Benzazetes (1-Azabenzocyclobutenes)[1]

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Flash vacuum pyrolysis of 4-phenyl-1,2,3-benzotriazine (1) at 420° gives the bright red 2-phenylbenzazete (2) which is stable up to *ca.* −40° but which dimerises at higher temperatures. The azete (2) reacts with dilute aqueous acid and with phenylhydrazine to give *o*-aminobenzophenone and its phenylhydrazone, respectively. It undergoes cycloaddition reactions with conjugated dienes to give a variety of new heterocyclic systems; since these contain the labile azetine ring they mostly rearrange spontaneously to other heterocyclic systems. Thus diphenylisobenzofuran gives a primary adduct (16) which is isolable, but cyclopentadiene gives a hydrated product (18); carbon monoxide is extruded spontaneously from the tetraphenylcyclopentadienone adduct (20) to give the benzazocine (21), and nitrogen is similarly lost from the dipyridyltetrazine adduct to give the 1,3,4-benzotriazocine (22), the first example of this ring system. 4-Chloro-2-phenylbenzazete, 2-(*p*-methoxyphenyl)-benzazete, and 2-phenylnaphth[2,3-*b*]azete (24) are formed similarly from the appropriate triazines; the last two are, as expected, much more stable than 2-phenylbenzazete (2), compound (24) even having appreciable stability in the solid state at room temperature.

Flash pyrolysis of 4-phenyl-1,2,3-benzotriazine 3-oxide (27) gave 3-phenyl-2,1-benzisoxazole and acridone, possibly *via* 2-phenylbenzazete *N*-oxide (28), together with 3-phenylindazole, probably formed by rearrangement of (27) to 2-nitroso-3-phenylindazole and thermal denitrosation.

IN the preceding paper[2] we described the reasoning and experiments which led to our study of the pyrolysis of 4-substituted 1,2,3-benzotriazines as a route to benzazetes, derivatives of the unknown azacyclobutadiene system.

4-Phenyl-1,2,3-benzotriazine (1) was pyrolysed by sublimation through an oven maintained at 420—450° and 10^{-3} Torr. This was carried out in an apparatus similar to that previously described[3] except for a modification to the cold finger region to allow for the direct injection of trapping agents on to the pyrolysate. The products condensed as a bright red deposit on the cold receiver maintained at —78°. The main component of this deposit was 2-phenylbenzazete (2) (at least 64% †) together with biphenylene (3), 9-phenylacridine (4), benzonitrile, and unchanged benzotriazine. The above temperature range for the oven was found to be the optimum; below 400° benzotriazine was recovered almost quantitatively and above 500° considerable charring occurred and biphenylene and benzonitrile were the only products formed in appreciable amounts.

Evidence that 2-phenylbenzazete is the main component of the red deposit on the cold receiver is as follows. On warming to room temperature the deposit became pale yellow and a dimer of 2-phenylbenzazete was isolated, together with the other previously mentioned products, after preparative layer chromatography on silica gel. The red colour is consistent with the presence of monomeric 2-phenylbenzazete since the known stable cyclobutanaphthalene (5)[4] is also bright red.

Analytical and mass spectral data clearly establish the overall constitution of the 2-phenylbenzazete dimer, but its precise structure is not yet known. The two possible 'linear' dimeric structures (6) and (7) are readily eliminated, however; the former by an independent synthesis[5] and the latter by the ready conversion of the dimer into 9-phenylacridine either thermally or with ethanolic hydrochloric acid. This last reaction is consistent with any of the 'angular' dimeric structures (8)—(11) expected by analogy with the dimerisation of benzocyclobutene,[6] *i.e.* Diels–Alder dimerisation followed by electrocyclic ring opening, shown for the formation of (8). The problem of this dimer structure is further complicated since each of the angular dimers (8)—(11) has a dibenzodiazocine valence bond isomer [*e.g.* (8) $\rightleftharpoons$ (12)] and indeed such isomers seem likely intermediates in the conversion to 9-phenylacridine. Since there is evidence that dibenzo[*a*,*d*]-cyclo-octene (14) itself readily rearranges to dibenzosemibullvalene (15),[7] an analogous set of diazasemibullvalene structures [*e.g.* (13)] must also be considered

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† The yield of 2-phenylbenzazete could only be ascertained indirectly by further reaction with a suitable reagent or by allowing the azete to dimerise (see below). This yield represents the highest yield of a product derived from the azete.

[1] Preliminary communication, B. M. Adger, M. Keating, C. W. Rees, and R. C. Storr, *J.C.S. Chem. Comm.*, 1973, 19.

[2] B. M. Adger, M. Keating, C. W. Rees, and R. C. Storr, preceding paper.

[3] D. J. Anderson, T. L. Gilchrist, D. C. Horwell, C. W. Rees, and E. Stanton, *J.C.S. Perkin I*, 1972, 1317.

[4] M. P. Cava, B. Hwang, and J. P. Van Meter, *J. Amer. Chem. Soc.*, 1963, **85**, 4032; for a recent and even closer analogue, 1,2-diphenyltetramethylbenzocyclobutene, see H. Straub, *Angew. Chem. Internat. Edn.*, 1974, **13**, 405.

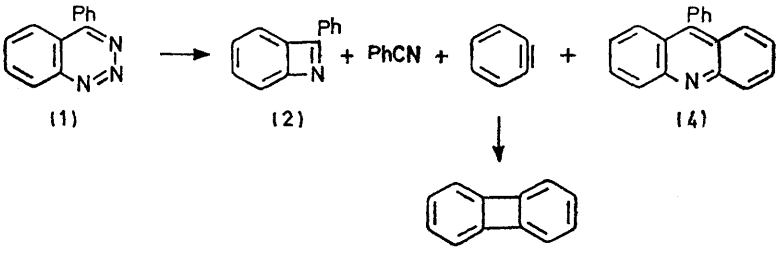
[5] A. Sondheimer, *Ber.*, 1896, **29**, 1273.

