2-Phenylbenzazete, an Azacyclobutadiene

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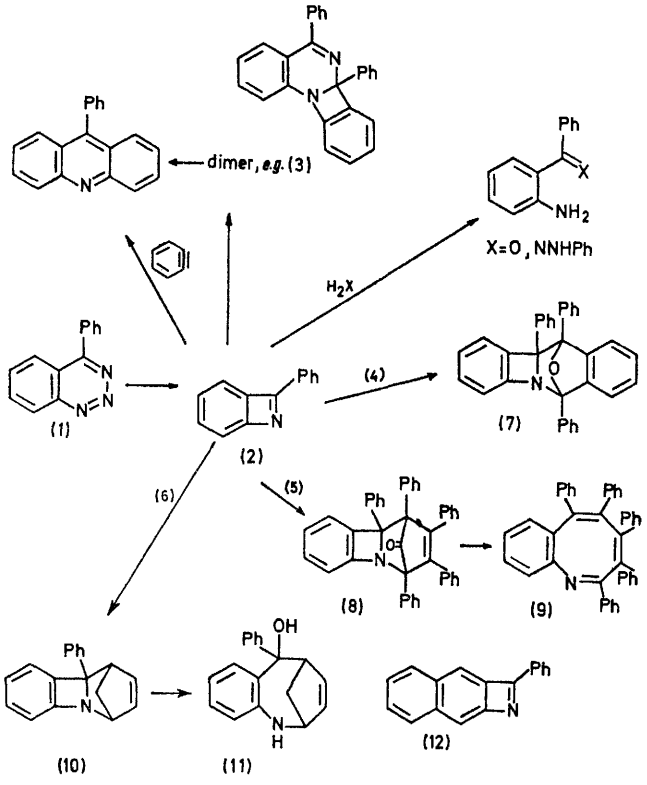
Summary 2-Phenylbenzazete (**2**), the first heterocyclic analogue of cyclobutadiene, is formed by vapour phase pyrolysis of 4-phenylbenzo-1,2,3-triazine; it dimerises and reacts with nucleophiles and dienes very rapidly but is surprisingly stable at −80°; 2-phenylnaphth[2,3-*b*]-azete (**12**), formed similarly, is even appreciably stable at room temperature.

IN spite of their theoretical significance and synthetic potential no heterocyclic analogues of cyclobutadiene have been reported.† Benzo-1,2,3-triazines[1] are therefore of interest since by extrusion of nitrogen they could yield benzazetes where the 4π-azacyclobutadiene system is stabilised by benzo fusion.



Vapour phase flash pyrolysis (0·03 Torr) of 4-phenylbenzo-1,2,3-triazine (**1**) above 500° gives biphenylene (40%) as the major product, presumably by dimerisation of benzyne produced by complete fragmentation of the triazine ring.[1] However, pyrolysis at 420—450° gives a dark red deposit on the cold receiver maintained at −80°. This contains biphenylene (*ca.* 20%), 9-phenylacridine (*ca.* 15%), unchanged benzotriazine (*ca.* 5%), and the red‡ 2-phenylbenzazete (**2**) (*ca.* 60%). Surprisingly, this last product is stable at −80°, but it is converted into a pale yellow solid (50%),§ m.p. 177—178°, as the receiver is allowed to warm to room temperature. This is clearly a dimer of 2-phenylbenzazete from analytical and mass spectral data. Its quantitative conversion into 9-phenylacridine, either thermally or with ethanolic hydrochloric acid under reflux, is consistent with any of the four possible angular dimers such as (**3**), which are analogous to that formed by benzocyclobutadiene. Of the two possible linear dimers, the dibenzo-1,2- and -1,5-diazocines, the latter is eliminated by comparison with an authentic specimen[2] and the former is incompatible with the conversion into 9-phenylacridine.

Monomeric 2-phenylbenzazete can be intercepted when nucleophiles or conjugated dienes are injected directly onto the cold pyrolysate at about −40° or below.¶ When dilute aqueous sulphuric acid is added in tetrahydrofuran solution, *o*-aminobenzophenone (50%) is formed by acid-catalysed addition of water to the imine bond, followed by opening of the four-membered azetine ring. Similar treatment with phenylhydrazine gives *o*-aminobenzophenone phenylhydrazone (60%) directly.

Cycloadditions are observed with diphenylisobenzofuran (**4**), tetraphenylcyclopentadienone (**5**), and cyclopentadiene (**6**). The isobenzofuran gives a single stable primary adduct (**7**) (55%), m.p. 171—172°, presumably having the expected *endo* configuration. With the other dienes the initial 1:1-adducts are not isolated because of strain in the azetine rings. This is relieved in the tetraphenylcyclopentadienone adduct (**8**) by extrusion of carbon monoxide to give the benzazocine (**9**) (52%), m.p. 189—190°, λ_{max} ($CHCl_3$) 254 nm (ϵ 35,900), and in the cyclopentadiene adduct (**10**) by hydration during work-up to give the amino-alcohol (**11**) (36%), m.p. 126—130° (decomp.). The susceptibility of 1-phenylbenzazetine to ring opening by nucleophiles has already been demonstrated.[3]

Like benzocyclobutadiene, 2-phenylbenzazete (**2**) does not react with added dienophiles (dimethyl acetylenedicarboxylate, but-2-yne, cyclopentene, or 1-dimethylaminopropyne) although it is possible that 9-phenylacridine formed in the pyrolysis could result from its reaction with the benzyne also produced.

2-Phenylnaphth[2,3-*b*]azete (**12**) is a similar red solid formed by pyrolysis (470°/0·03 Torr) of 4-phenyl-1,2,3-naphtho[2,3-*d*]triazine, m.p. 194—195°, and, as expected, is much more stable than (**2**). Even after the pyrolysate has been allowed to stand at room temperature for 1 h before injection of dilute aqueous sulphuric acid in tetrahydrofuran, 2-amino-3-benzoylnaphthalene is obtained in reasonable yield (25%). However, (**12**) dimerises very rapidly in solution and on attempted purification so that, as yet, we have been unable to obtain reliable spectroscopic data for it.

The obvious application of these highly reactive, but easily generated benzazetes to the synthesis of new heterocyclic systems is being investigated.

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† Several unsubstantiated claims of such systems appear in the early literature; see *e,g.* S. A. Ballard and D. S. Melstrom in 'Heterocyclic Compounds,' vol. I, ed. R. C. Elderfield, John Wiley, New York, 1950, p. 78.

‡ A red colour is to be expected for 2-phenylbenzazete by analogy with known cyclobutadiene derivatives.[4] The red colour disappears as the benzazete dimerises or reacts with added reagents.

§ All yields are based on the amount of triazine pyrolysed.

¶ Control experiments show that the products of these reactions are not formed from the starting benzotriazine or the benzazete dimer.

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[2] A. Sondheimer, *Ber.*, 1896, **29**, 1273.
[3] E. M. Burgess and L. McCullagh, *J. Amer. Chem. Soc.*, 1966, **88**, 1580.
[4] M. P. Cava, B. Hwang, and J. P. Van Meter, *J. Amer. Chem. Soc.*, 1963, **85**, 4032; M. P. Cava and B. Hwang, *Tetrahedron Letters*, 1965, 2297.