Reaction of Diphenylketen with N-Alkyl Nitrones

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Summary Diphenylketen reacts with the N-alkyl nitrones (3) to form β -lactams (4) and oxazolones (5).

The reaction of nitrones with cumulenes has been shown¹ to proceed with a rearrangement, leading to products other than the expected 1,3-dipolar adducts. Our own work2 with the reaction of diaryl nitrones with ketens has shown that the normal reaction pathway for these compounds involves initial formation of a zwitterion (1) followed by sigmatropic rearrangement to (2), one or more further steps leading to the observed products. We now report studies on the reaction of ketens with N-alkyl nitrones for which no similar reaction path is available.

Diphenylketen reacted with the N-methyl nitrone (3a) in benzene to give two products. One, C₂₈H₂₁NO, m.p. 201°, was identified as the β -lactam (4) by the i.r. spectrum and comparison with a synthetic specimen obtained by addition of diphenylketen to N-methylfluorenoneimine. The product presumably arises by deoxygenation of (3a) to the imine, which subsequently reacts with more diphenylketen. The second product, C₂₈H₂₁NO₂, m.p. 145°, has a molecular formula corresponding to a 1:1 adduct of keten and nitrone, and is assigned the structure (5) rather than that of the expected 1,3-dipolar adduct (6) on the basis of spectroscopic data and degradative evidence. Reduction of the adduct with lithium aluminium hydride gave a dihydroderivative (7), m.p. 177°, containing a methyl group, a methine group, and a hydroxy-group, which decomposed during chromatography on silica gel to give fluorenone in almost quantitative yield. Treatment of the adduct with benzylamine in methanol gave, amongst other products, a compound with properties similar to those of 2-methylamino-2,2-diphenylacetic acid, which was reduced by lithium aluminium hydride to the amino-alcohol (8) and identified by comparison with a synthetic specimen.

On boiling a solution of the adduct (5) in benzene, a dark green colour developed, whereas boiling the adduct in benzene in the presence of dimethyl acetylenedicarboxylate leads to formation of a compound C₃₃H₂₇NO₄, m.p. 196°, with spectroscopic properties consistent with the structure (9). We believe the green colour is due to formation of a stable ylide (10) formed by loss of carbon dioxide from (5).

Reaction of diphenylketen with the N-ethyl and N-isopropyl nitrones (3b,c) gave products similar to (4) and (5). The mechanism of formation of (5) is not clear, although it can be rationalised in terms of the mechanism suggested by Cum¹ for the reaction of allenes and nitrones.

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PhCH=N (1) (2) Ph (3) (4) (a) R = Me (b) R = Et (c) R = Pri (5) (6) Ph2CCH2OH MeNH (7) (8) Ph CO,Me CO,Me (9) (10) (11)

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