[6] M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.*, 1956, **78**, 500; 1957, **79**, 1701.

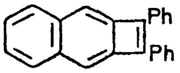
[7] G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, 1965, **87**, 131; W. Merk and R. Pettit, *ibid.*, 1967, **89**, 4787.

for the 2-phenylbenzazete dimer. We are investigating this possibility.

More convincing evidence for 2-phenylbenzazete comes from trapping experiments with added nucleophiles and dienes. These were introduced through the inlet after disconnection of the pump and introduction of nitrogen into the system, the pyrolysate temperature still being below about −60°. In each case the benzazete adduct was separated from the other pyrolysis products, after the mixture had warmed to room temperature, by preparative layer chromatography.



(1) (2) (4) (3)



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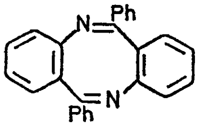
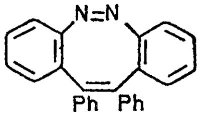
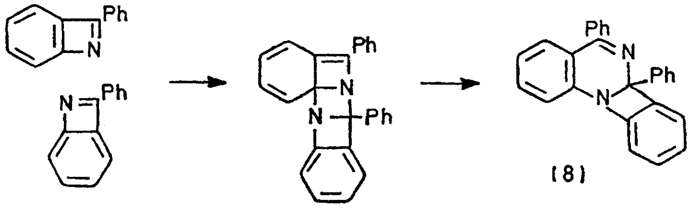


(6)



(7)



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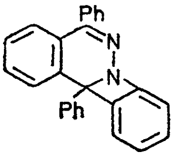

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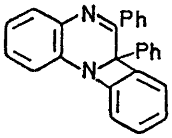

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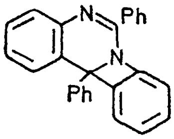
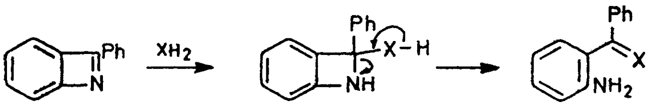


(11)

When tetrahydrofuran containing dilute aqueous sulphuric acid or phenylhydrazine was added to the cold pyrolysate, *o*-aminobenzophenone or its phenylhydrazone, respectively, was produced at the expense of the dimer. These products are readily explained in terms of nucleophilic addition to the reactive imine followed by cleavage of the unstable azetine so formed (Scheme 1). The benzazete did not react significantly with water; acid catalysis was necessary. Control experiments showed that in these and later trapping experiments, unchanged benzotriazine, the dimer, and any other product present in the pyrolysate did not react with the added reagent.



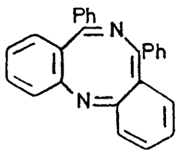
X = O or N·NHPh

SCHEME 1

2-Phenylbenzazete also reacted efficiently with a variety of dienes when these were injected in solution on to the pyrolysate at low temperature. In only one case however was the primary adduct isolated. Thus with the highly reactive 1,3-diphenylisobenzofuran a moderately stable 1 : 1 adduct was produced for which spectral data are consistent with structure (16). Since only one isomer was detected this is probably the more generally favoured *endo*-isomer.

With cyclopentadiene, the amino-alcohol (18) was obtained after chromatographic work-up. This is a homogeneous single product which shows N–H and O–H stretching absorptions in its i.r. spectrum and n.m.r. signals corresponding to NH and OH and aromatic, olefinic, bridgehead, and bridging methylene protons. The relative stereochemistry about carbon atoms *a* and *b* is not known. In this case strain in the initial azetine cycloadduct (17) is relieved by hydration, possibly during chromatography. Precedent for this is found in the only previously reported 1,2-dihydrobenzazete (19), which underwent similar ring cleavage with acetic acid in refluxing benzene and with aniline at 30°.[8] In this case the lower reactivity is to be anticipated because of the stabilising *N*-phenyl substituent and the lack of additional strain caused by the five-membered ring in (17).

With tetraphenylcyclopentadienone, ring strain in the initial adduct (20) is relieved by carbon monoxide extrusion, probably in concert with azetine bond cleavage, and the benzazocine (21) was isolated. Lack of reaction of this benzazocine with 4-phenyl-1,2,4-triazoline-3,5-dione suggests that it exists as the eight-membered ring structure rather than as a bicyclic valence tautomer. This reaction with tetraphenylcyclopentadienone gives some indication of the potential scope of benzazetes in synthesis since benzazocines have only recently been reported.[9] This was further underlined by the formation of the first 1,2,4-benzotriazocine (22) by reaction of 2-phenylbenzazete with 3,6-bis-(2-pyridyl)-1,2,4,5-tetrazine. In this case Diels–Alder addition is accompanied by spontaneous extrusion of nitrogen and σ-bond cleavage.



