Cycloaddition of an Aziridine to Ketens

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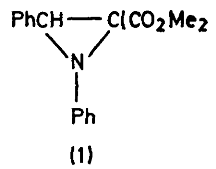
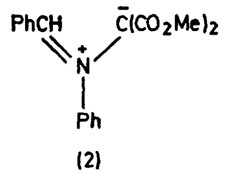
Summary The azomethine ylide arising from the cleavage of dimethyl 1,3-diphenylaziridine-2,2-dicarboxylate adds preferentially to the C=O bond of ketens to give 5-methyleneoxazolidines with two ester groups on C(4).

The reactions of 1,3-dipoles and heteromultiple bonds have been studied,[1,2] but to our knowledge the addition of an azomethine ylide to ketens has not been reported.

Previously[3–5] we have studied the azomethine ylide (**2**) resulting from the thermal cleavage of aziridine (**1**). Addition of this dipole to diphenylketen in boiling toluene gives the oxazolidine (**3a**; R = Ph). and the isomeric pyrrolidone (**4**) in the ratio 80:20 (n.m.r. estimation). With keten itself only the oxazolidine (**3b**; R = H) is formed. The reaction takes place at 110—120°, gaseous keten being bubbled through the liquid aziridine.

In the presence of the azomethine ylide (**2**), the oxazolidine (**3a**) does not isomerize into pyrrolidone (**4**) under the reaction conditions and *vice versa*.


(1)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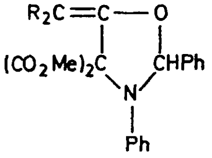
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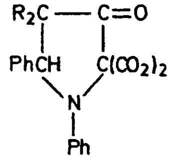
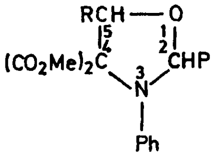

(4)

a; R = Ph
b; R = H

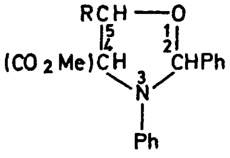
Spectroscopic data show that compound (**4**) is a pyrrolidone (n.m.r. spectra, absence of $\nu_{C=C}$ from i.r. spectra, and analogy of the u.v. spectra with those of *N*-phenylpyrrolidones). The possibility of an isomeric structure [opposite direction of the addition of (**2**) to the C=C bond] is not ruled out, and is being investigated. Nevertheless the proposed structure (**4**), seems to be more soundly based because we have already shown[3–5] that the carbon atom of the ylide (**2**) which is substituted by two ester groups is never bonded to the sp^2 carbon atom of a dipolarophile when this atom is disubstituted.

The structures of the oxazolidines (**3**) were confirmed chemically as follows.

(a) Catalytic reduction of (**3b**) (10% Pd/C; 1 atm) gives a quantitative yield of the two epimeric oxazolidines (**5b**) and (**5′b**) (ratio 75: 25). Additions of azomethine ylide (**2**) to acetaldehyde[4] gives the same oxazolidines (**5b**) and (**5′b**) (ratio 95:5), 60% yield after one week in boiling benzene [(**5b**): m.p. 122°; δ (CDCl$_3$) 6·24 (s, 2-H) 4·49 (q, *J* 6·4 Hz, 5-H) and 3·67 and 3·82 (2s, Me ester) p.p.m.; (**5′b**): δ (CDCl$_3$) 6·11 (s, H_2), 4·83 (q, *J* 7·4 Hz, 5-H), and 3·51 and 3·92 (2s, Me ester) p.p.m.].



(5) and (5′)



(6) and (6′)

a; R = Ph$_2$CH

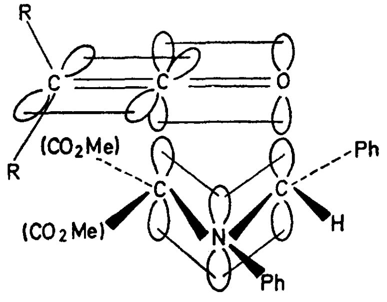
b; R = Me

(b) Ozonolysis of (**3a**) leads to benzophenone. Catalytic reduction of (**3a**) is not quantitative (Adams catalyst; 1 atm) but the resulting compound has the structure (**5a**) [δ (CDCl$_3$) 6·04 (s, 2-H), 5·39 (d, 5-H), 4·59 (d, H^A out of ring, $J_{5,A}$ 9·1 Hz) p.p.m.]. Addition of (**2**) to diphenylacetaldehyde affords the other epimer (**5′a**) [δ (CDCl$_3$) 6·15 (s, 2-H), 5·42 (d, 5-H), and 4·55 (d, H^A), $J_{5,A}$ 8·0 Hz) p.p.m.].

(c) After treatment with piperidine in refluxing benzene (**5b**) gives two epimeric oxazolidines (**6b**) and (**6′b**); (**5′a**) gives compound (**6a**) (only one epimer) [(**6b**): δ (CDCl$_3$) 6·02 (s, 2-H), 4·05 (d, 4-H); 3·76 (s, Me ester) p.p.m.; (**6′b**): (not separated from **6b**) δ (CDCl$_3$) 6·16 (s, 2-H), 3·66 (s, Me ester); the 4-H doublet appears with the 5-H signals of (**6b**) and (**6′b**) between 4·30 and 4·60 p.p.m.; (**6a**): m.p. 72–74°; δ (CDCl$_3$) 6·01 (s, 2-H), 5·17 dd, 5-H), 4·20 (d, 4-H and H^A), 3·51 (s, Me ester) p.p.m.].

These results show that during the addition to aldehydes and ketens, aziridine (**1**) undergoes cleavage of the C–C bond and not cleavage of the C–N bond as has been observed in some cases with other aziridines.[6,7]

In conclusion, the azomethine ylide prefer to react with the carbonyl group of ketens, and the orientation of the addition has been established. Addition to the C=C bond is observed only with a disubstituted keten. Structure A may explain this reactivity: a bulky R substituent hinders the approach of the π electron system of the carbonyl group and therefore addition to the olefinic bond becomes possible. Such an interaction has been postulated by Andrews and Day[8] to explain the orientation of the addition of diphenyldiazomethane to the γγ-dimethylallenic esters.



(A)

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