

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

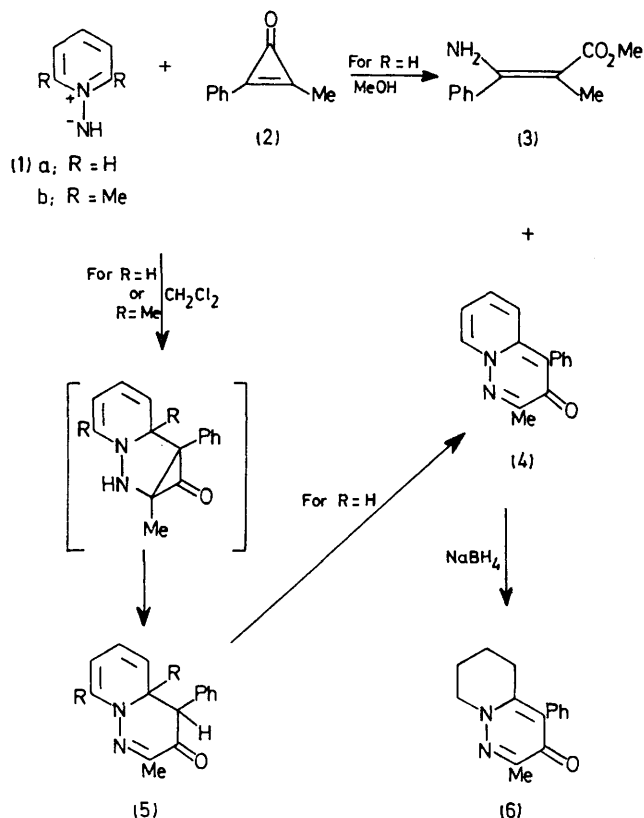
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**Summary** Pyridine *N*-imide (**1a**) reacts with methylphenylcyclopropenone (**2**) in methanol to give a  $\beta$ -aminoester (**3**) and the first reported 3*H*-pyrido[1,2-*b*]pyridazin-3-one (**4**); reaction in dichloromethane permitted isolation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

PYRIDINE *N*-IMIDE (**1a**) has been shown<sup>1</sup> to react as a nucleophile with diphenylcyclopropenone in methanol to produce methyl  $\alpha$ -phenyl- $\beta$ -amino-*trans*-cinnamate in high yield. In the course of investigating the mode of ring opening of the unsymmetrical methylphenylcyclopropenone<sup>2</sup> (**2**) in methanol, we have observed the formation of both the  $\beta$ -amino-ester (**3**) (31%, oil, unstable with respect to hydrolysis to the  $\beta$ -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**),  $\delta$  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  $\delta$  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).<sup>3</sup> 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.<sup>4</sup>

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<sup>3</sup> T. Sasaki, K. Kanematsu, and A. Kakehi, *J. Org. Chem.*, 1971, **36**, 2451; J. W. Lown and K. Matsumoto, *Canad. J. Chem.*, 1972, **50**, 584.

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