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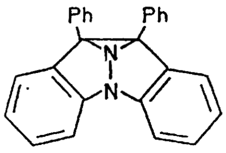

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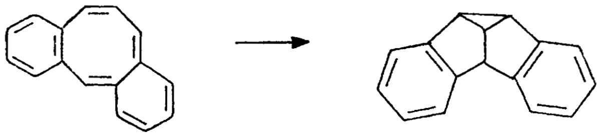

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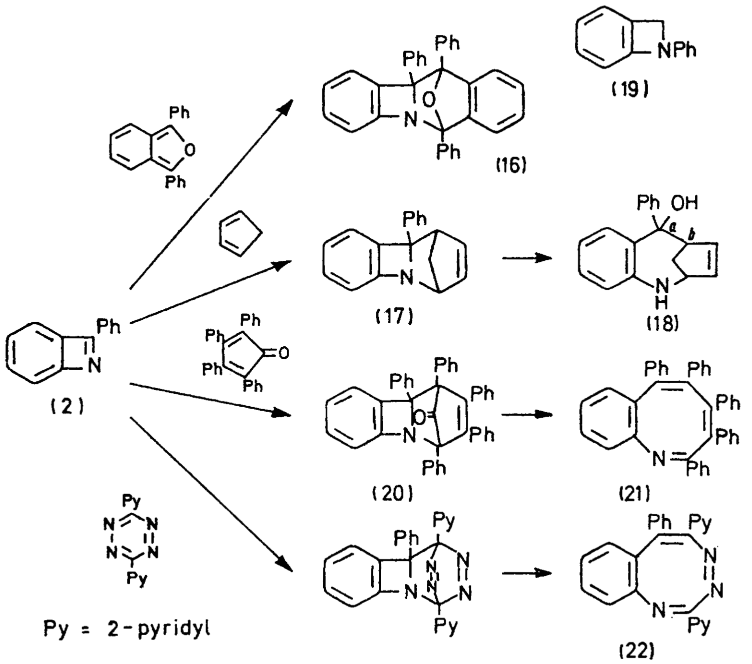

(19) (16) (17) (18) (2) (20) (21) (22)

Like benzocyclobutene, 2-phenylbenzazete shows little tendency to act as a diene in Diels–Alder reactions. Thus no reaction was observed with cyclopentene, but-2-yne, *N*-phenylmaleimide, or 1-diethylaminopropyne. The only examples of diene activity are in the dimerisation and, possibly, in the formation of 9-phenylacridine in the pyrolysis which can be rationalised in terms of a gas-phase reaction of 2-phenylbenzazete with the benzyne produced by complete fragmentation of the starting benzotriazine.

The preceding reactions establish that 2-phenylbenzazete is formed in the pyrolysis of 4-phenyl-1,2,3-benzotriazine. Most remarkable is the high stability of the species at only moderately low temperatures (−78 to −40°). This stability for such an antiaromatic system must result largely from benzo-fusion and conjugative stabilisation of the imine function. Predictably, enhancement of either of these effects leads to even more stable azetes.

Thus pyrolysis of the naphtho[2,3-*d*]triazine (23) gave the stabilised 2-phenylnaphth[2,3-*b*]azete (24) as an orange solid contaminated with traces of dibenzo[*b*,*h*]biphenylene. The orange colour persisted in the solid even at room temperature but in dichloromethane

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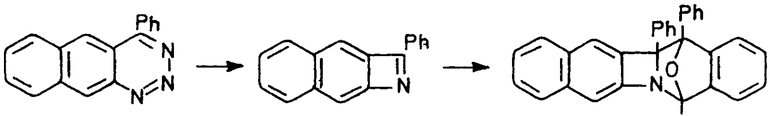
[8] E. M. Burgess and L. McCullagh, *J. Amer. Chem. Soc.*, 1966, **88**, 1580.

[9] L. A. Paquette, L. B. Anderson, J. F. Hansen, S. A. Lang, and H. Berk, *J. Amer. Chem. Soc.*, 1972, **94**, 4907.

solution was very rapidly discharged with the simultaneous deposition of a pale yellow, highly insoluble compound having spectral and mass spectral properties as expected for a dimer of the naphthazete (24). In spite of this extremely rapid dimerisation the naphthazete was intercepted in good yield with diphenylisobenzofuran. The adduct (25) was of limited stability however and was extremely insoluble, making complete purification impossible. Significantly the adduct was also formed, although in much lower yield, when the isobenzofuran was added after the pyrolysate had been left at room temperature for 2 h. Addition of 2N-sulphuric acid in tetrahydrofuran to the pyrolysate gave 2-amino-3-benzoylnaphthalene by hydration of the azete; again this reaction was observed, although to a lesser extent, when addition of the acid solution was delayed for 2 h.

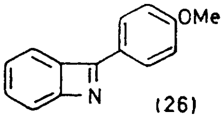


(23) (24) (25)

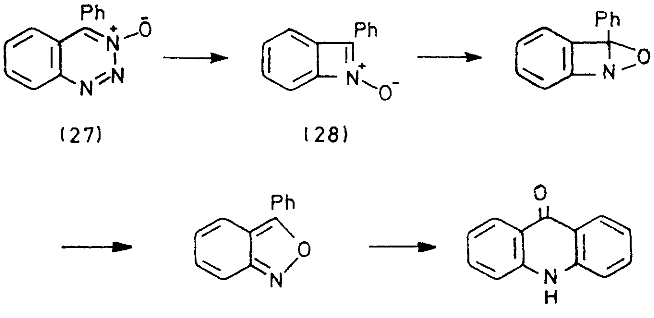
An even more dramatic effect was observed for the conjugatively stabilised 2-(*p*-methoxyphenyl)benzazete (26) produced by pyrolysis of 4-(*p*-methoxyphenyl)-1,2,3-benzotriazine. This azete dimerised only slowly in solution, its red colour persisting for several hours. Although it reacted rapidly with dilute sulphuric acid in tetrahydrofuran the cycloaddition reactions with tetraphenylcyclopentadienone and diphenylisobenzofuran, to give products exactly analogous to those from 2-phenylbenzazete, were sluggish at room temperature. It is only contamination by biphenylene, *p*-methoxybenzonitrile, and 9-*p*-methoxyphenylacridine in the pyrolysate which has so far prevented us from obtaining reliable spectroscopic data for this azete (26). The observation of two methoxy-absorptions in the n.m.r. spectrum of the dimer of (26) is consistent with an angular mode of dimerisation but does not help to differentiate between structures analogous to (8)—(11) for the azete dimers.

