Cycloaddition of 2-Phenylbenzazete to Diphenylketen

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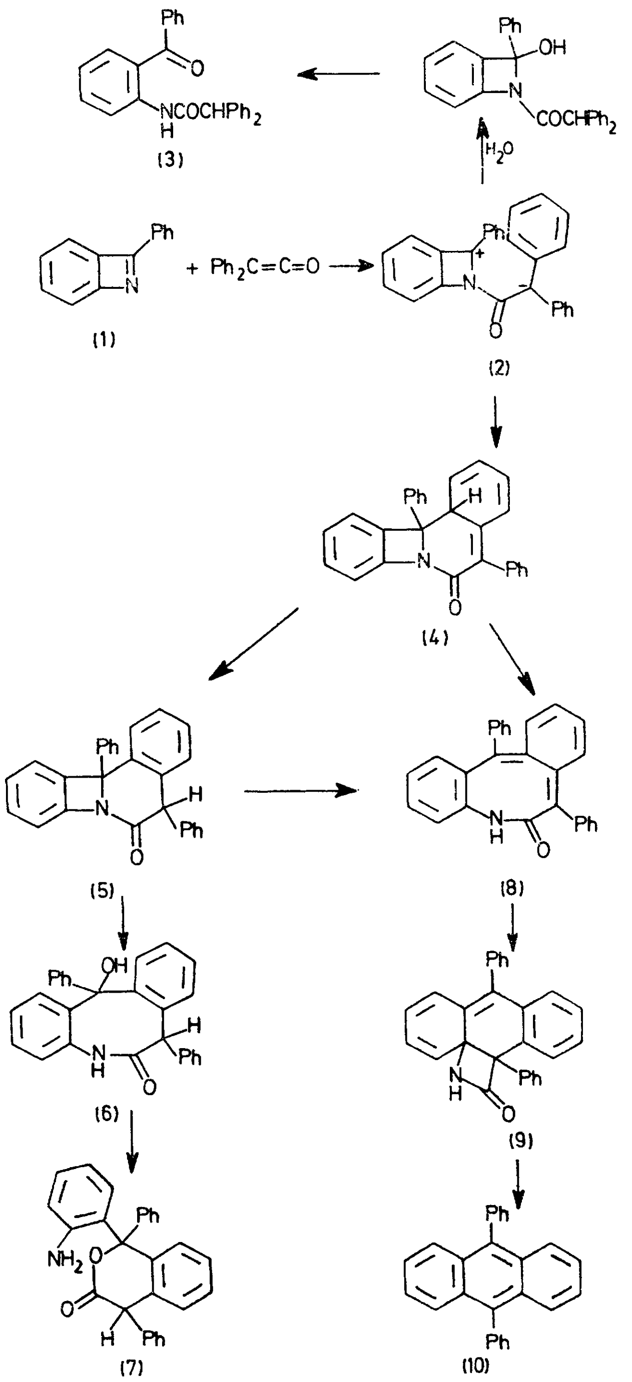
Summary Formation of 9,10-diphenylanthracene and the benzazetine (**5**) from 2-phenylbenzazete (**1**) and diphenylketen involves a stepwise 2+4 cycloaddition in which the keten acts formally as a diene; the benzazetine (**5**) gives diphenylanthracene at high temperature.

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—230 °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 δ 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 azetine 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—141 °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 azetine 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 azetine 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 ($_{\sigma}2_s+_{\pi}2_s+_{\sigma}2_s$) which relieves the strain of the azetine 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.