Synthesis of a 3*H*-Pyrido[1,2-*b*]pyridazin-3-one from Pyridine *N*-Imide and Methylphenylcyclopropenone

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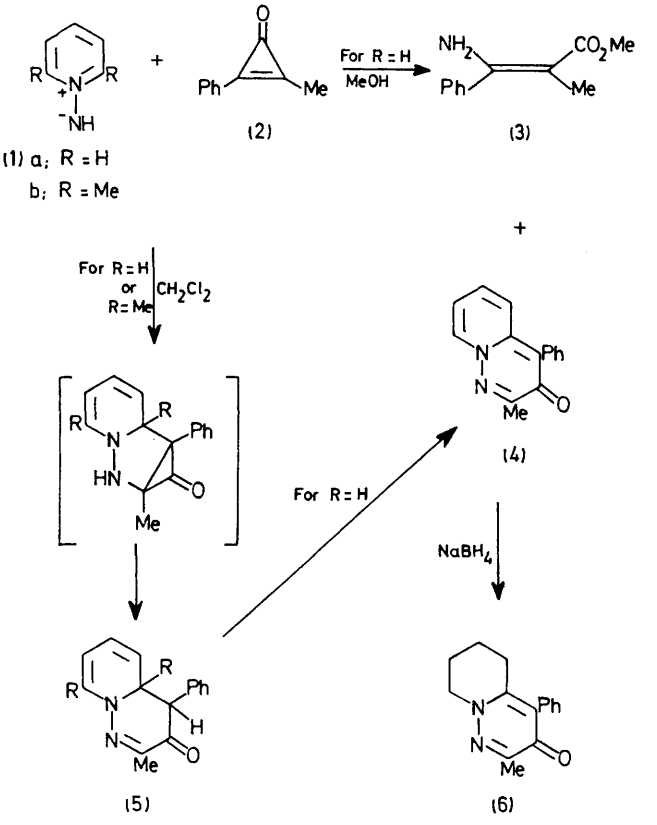
Summary Pyridine *N*-imide (**1a**) reacts with methylphenylcyclopropenone (**2**) in methanol to give a β-aminoester (**3**) and the first reported 3*H*-pyrido[1,2-*b*]pyridazin-3-one (**4**); reaction in dichloromethane permitted isolation of the intermediate (**5a**).

PYRIDINE *N*-IMIDE (**1a**) has been shown[1] to react as a nucleophile with diphenylcyclopropenone in methanol to produce methyl α-phenyl-β-amino-*trans*-cinnamate in high yield. In the course of investigating the mode of ring opening of the unsymmetrical methylphenylcyclopropenone[2] (**2**) in methanol, we have observed the formation of both the β-amino-ester (**3**) (31%, oil, unstable with respect to hydrolysis to the β-ketoester) and the 3*H*-pyrido[1,2-*b*]pyridazin-3-one (**4**) (67%, m.p. 201—203 °C). When the reaction was carried out in dichloromethane for 17 h, an intermediate (**5a**) (69%) was isolated in addition to (**4**) (27%). On standing, (**5a**) was readily oxidized to (**4**). This intermediate was also observed in methanol during shorter reaction times. Evidence for the isomer with a phenyl group in the 4-position was obtained from the n.m.r. spectrum of (**5a**), δ 3·75 (1H, d, H-4). Reaction of (**1b**) with (**2**) afforded (**5b**) (19%) the n.m.r. spectrum of which showed a singlet (1H) at δ 3·40, thus confirming the assignment. Treatment of (**4**) with an excess of sodium borohydride in ethanol produced (**6**) (61%, m.p. 164—166 °C).

This reaction of (**2**) apparently involves participation of (**1a**) not only as a nucleophile, as in the case of diphenylcyclopropenone, but also as a 1,3-dipolar compound. This result may also be contrasted with those obtained previously in the reactions of diphenylcyclopropenone with pyridine *N*-(acylimides).[3] In these cases, reaction led exclusively to formation of 2,4,5-trisubstituted-6*H*-1,3-oxazin-6-ones by a pathway involving initial nucleophilic attack of the imide on the cyclopropenone ring followed by elimination of pyridine. Thus, the present report represents the first example of a possible 1,3-dipolar addition of a pyridine *N*-imide to a cyclopropenone, further illustrating the effect of substituents on the reactivity of the cyclopropenone ring.[4]



The authors acknowledge financial assistance of Financiadora de Estudos e Projetos.

(*Received*, 19*th December* 1975; *Com.* 1403.)

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[4] For a recent review of cyclopropenone chemistry, see K. T. Potts and J. S. Baum, *Chem. Rev.*, 1974, **74**, 189.