Enhanced stability of the benzazete system might also be expected to result from the reduced C–N bond order in benzazete *N*-oxides such as (28). We therefore investigated the pyrolysis of 4-phenyl-1,2,3-benzotriazine 3-oxide (27). Although the photolysis of many aromatic *N*-oxides, including (27),[10] has been extensively studied, pyrolysis of such systems has been neglected. Pyrolysis of the *N*-oxide (27) at 420° gave 3-phenyl-2,1-benzisoxazole (29), 3-phenylindazole (31), and acridone (30). Formation of the 3-phenylbenzisoxazole and acridone can be explained in terms of the intermediacy of 2-phenylbenzazete 1-oxide (28), as shown in Scheme 2, but an alternative mechanism cannot be discounted since 4-phenylbenzotriazine 3-oxide is known to be converted into *o*-azidobenzophenone on heating (see ref. 10). This would in turn lead to (29) and then to (30) since 3-phenyl-2,1-benzisoxazole is known to rearrange thermally to acridone.[11] Formation of 3-phenylindazole must involve a different pathway, such as that shown in Scheme 3. A similar mechanism has been proposed to account for the formation of 3-phenylindazole by photolysis of the *N*-oxide (27).[9]

The above pyrolysis of the *N*-oxide (27) indicates that benzazete *N*-oxides, if formed, are not markedly more stable thermally than the azetes. An alternative attempt to obtain 2-phenylbenzazete *N*-oxide by low temperature peroxidation of the benzazete (2) with *m*-chloroperbenzoic acid also failed since oxidation did not compete with dimerisation.



(26)



(27) (28) (29) (30)

Scheme 2

Initial experiments suggest that benzazetes may also be formed in solution by photolysis of 1,2,3-benzotriazines. Thus irradiation of 4-phenylbenzotriazine (1) in tetrahydrofuran with a medium-pressure mercury lamp and quartz filter gave a dimer of 2-phenylbenzazete identical with that from the pyrolysis. 2-Aminobenzophenone was produced by irradiation in wet tetrahydrofuran. It is however possible that the 2-aminobenzophenone could have resulted from hydration of photoexcited triazine and not from benzazete. Control experiments showed that 4-phenylbenzotriazine was not converted into 2-aminobenzophenone under these conditions in the absence of irradiation. 2-Phenylbenzazete (2) was not intercepted when irradiation was conducted in the presence of tetraphenylcyclopentadienone or cyclopentadiene, probably because of the photoinstability of the adducts, though dimer formation was suppressed in the presence of these dienes.

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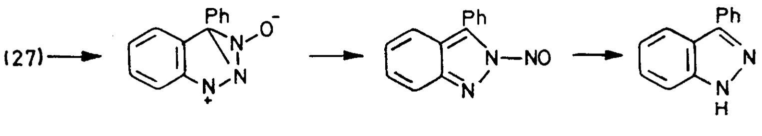
[10] W. M. Horspool, J. R. Kershaw, A. W. Murray, and G. M. Stevenson, *J. Amer. Chem. Soc.*, 1973, **95**, 2390.

[11] J. M. F. Gagan in 'Acridines,' ed. R. M. Acheson, 2nd edn., Wiley, London, 1973, p. 177.

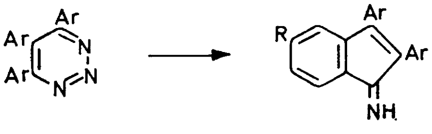
Attempts to generate benzazetes with substituents other than a 2-aryl group have so far been unsuccessful. 4-Methyl-1,2,3-benzotriazine was either recovered unchanged from pyrolysis or at slightly higher temperatures underwent complete fragmentation to give benzyne and hence biphenylene. 4-Methoxy-1,2,3-benzotriazine was either recovered unchanged or gave a complex mixture of unidentified products. No evidence was found for 2-methoxybenzazete, which we anticipated would be highly stabilised; this azete, like the starting triazine, could readily suffer O ⟶ N methyl migration. On the other hand, on pyrolysis at 420°, 6-chloro-4-phenyl-1,2,3-benzotriazine gave a bright red azete which was isolated as its dimer after warming to room temperature.



(31)

Scheme 3

Pyrolysis of monocyclic 1,2,3-triazines could in principle lead to unfused azetes; indeed this has been convincingly demonstrated by Gompper and his co-workers in the formation of tris(dimethylamino)azete.[12] However the monocyclic 4,5,6-triphenyl-1,2,3-triazine underwent complete fragmentation on vapour-phase pyrolysis to give diphenylacetylene, benzonitrile, and nitrogen; no conditions were found for partial fragmentation of the triazine. Recently however it has been reported[13] that prolonged heating of various monocyclic triaryltriazines at the m.p. led to the extrusion of nitrogen and formation of indenimines (32). No evidence for an intermediate azete was presented or considered. In contrast, a careful search in our benzotriazine pyrolysis revealed no trace of fluorenone imines.



(32)

Similarly, pyrolysis of 1,2,4-benzotriazines could also give benzazetes. However these triazines are considerably more stable than the corresponding 1,2,3-isomers.[2] No fragmentation occurred below 700° and above this temperature benzyne (and hence biphenylene) was produced. The characteristic red colour of 2-phenylbenzazete was never observed in the pyrolysis of 3-phenyl-1,2,4-benzotriazine.

