

## The Reaction of Ketens with Imines in Methanol

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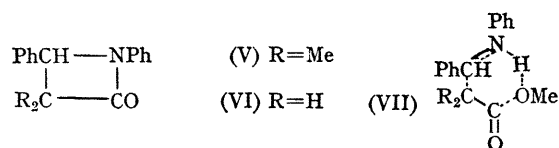
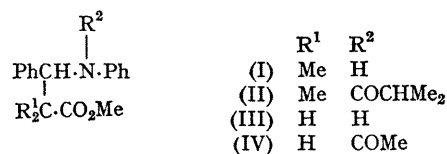
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**Summary** Benzylideneaniline reacts with dimethylketen in methanol to give (I) and a small amount of (II).

7.77 (1H, sept.), 8.98 (3H, d), 9.12 (3H, d),  $\nu_{\max}$  (KBr disc) 1725, 1664  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  (EtOH) 259, 264, nm. ( $\log \epsilon$  2.66,

The cycloaddition reaction of ketens with imines has recently been shown to proceed *via* zwitterionic intermediates.<sup>1</sup> One technique used in the investigation has been to trap the zwitterions by quenching a partly completed reaction with methanol or water. We have examined the reaction of ketens with imines using methanol as the solvent and in these circumstances a totally different reaction is observed.

Treatment of a methanolic solution of benzylideneaniline with dimethylketen gave two products, identified as (I) (51%), m.p. 121°,  $\tau$  ( $\text{CDCl}_3$ ) 2.6—3.7 (10H, m), 5.22 (1H, broad signal), 5.51 (1H, s), 6.40 (3H, s), 8.75 (3H, s), 8.85 (3H, s),  $\nu_{\max}$  ( $\text{CHCl}_3$ ) 3425, (KBr disc) 1717  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  (EtOH) 247, 296 nm. ( $\log \epsilon$  4.16, 3.29), and (II) (5%), m.p. 107°,  $\tau$  ( $\text{CDCl}_3$ ) 2.5—3.7 (10H, m), 3.88 (1H, s), 6.35 (3H, s),



2.54). The latter is a minor product clearly arising by acylation of the former by an excess of dimethylketen. A

similar reaction of keten with methanolic benzylidene-aniline at 0° gives (III) and (IV).

The mild conditions of the reaction preclude the intermediate formation and solvolysis of the  $\beta$ -lactams. In the reaction of dimethylketen, (V) cannot be detected in the reaction mixture by t.l.c., and it seems unlikely that the keten cycloadduct (VI) would be formed.<sup>2</sup> Formation of

(I) and (III) could plausibly be explained by a cyclic process involving a transition state like (VII), reaction occurring between a molecule of the keten and a hydrogen-bonded methanol-imine complex. Similar cyclic processes have been shown to occur in the reaction of ketens with alcohols,<sup>3</sup> amines,<sup>4</sup> and carboxylic acids.<sup>5</sup>

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<sup>2</sup> H. Staudinger, *Ber.*, 1917, **50**, 1035.

<sup>3</sup> A. Tille and H. Pracejus, *Chem. Ber.*, 1967, **100**, 196; P. J. Lillford and D. P. N. Satchell, *J. Chem. Soc. (B)*, 1968, 889.

<sup>4</sup> P. J. Lillford and D. P. N. Satchell, *J. Chem. Soc. (B)*, 1968, 54.

<sup>5</sup> J. M. Briody, P. J. Lillford, and D. P. N. Satchell, *J. Chem. Soc. (B)*, 1968, 885.