

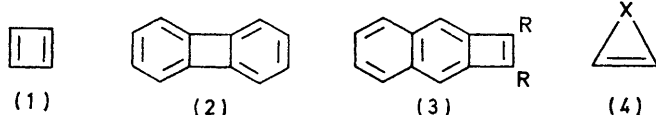
Attempted Routes to Benzazetes¹

By Brian M. Adger, Martin Keating, Charles W. Rees,* and Richard C. Storr,* The Robert Robinson Laboratories, University of Liverpool, P.O. Box 147, Liverpool L69 3BX

Vapour phase pyrolysis of the *N*-indazol-2-yl-*SS*-dimethylsulphoximides (21; R = H or Me) and of 3-methyl-indazol-2-ylimino(triphenyl)phosphorane (22) gave *cis,cis*-hepta- and octa-2,4-dien-6-ynenitriles; these could not be induced to isomerise to benzazetes. Pyrolysis of 1,2,3-benzotriazines above 450° resulted in fragmentation of the triazine ring to give benzyne, which dimerised to give biphenylene in good yield. 6-Methylpyrido[3,2-*d*]-[1,2,3]triazine however gave 6-methylpyridine-2-carbonitrile rather than the diazabiphenylenes. 1,2,4-Benzotriazines also gave benzyne but only at temperatures above 800°; quinazoline, phthalazine, 2,3-diphenylquinoxaline, and 2-methyl-3,1-benzoxazin-4-one were unchanged at this temperature.

OVER the last few years the chemistry of cyclobutadiene (1), the classic antiaromatic 4 π hydrocarbon, has been extensively studied,^{2,3} particularly since its stabilisation by formation of complexes with metals was developed.⁴ It is a highly reactive, transient species. However its di-benzo-derivative, biphenylene (2) is extremely stable, although single benzo-fusion has led to cyclobutadiene derivatives sufficiently stable for isolation only in the cases of the dibromo- and diphenyl-naphthocyclobutenes† (3; R = Br or Ph).⁵

Although the formally antiaromatic oxirens, thiirens, and 1*H*-azirines (4; X = O, S, or NR) have been



postulated as reaction intermediates⁶ no closer 4 π -heterocyclic analogues of cyclobutadiene have been produced.† Several early reports of the azete (azacyclobutadiene) system (5) have been shown to be incorrect⁷ and recently a promising attempt to generate an azete by retro-Diels-Alder reaction of an apparently ideal precursor (6) failed.⁸

Triphenylazete (7) has been suggested, though without supporting evidence, as a possible reactive intermediate in the photolysis of the triazafulvenes (8) and (9).⁹

A negative resonance energy of 15.5 kcal mol⁻¹ has been calculated for azete.¹⁰ This is somewhat less than that for cyclobutadiene (-18 kcal mol⁻¹)³ but sufficiently large to allow the prediction that azacyclobutadiene would exist only as an extremely reactive, transient species. The generation of azetes is thus of both considerable theoretical and potential synthetic interest.

† *Editor's note.* In accord with IUPAC/*Chemical Abstracts* recommendations for fusion nomenclature, the termination '-cycloalkene' as used here implies *maximum* unsaturation of the whole of a fused polycyclic skeleton. However, names such as 'benzocyclobutene', 'naphthocyclobutene', 'dibenzocyclo-octene', etc. have been employed frequently in the literature to refer to structures in which the 'cycloalkene' unit contains only one formal double bond.

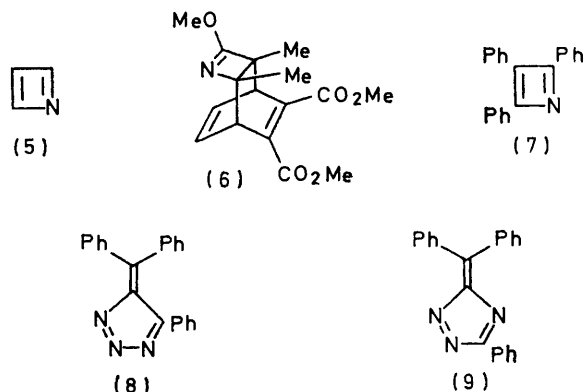
‡ Tris(dimethylamino)azete has been reported very recently: G. Seybold, U. Jersak, and R. Gompper, *Angew. Chem. Internat. Edn.*, 1973, **12**, 847.

