—S or oxidation to diketone analogue), 444 (M^+—N≡C–C–C≡N), 431 (M^+—Ph), 286 (M^+—Ph_2C_3S), and 222 (Ph_2C_3S); ν_{max} 2230 (C≡N), 1560, 1165 and 1315 (S=C–N=) cm^{-1}; λ_{max} (EtOH) 394 (log ε 4·59), 317 (4·37), and 263 (4·56) nm; ^{1}H n.m.r. spectrum shows only aromatic protons]. Compound (**7**) is stable as a solid but unstable in solution. Apparently, (**1**) reacts as a nucleophile and another molecule of (**2b**) is involved in the subsequent step (Scheme). This is supported by the fact that the reaction of either isoquinolinium, 4-methylpyridinium, or dimethylsulphonium[5] dicyanomethylide with (**2b**) produces (**7**). At present, assignment of structure (**7**) is mainly based on mechanistic considerations[1,6,7] which do not favour the alternative structure (**8**).§ Initial nucleophilic attack of (**1**) on the carbon–carbon double bond of (**2b**), followed by rearrangement, leads to the thioketen intermediate (**5**)[6] which undergoes an electrocyclic reaction to form the dipolar intermediate (**6**) with the positive charge stabilized as an azabenzyne. The intermediate (**6**) reacts as a nucleophile with (**2b**) and the subsequent rearrangement gives (**7**). The alternative dipolar form (**9**) is unlikely since it has a positive charge next to a cyano group. A concerted attack of (**2b**) on (**5**) would be also possible. Attempts to quench the intermediate (**5**) or (**6**) with methanol were unsuccessful (*cf.* ref. 6).

Thus, this is the first reported case in which (**2a**) and (**2b**) behave in a different manner towards a pyridinium ylide. A chemical difference between (**2a**) and (**2b**) has also been observed in the reaction with tetracyanoethylene oxide.[7]

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† Satisfactory analytical data were obtained for this compound.

‡ No appreciable reaction occurs at room temperature. Since the reaction of either isoquinolinium or 4-methylpyridinium dicyanomethylide with (2a) results in the formation of a complex mixture of products, an example of a 1,3-dipolar addition of pyridinium ylide to cyclopropenone may still be an exceptional case.

§ We are indebted to the referees for this discussion.

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