In conclusion, pyrolysis of 4-aryl-1,2,3-benzotriazines has provided a route to the first azacyclobutadiene derivatives. The synthetic potential of such species is already apparent and should provide a stimulus for further investigation into antiaromatic heterocyclic systems.

EXPERIMENTAL

Pyrolyses were carried out with the apparatus described previously[3] modified by the addition of an inlet facility to allow direct introduction of reactant solutions onto the pyrolysate. This was conveniently effected after inlet of nitrogen and inversion of the combined pyrolysis tube and receiver. To minimise warming of the pyrolysate the reactant solution was precooled (−78°) and added immediately.

Pyrolysis of 4-*Phenyl*-1,2,3-*benzotriazine*.[14]—The pyrolyses were performed over a range of oven temperatures in order to find the optimum conditions. The sublimation temperature was maintained at 160° and the pressure at 10^{-3} Torr. The pyrolyses were carried out with 150 mg portions of pure triazine. The pyrolysate was collected on a solid carbon dioxide–acetone-cooled receiver and was allowed to warm to room temperature under nitrogen. The components were then separated by chromatography on a silica gel preparative layer chromatography (p.l.c.) plate by elution with ether–petroleum (1 : 4) and, where applicable, characterised by comparison with authentic samples.

Below 400°, 4-phenyl-1,2,3-benzotriazine was recovered unchanged (95%). In the range 420—450° a dark red oil collected on the cold receiver. At 420° this consisted (after warming to room temperature, when the colour changed to yellow) of a mixture of 4-phenyl-1,2,3-benzotriazine (12%), benzonitrile (13%), 9-phenylacridine (7%) (authentic sample prepared by the method of Bernthsen[15]), biphenylene (10%), and a dimer of 2-phenylbenzazete (51%). This dimer crystallised as pale yellow needles from ethanol, m.p. 177—178° (Found: C, 87·0; H, 5·1; N, 7·8. Calc. for $C_{26}H_{18}N_2$: C, 87·1; H, 5·1; N, 7·8%), $\nu_{max.}$ 1620, 1600, 1580, 1400, 1350, 770, 750, 730, and 700 cm^{-1}, $\lambda_{max.}$ 222·5 (ε 21,900), 247 (25,100), 287 (15,500), and 355 nm (7080), *m*/*e* 358 (M^+, 100%), 281 (96), 255 (99), 254 (98), 226 (18), 177 (31), 151 (16), 103 (15), and 77 (17).

Above 500° considerable charring occurred and the yield of dimer was lower (5%). Biphenylene (55%), 9-phenylacridine (12%), and benzonitrile (52%) were also isolated.

Reactions of 2-*Phenylbenzazete*.—4-Phenyl-1,2,3-benzotriazine (150 mg) was pyrolysed at 420° as described above. After the introduction of nitrogen, a solution of the trapping agent (precooled to −78°) was added directly to the dark red pyrolysate on the cold receiver at −78°. The mixture was then allowed to warm to room temperature. In all experiments traces of the 2-phenylbenzazete dimer, 9-phenylacridine, biphenylene, and unchanged 4-phenyl-1,2,3-benzotriazine were detected by t.l.c. The main product was separated from these minor components by p.l.c. as described below.

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[12] G. Seybold, U. Jersak, and R. Gompper, *Angew. Chem. Internat. Edn.*, 1973, **12**, 847.

[13] H. von Neunhoeffer, H. D. Vötter, and M. Gais-Mutterer, *Tetrahedron Letters*, 1973, 219.

[14] B. M. Adger, S. Bradbury, M. Keating, C. W. Rees, R. C. Storr, and M. T. Williams, *J.C.S. Perkin I*, 1975, 31.

[15] A. Bernthsen, *Annalen*, 1884, **224**, 13.

(i) *With dilute acid.* A solution (15 ml) containing 10% (v/v) of 2N-sulphuric acid in tetrahydrofuran was added to the pyrolysate at −78°. After warming to room temperature evaporation of the resulting pale yellow solution followed by p.l.c. of the residue on silica gel with ether–petroleum (1 : 1) as eluant gave 2-aminobenzophenone (90 mg, 64%).

(ii) *With phenylhydrazine.* A solution of phenylhydrazine (150 mg) in dichloromethane (15 ml) was added to the pyrolysate at −78°. Evaporation of the resulting solution followed by p.l.c. of the residue [ether–petroleum (1 : 1) as eluant] gave 2-aminobenzophenone phenylhydrazone (130 mg, 62%), m.p. 127—128°, identical with an authentic specimen prepared from 2-aminobenzophenone and phenylhydrazine.

(iii) *With cyclopentadiene.* A solution of cyclopentadiene (3 ml) in dichloromethane (15 ml) was added to the pyrolysate at −78°. After warming to room temperature, the resulting pale yellow solution was evaporated and the residue subjected to p.l.c. on silica gel with ether–petroleum (1 : 3) as eluant. This gave 1,2,5,6-*tetrahydro*-6-*phenyl*-2,5-*methano*-1-*benzazocin*-6-*ol* (18) (45 mg, 36%) as an unstable and rapidly darkening solid, m.p. 126—130° (decomp.) (Found: M^+, 263·13098. $C_{18}H_{17}NO$ requires M, 263·13100), $\nu_{max.}$ 3400 (OH), 3300 (NH), 1610, 1310, 1010, 980, 760, and 740 cm^{-1}, τ ($CDCl_3$) 1·20—3·40 (9H, aromatic), 4·34 (2H, m, olefinic), 5·74 (1H, m, allylic), 6·75br (2H, m, OH and NH), 6·90 (1H, m, allylic), and 7·42—7·95 (2H, m, bridging CH_2), *m/e* 263 (M^+, 33%), 197 (95), 196 (100), 120 (25), and 77 (20).

