Reaction of a Nitrile Ylide with Functional Methylenecyclopropenes. A New Synthesis of Substituted Pyridines

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Summary The nitrile ylide (**1**) adds to the cyclic double bond of functional methylenecyclopropenes to give a pyridine; this reaction probably implies the formation of a methylenecyclopropane which has been isolated in one case.

THE addition of the nitrile ylide (**1**), prepared according to Huisgen *et al.*[1] in benzene solution, to the methylenecyclopropenes (**2a**)—(**2e**) leads with quantitative yields to the pyridines (**4**) [in the tautomeric form (**4′**) except for (**4a**)]. The bicyclic methylenecyclopropane (**3**) isolated in one case, is thought to be an intermediate of the reaction.

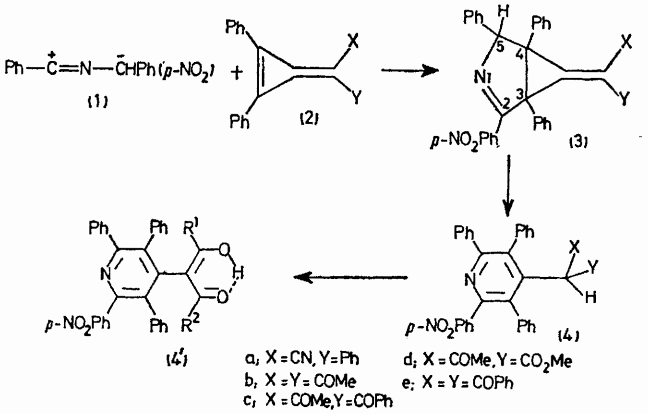
The synthesis of compounds (**2a**),[2] (**2b**), and (**2c**)[3] is described in the literature. Olefins (**2d**) and (**2e**) have been prepared according to the method described by Eicher *et al.*[3] in 70 and 80% yield respectively. The i.r. and n.m.r. spectra are in agreement with the assigned structure (particularly a strong absorption at 1825—1830 cm^{-1} due to the cyclopropene ring).

TABLE

			%		δ ($CDCl_3$)	
	R^1	R^2	yield[b]	m.p./°C	OH	R^1 or R^2
(**4′b**)	Me	Me	64	177	16·85	1·80
(**4′c**)	Me	Ph	64	160	17·76	2·80
(**4′d**)[c]	Me	OMe	65	214	12·62	3·60; 1·56
(**4′e**)	Ph	Ph	71	226	18·60	—

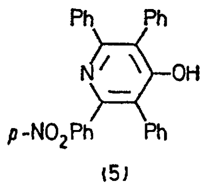
[a] Satisfactory microanalyses were obtained for all compounds. [b] Yield of pure recrystallised sample. [c] I.r. (Nujol) 1648 cm^{-1}, chelated ester carbonyl.

The pyridine (**4a**) formed has m.p. = 197 °C, n.m.r. ($CDCl_3$) δ 5·44 (1H s); m.s., 543 (M^+), 513 (M^+ − NO), 496 (M^+ − NO_2), 425 (M^+ − CH(Ph)CN). Data for the pyridines (**4′b**)—(**4′e**) is shown in the Table.



The bicyclic compound (**3**) is isolated only in the case of (**3a**). After 10 h reflux in benzene, the reaction between (**1**) and (**2a**) is quantitative and leads to a (**1** : **1**) mixture of (**3a**) and (**4a**) which may be separated. The ratio (**3a**) : (**4a**) decreases when heating is maintained more than 10 h. In boiling benzene (10 h) (**3a**) gives a quantitative yield of (**4a**). The same result is obtained at 220 °C during 1 min.

The spectroscopic data for (**3a**) are in agreement with the proposed structure,† i.r. (Nujol) $\nu_{\equiv CN}$ 2210 cm^{-1} [lacking in the spectrum of (**4a**)], ^{1}H n.m.r. (δ, $CDCl_3$) 6·60 (1H, s), ^{13}C n.m.r. (δ, $CDCl_3$) 55·0 and 56·8 (bridgehead carbon atoms), 83·2 (tertiary carbon atom split by one H). The ^{13}C spectrum of (**4a**) exhibits only one signal (38·0 p.p.m.) due to an sp^3 carbon. In the m.s. of (**3a**) the ion (M^+ − CH(Ph)CN) does not appear.



(5)

This reaction gives a new route to substituted pyridines. We have now shown that the method can also be used for nitrile ylides resulting from the photochemical cleavage of 1-azirines.

The results are also of interest as reactions of 1,3-dipoles with methylenecyclopropenes and cyclopropenones. Previous reports on these reactions have dealt essentially with azomethine ylides[4] and diazoalkanes.[5] With these dipoles the formation of the primary addition product (usually on the cyclic double bond) is postulated, but this product, which rearranges in a complex way, has never been isolated. The reaction between the nitrile ylide (**1**) and (**2a**) allows us to isolate the primary cycloaddition compound and to check its thermal rearrangement to pyridine (probably 1,5 sigmatropic rearrangement(s) with the possibility of prototropy).

Diphenylcyclopropenone also reacts with (**1**) and leads directly with a good yield to the 4-hydroxypyridine (**5**) (or to the tautomeric 4-pyridone), [m.p. 297 °C, i.r. (Nujol) 3230 cm^{-1} (OH or NH), m.s. 444 (M^+), 427 (M^+ − OH), 414 (M^+ − NO), 398 (M^+ − NO_2)].

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† The stereochemistry of C(5) in (**3a**) is not established.

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