

Cycloaddition of 2-Phenylbenzazete to Diphenylketen

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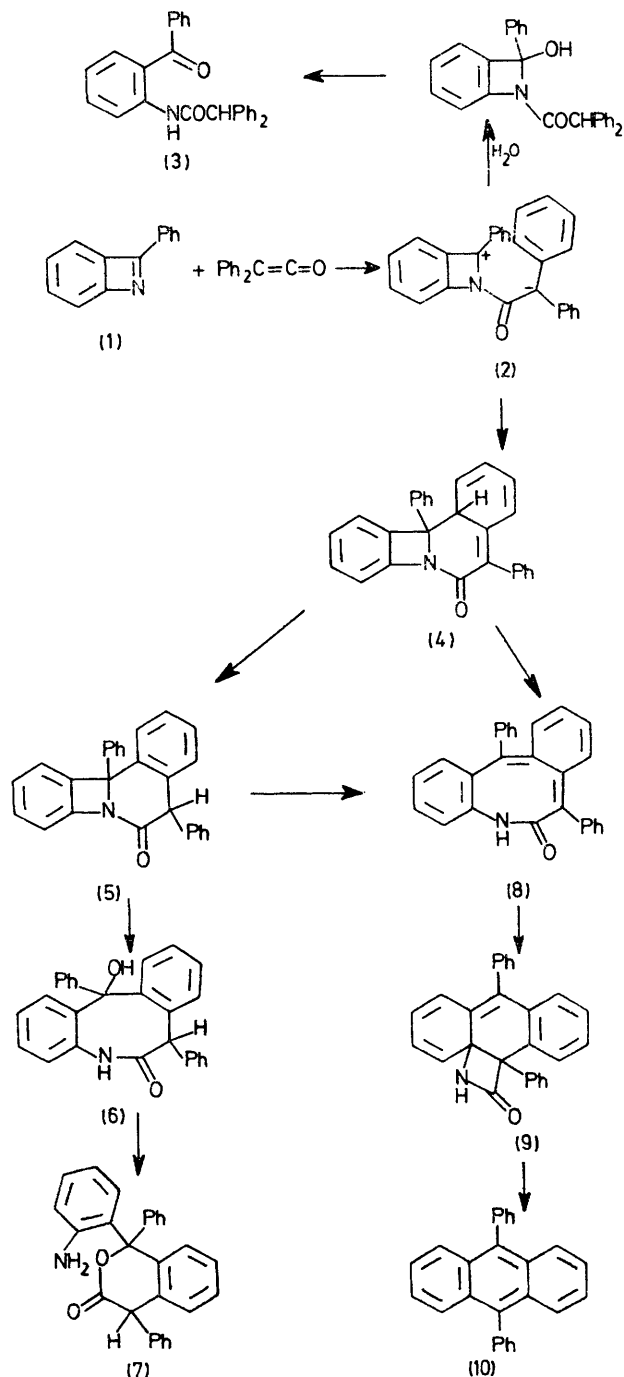
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Summary Formation of 9,10-diphenylanthracene and the benzazetine (5) from 2-phenylbenzazete (1) and diphenylketen involves a stepwise 2+4 cycloaddition in which the keten acts formally as a diene; the benzazetine (5) gives diphenylanthracene at high temperature.

IMINES have been observed to give 1:1 (β -lactam) and 1:2 adducts with ketens.¹ We now report that the highly reactive imine, 2-phenylbenzazete, reacts with diphenylketen to give a new type of 1:1 adduct.

The pyrolysate from 4-phenylbenzotriazine contains 2-phenylbenzazete (1) as the main component, the azete

being stable at -80°C .² Addition of diphenylketen in cold ether (*ca.* -20°C) to the pyrolysate followed by warming



to room temperature gave, on chromatographic work up, the 1:1 adduct (5) (30%), m.p. $228\text{--}230^{\circ}\text{C}$.[†] Evidence for the structure of this adduct is the carbonyl absorption at 1685 cm^{-1} and the absence of any N-H absorption in the i.r. spectrum, the presence only of benzenoid absorption in the u.v. spectrum, and the appearance of the methine proton at $\delta\ 5.01$ in the n.m.r. spectrum; that this absorption is a sharp singlet suggests that the compound isolated is one stereoisomeric form of (5). Chemical evidence comes from the pyrolysis described later. Moreover, attempted hydrolysis with hydrochloric acid in chloroform gave an equimolar mixture of the two diastereoisomeric lactones (7). Hydrolytic cleavage of the strained azetidine ring to give the amido-alcohol (6) is to be expected and (7) would then result from transacylation.

When the addition of diphenylketen to the azete was carried out in HCl-free dichloromethane in place of ether, the adduct (5) was again formed but in slightly lower yield. However, 9,10-diphenylanthracene (10) (*ca.* 5%) was now observed as a new product. Increasing amounts of (10) (15%) and correspondingly lower yields of (5) (20%) were obtained when the CH_2Cl_2 was not purified by passage through basic alumina. Control experiments showed that the adduct (5) was not converted into diphenylanthracene under the experimental conditions. However pyrolysis of the adduct (5) in the vapour phase at 420°C and 0.1 Torr did give the diphenylanthracene (60%).

We rationalise the above transformations in terms of an initial 4+2 addition of the keten to the azete to give the adduct (4).[‡] This addition almost certainly proceeds through the zwitterion (2) since when the reaction is carried out in moist ether or acetonitrile this is intercepted by water to give the amidoketone (3), m.p. $140\text{--}141^{\circ}\text{C}$, synthesised independently, in addition to the adduct (5). Control experiments show that the amidoketone (3) does not arise by hydration of the adduct (5) or by addition of diphenylacetic acid to the azete. Aromatisation of the initial adduct (4) by a 1,3 H shift to carbon would give the observed product (5). An alternative shift to nitrogen with concomitant cleavage of the azetidine ring would give the *o*-quinonoid dibenzazocinone (8) which by electrocyclic closure to (9) and extrusion of cyanic acid could lead to diphenylanthracene (10). The hydrogen shift to nitrogen is clearly acid catalysed; this is understandable if the azetidine bond cleavage is assisted by protonation on nitrogen.

Thermal conversion of the adduct (5) into 9,10-diphenylanthracene can also be explained by way of the intermediate (8), which could be formed by an intramolecular 1,5-H shift ($\sigma_2^2 + \pi_2^2 + \sigma_2^2$) which relieves the strain of the azetidine ring.

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[†] Percentage yield based on 4-phenylbenzotriazine pyrolysed; assuming 60% conversion of triazine into azete (see ref. 2) this represents a yield of 50% based on azete. Satisfactory analytical and mass spectral data were obtained for all new compounds.

[‡] Formal Diels-Alder adducts of diphenylketen in which the keten acts as a diene are rare; see, however, J. E. Baldwin and D. S. Johnson, *J. Org. Chem.*, 1973, **38**, 2147; L. A. Feiler, R. Huisgen, and P. Koppitz, *J. Amer. Chem. Soc.*, 1974, **96**, 2270.

¹ D. J. Anderson and A. Hassner, *Synthesis*, 1975, 483 and references therein; D. H. Aue and D. Thomas, *J. Org. Chem.*, 1975, **40**, 2552 and references therein.

² B. M. Adger, C. W. Rees, and R. C. Storr, *J.C.S. Perkin I*, 1975, 45.