(iv) *With tetraphenylcyclopentadienone.* A solution of tetraphenylcyclopentadienone (200 mg) in dichloromethane (15 ml) was added to the pyrolysate at −78°. The resulting solution was allowed to warm to room temperature and evaporated, and the residue was subjected to p.l.c. on silica gel with ether–petroleum (1 : 9) as eluant, to give 2,3,4,5,6-*pentaphenyl*-1-*benzazocine* (21) (180 mg, 52%) as needles from benzene–hexane, m.p. 188—189° (Found: C, 91·8; H, 5·6; N, 2·8. $C_{41}H_{29}N$ requires C, 91·9; H, 5·4; N, 2·6%), $\nu_{max.}$ 1620, 1600, 1580, 1500, 1460, 1455, 1200, 1160, 780, 770, 760, and 700 cm^{-1}, *m/e* 535 (M^+, 100%), 487 (15), 398 (52), 380 (20), 357 (22), 304 (12), 268 (16), 227 (24), 189 (26), 165 (10), and 105 (15).

(v) *With* 1,3-*diphenylisobenzofuran*.[16] A solution of 1,3-diphenylisobenzofuran (200 mg) in dichloromethane (15 ml) was added to the pyrolysate at −78°. The standard work-up procedure [p.l.c. on silica gel with ether–petroleum (1 : 9) as eluant] gave 11,11a-*dihydro*-6,11,11a-*triphenyl*-6,11-*epoxy*-6H-[1]*benzazeto*[1,2-b]*isoquinoline* (16) (183 mg, 54%) as needles from benzene–hexane, m.p. 171—172° (Found: M^+, 449·17729. $C_{33}H_{23}NO$ requires M, 449·17727) (Found: C, 86·6; H, 5·2; N, 3·4. $C_{33}H_{23}NO,0·5H_2O$ requires C, 86·5; H, 5·2; N, 3·2%), $\nu_{max.}$ 1640, 1600, 1485, 1370, 1340, 1300, 1180, 1000, 950, 920, 755, 720, and 700 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 273 nm (ε 3360), *m/e* 449 (M^+, 25%), 421 (2), 344 (10), 270 (100), 239 (27), 195 (95), 180 (20), 162 (41), 120 (21), and 103 (31).

(vi) *With* 3,6-*bis*-(2-*pyridyl*)-1,2,4,5-*tetrazine*.[17] A solution of the tetrazine (200 mg) in dichloromethane was added to the pyrolysate at −78°. The resulting solution was allowed to warm to room temperature and then evaporated to dryness. The deep purple residue was extracted with ether (3 × 10 ml) and the insoluble tetrazine was filtered off to leave a bright yellow solution. This was evaporated and the residue was subjected to p.l.c. on silica gel with ether–petroleum (1 : 3) as eluant to give 6-*phenyl*-2,5-*bis*-(2-*pyridyl*)-1,3,4-*benzotriazocine* (22) (97 mg, 25%) as bright yellow prisms from ethanol, m.p. 78—79° (Found: C, 77·0; H, 4·4; N, 18·0. $C_{25}H_{17}N_5$ requires C, 77·5; H, 4·4; N, 18·1%), $\nu_{max.}$ 1600, 1580, 1240, 1160, 1120, 1000, 960, 920, 770, 740, and 700 cm^{-1}, $\lambda_{max.}$ 240 (ε 48,500) and 304 nm (44,180), *m/e* 387 (M^+, 5%), 358 (20), 269 (50), 252 (43), 207 (47), 179 (100), and 152 (41).

No products other than the expected 2-phenylbenzazete dimer, biphenylene, benzonitrile, and 9-phenylacridine were observed when solutions of the following dienes (150 mg) in dichloromethane (15 ml) were added to the pyrolysate; cyclohexa-1,3-diene, tetrachlorodimethoxycyclopentadiene,[18] 1,2-diaza-3,5-diphenylcyclopenta-2,5-dien-4-one,[19] and 1,2-diaza-3,7-diphenylnorcaradiene.[20] Similarly no adducts were detected when the pyrolysate was treated with solutions of cyclopentene, but-2-yne, 1-diethylaminopropyne, or *N*-phenylmaleimide.

Pyrolysis of 6-*Chloro*-4-*phenyl*-1,2,3-*benzotriazine*.[14]—This triazine was pyrolysed as described for 4-phenyl-1,2,3-benzotriazine. Below 400° 6-chloro-4-phenyl-1,2,3-benzotriazine was recovered unchanged. At 420° a dark red oil collected on the cold receiver. This was allowed to warm to room temperature under nitrogen and subjected to p.l.c. on silica gel with ether–petroleum (1 : 5) as eluant to give 6-chloro-4-phenyl-1,2,3-benzotriazine (40%), benzonitrile (25%), a mixture of 2,6- and 2,7-dichlorobiphenylene (40%), and a dimer of 4-chloro-2-phenylbenzazete (6%). The dimer crystallised from ethanol as needles, m.p. 180—181° (Found: C, 73·1; H, 3·9; N, 6·3. Calc. for $C_{26}H_{16}Cl_2N_2$: C, 73·1; H, 3·7; N, 6·5%), $\nu_{max.}$ 1630, 1605, 1580, 1390, 1320, 1300, 1100, 960, 820, and 700 cm^{-1}, $\lambda_{max.}$ 222 (ε 22,000), 246 (24,900), 273 (14,200), and 352 nm (7000), *m/e* 426 (M^+, 100%), 387 (5), 322 (20), 288 (15), 252 (10), 213 (21), 177 (11), and 126 (8).

