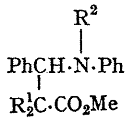
The Reaction of Ketens with Imines in Methanol

By S. A. PROCTER
(*Dept. of Pure and Applied Science, Doncaster College of Technology*)
and P. D. ENGLISH and G. A. TAYLOR*
(*Dept. of Chemistry, University of Sheffield* S3 7HF)

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

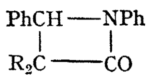
THE cycloaddition reaction of ketens with imines has recently been shown to proceed *via* zwitterionic intermediates.[1] One technique used in the investigation has been to trap the zwitterions by quenching a partly completed reaction with methanol or water. We have examined the reaction of ketens with 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°, τ ($CDCl_3$) 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), ν_{max} ($CHCl_3$) 3425, (KBr disc) 1717 cm.$^{-1}$, λ_{max} (EtOH) 247, 296 nm. (log ε 4·16, 3·29), and (II) (5%), m.p. 107°, τ ($CDCl_3$) 2·5—3·7 (10H, m), 3·88 (1H, s), 6·35 (3H, s), 7·77 (1H, sept.), 8·98 (3H, d), 9·12 (3H, d), ν_{max} (KBr disc) 1725, 1664 cm.$^{-1}$, λ_{max} (EtOH) 259, 264, nm. (log ε 2·66, 2·54). The latter is a minor product clearly arising by acylation of the former by an excess of dimethylketen. A



$$\begin{array}{c} R^2 \\ | \\ PhCH{\cdot}N{\cdot}Ph \\ | \\ R^1_2C{\cdot}CO_2Me \end{array}$$

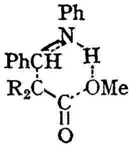
	R^1	R^2
(I)	Me	H
(II)	Me	$COCHMe_2$
(III)	H	H
(IV)	H	COMe



(V) R=Me

(VI) R=H

(VII)



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

The mild conditions of the reaction preclude the intermediate formation and solvolysis of the β-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.[2] 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,[3] amines,[4] and carboxylic acids.[5]

(*Received, June 23rd*, 1969; *Com.* 901.)

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