Above 500°, considerable charring occurred and the yield of all products was lower. In view of the low yield of 4-chloro-2-phenylbenzazete obtained in this pyrolysis, no trapping experiments were conducted.

Pyrolysis of 4-(p-*Methoxyphenyl*)-1,2,3-*benzotriazine*.[14]—Pyrolysis of this triazine was carried out as described for 4-phenyl-1,2,3-benzotriazine. Below 400°, the triazine was recovered unchanged. At 420° a dark red oil collected on the cold receiver. This was allowed to warm to room temperature under nitrogen and the components were separated by p.l.c. on silica gel with ether–petroleum (1 : 9) as eluant to give unchanged triazine (15%), *p*-methoxybenzonitrile (10%), biphenylene (9%), and a dimer of 2-(*p*-methoxyphenyl)benzazete (21%). This dimer crystallised from ethanol as pale yellow needles, m.p. 185—187° (Found: C, 80·0; H, 5·3; N, 6·8. Calc. for $C_{28}H_{22}N_2O_2$: C, 80·3; H, 5·3; N, 6·7%), $\nu_{max.}$ 1620, 1600, 1390, 1260, 1180, 1030, 850, 750, and 740 cm^{-1}, $\lambda_{max.}$ 224 (ε 22,000), 250 (25,200), 290 (15,100), and 361 nm (7000), τ ($CDCl_3$) 2·51 (m, aromatic), 6·11 (3H, s, OCH_3), and 6·23 (3H, s, OCH_3), *m/e* 418 (M^+, 100%), 403 (9), 388 (10), 387 (21), 356 (20), 311 (35), 285 (92), 241 (12), 209 (19), and 135 (15).

At 500° charring occurred and *p*-methoxybenzonitrile

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[18] J. S. Newcomer and E. T. McBee, *J. Amer. Chem. Soc.*, 1949, **71**, 946.

[19] P. J. Fagan and M. J. Nye, *Chem. Comm.*, 1971, 537.

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(44%) and biphenylene (40%) were the only products isolated.

Reactions of 2-(p-*Methoxyphenyl*)*benzazete*.—These trapping experiments were carried out as described for 2-phenylbenzazete except that the reaction mixtures resulting from addition of the dienes were set aside for several hours after attaining room temperature. During this time the red colour of the azete faded and t.l.c. indicated that the yield of adduct rose to a maximum. Work-up procedures were exactly as before.

(i) *With* 1,3-*diphenylisobenzofuran*. This gave 11,11a-*dihydro*-11a-(p-*methoxyphenyl*)-6,11-*diphenyl*-6,11-*epoxy*-6H-[1]*benzazeto*[1,2-b]*isoquinoline* (48%) as a pale yellow solid which was crystallised with difficulty and slight decomposition from ethanol as needles, m.p. 142—144° (Found: C, 85·7; H, 5·5. $C_{34}H_{25}NO_2$ requires C, 85·2; H, 5·2%), $\nu_{max.}$ 1600, 1590, 1510, 1370, 1250, 1170, 1040, 1030, 840, 820, 800, 755, 740, and 700 cm^{-1}, τ ($CDCl_3$) 2·00—3·50 (22H, m, aromatic) and 6·18 (3H, s, OCH_3), *m/e* 479 (M^+, 2%), 464 (20), 448 (30), 347 (22), 270 (100), 239 (10), 226 (11), 165 (9), and 135 (15).

(ii) *With tetraphenylcyclopentadienone*. This gave 6-(*p*-methoxyphenyl)-2,3,4,5-tetraphenyl-1-benzazocine (36%), m.p. 198—199° (from benzene), $\nu_{max.}$ 1620, 1600, 1590, 1505, 1490, 1370, 1240, 1170, 1030, 835, 800, 770, 765, 730, and 700 cm^{-1}, τ ($CDCl_3$) 2·05—3·60 (27H, m, aromatic), 6·19 (3H, s, OCH_3), *m/e* 565 (M^+, 100%), 516 (10), 487 (95), 457 (23), 443 (12), 385 (11), 281 (20), 224 (19), 176 (11), and 118 (8). It was impossible to free this adduct from traces of tetraphenylcyclopentadienone.

(iii) *With dilute acid*. Dilute sulphuric acid in tetrahydrofuran gave 2-amino-4′-methoxybenzophenone (50%).

(iv) *With phenylhydrazine*. This gave 2-amino-4′-methoxybenzophenone phenylhydrazone (51%), as yellow crystals from ethanol, m.p. 181—182°, identical with an authentic specimen made from 2-amino-4′-methoxybenzophenone and phenylhydrazine.

Pyrolysis of 4-*Phenylnaphtho*[2,3-d][1,2,3]*triazine* (23).[14]—The optimum oven temperature for pyrolysis of this triazine was found to be 470°. Below this temperature large amounts of triazine were recovered and above 490° there was excessive charring. The pyrolysate was a deep orange solid, the colour of which persisted for several hours at room temperature. The fresh pyrolysate was dissolved in dry dichloromethane and after several minutes a pale yellow solid, presumed to be a 2-phenylnaphth[2,3-*b*]azete dimer (21%), m.p. 310°, was precipitated. This could not be recrystallised owing to its extreme insolubility but the following data support this assignment (Found: M^+, 458·17830. Calc. for $C_{34}H_{22}N_2$: *M*, 458·17930), $\nu_{max.}$ 1620, 1600, 1500, 1285, 900, 760, and 695 cm^{-1}, *m/e* 458 (M^+, 100%), 382 (30), 354 (40), 333 (28), 289 (18), 229 (90), and 91 (68). The filtrate remaining after removal of this dimer was evaporated and the residue was chromatographed (p.l.c.) on a silica gel plate with ether–petroleum (1 : 4) as eluant to give dibenzo[*b*,*h*]biphenylene (4%), identical with an authentic specimen, and benzonitrile (4%).

Interception of 2-*Phenylnaphth*[2,3-b]*azete*.—(i) *With diphenylisobenzofuran*. The pyrolysate from 4-phenylnaphtho[2,3-*d*][1,2,3]triazine (100 mg) was allowed to warm to room temperature and a solution of diphenylisobenzofuran (120 mg) in dichloromethane (15 ml), also at room temperature, was added. Standard work-up by p.l.c. on silica gel gave 12,12a-*dihydro*-7,12,12a-*triphenyl*-7,12-*epoxy*-7H-*naphth*[2′,3′:3,4]*azeto*[1,2-b]*isoquinoline* (25) (30 mg, 15%), m.p. 152—154°, $\nu_{max.}$ 1630, 1600, 1580, 1300, 1180, 1140, 1010, 960, 750, and 700 cm^{-1}, *m/e* 499 (M^+, 10%), 315 (100), 286 (50), 245 (80), 229 (92), 210 (88), 165 (70), 126 (50), and 105 (98). The thermal instability and extreme insolubility of this compound made purification of a sample for analysis impossible.

When the pyrolysate was set aside at room temperature for 2 h before addition of the diphenylisobenzofuran solution the above adduct was isolated (3%); the major product was the dimer of 2-phenylnaphth[2,3-*b*]azete.

(ii) *With dilute acid*. The pyrolysate from 4-phenylnaphtho[2,3-*d*][1,2,3]triazine was treated at room temperature with a solution containing 10% (v/v) of 2N-sulphuric acid in tetrahydrofuran. This gave 2-amino-3-benzoylnaphthalene (46%), identical with an authentic specimen.

When the pyrolysate was set aside at room temperature for 2 h before addition of the acid solution, 2-amino-3-benzoylnaphthalene (4%) was obtained, the major product being the dimer of 2-phenylnaphth[2,3-*b*]azete.

Pyrolysis of 4-*Phenyl*-1,2,3-*benzotriazine* 3-*Oxide* (27).[21]—4-Phenyl-1,2,3-benzotriazine 3-oxide (150 mg) was pyrolysed as described above through an oven maintained at 420°. The pale yellow pyrolysate was allowed to warm to room temperature and chromatographed (p.l.c.) on a silica gel plate. Elution with ether–petroleum (1 : 1) gave (R_F 0·8) 3-phenyl-2,1-benzisoxazole (29) (30 mg, 25%), m.p. and mixed m.p. 51—52°, (R_F 0·4) 3-phenylindazole (31) (18 mg, 14%), m.p. and mixed m.p. 105—107°, and (R_F 0·25) acridone (30) (31 mg, 25%), m.p. and mixed m.p. 350°.

Pyrolysis of Triphenyl-1,2,3-*triazine*.[22]—Triphenyl-1,2,3-triazine (150 mg) was pyrolysed as described above. The triazine was extremely involatile requiring a sublimation temperature of 240° (10^{-3} Torr), which caused considerable decomposition during the sublimation. With an oven temperature below 400° starting material was recovered (70%). At 420° diphenylacetylene (40%) and starting material (16%) were isolated by p.l.c. At 460° diphenylacetylene was the only product isolated.

Photolysis of 4-*Phenyl*-1,2,3-*benzotriazine*.—4-Phenyl-1,2,3-benzotriazine (500 mg) was irradiated in dry degassed tetrahydrofuran (200 ml) for 3·5 h using a 125 W medium-pressure mercury lamp fitted with a quartz jacket. Evaporation of the tetrahydrofuran gave a residue which was chromatographed (p.l.c.) on silica gel plates with ether–petroleum (3 : 1) as eluant to give a 2-phenylbenzazete dimer identical with that obtained by pyrolysis of 4-phenyl-1,2,3-benzotriazine, and a trace of a yellow oil, possibly 7-phenylhepta-2,4-dien-6-ynonitrile, $\nu_{max.}$ ($CHCl_3$) 2200 (C≡N str.), 2100 (C≡C str.), 1600 (C=C str.), 1480, 1315, 1150, and 980 cm^{-1}. Unchanged 4-phenylbenzotriazine and polymeric material were also obtained.

Similar irradiation in tetrahydrofuran (200 ml) containing water (5 ml) gave *o*-aminobenzophenone (74 mg, 50%), m.p. and mixed m.p. 105—106°. This was isolated by evaporation of the tetrahydrofuran, addition of water, extraction with dichloromethane, and chromatography of the extracts on silica gel.

Pyrolysis of 2-*Phenylbenzazete Dimer*.—The dimer was sublimed at 170° and 0·01 Torr through an oven

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[21] J. Meisenheimer, O. Senn, and P. Zimmermann, *Ber.*, 1927, **60**, 1736.

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maintained at 475°. The resulting pyrolysate was subjected to p.l.c. on silica gel with ether–petroleum (1 : 3) as eluant to give 9-phenylacridine (95%) and benzonitrile.

Treatment of 2-Phenylbenzazete Dimer with Acid.—The dimer was heated under reflux in ethanolic hydrochloric acid (50% v/v) for 15 h. The resulting mixture was basified with sodium hydroxide solution and extracted with ether. The extracts were washed with water, dried, and evaporated to give 9-phenylacridine (90%).

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