¹ Preliminary communication, S. Bradbury, M. Keating, C. W. Rees, and R. C. Storr, *Chem. Comm.*, 1971, 827.

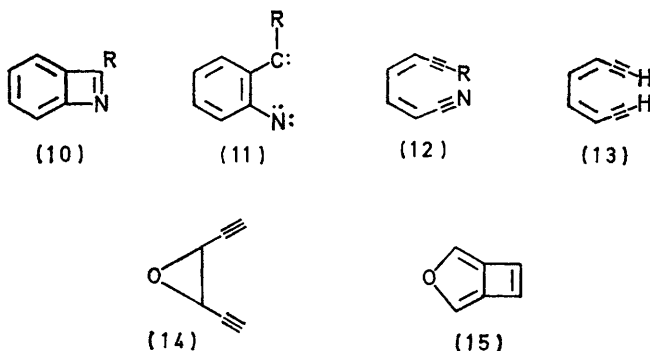
² M. P. Cava and M. J. Mitchell, 'Cyclobutadiene and Related Compounds,' Academic Press, New York, 1967; for further references see reference 6 in reference 3.

³ M. J. S. Dewar, M. C. Kohn, and N. Trinajstić, *J. Amer. Chem. Soc.*, 1971, **93**, 3437.

We chose to attempt the generation of a benzazete (10) where benzo-fusion should impart some stabilisation to



the system. Our initial approach involved the generation of species having the *o*-carbenophenylnitrene constitution (11) in the hope that these would collapse either



directly, or *via* the cyano-acetylene (12), to benzazete. This hope was fostered by the spontaneous and rapid formation of benzocyclobutene from the diacetylene (13).¹¹ Further precedent for this type of reaction comes

⁴ L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Amer. Chem. Soc.*, 1965, **87**, 3253.

⁵ 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.

⁶ M. J. S. Dewar and C. A. Ramsden, *J.C.S. Chem. Comm.*, 1973, 688, and references therein.

⁷ See S. A. Ballard and D. S. Melstrom in 'Heterocyclic Compounds,' vol. I, ed. R. C. Elderfield, Wiley, New York, 1960, p. 78.

⁸ T. Kakihana, J. F. Kelly, and L. A. Paquette, *J. Org. Chem.*, 1971, **36**, 435.

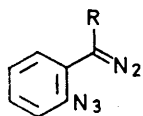
⁹ E. M. Burgess and J. P. Sanchez, *J. Org. Chem.*, 1973, **38**, 176.

¹⁰ M. J. S. Dewar and N. Trinajstić, *Theor. Chim. Acta*, 1970, **17**, 235.

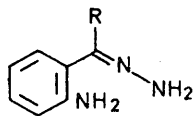
¹¹ G. H. Mitchell and F. Sondheimer, *J. Amer. Chem. Soc.*, 1969, **91**, 7520.

from the recent report of the formation of cyclobuta[*c*]-furan (15) from the diyne (14).¹²

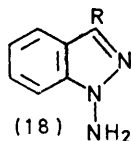
In the event, the obvious precursors to species with the desired constitution (11) did not extrude sufficient nitrogen and collapsed instead to 1,2,3-benzotriazines. Thus in the preceding paper¹³ we described how thermolysis of diazo-azides (16), oxidation of amino-hydrazones (17), and oxidation of 1- (18) and 2-aminoindazoles (19) provided valuable new synthetic entries into the 1,2,3-benzotriazine system (20). The diazo-azide (16; R = Me) on pyrolysis in bis-(2-methoxyethyl) ether did give a trace of cyano-acetylene (12; R = Me) but in insufficient quantity to be of further use.



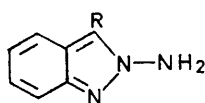
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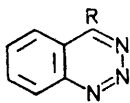
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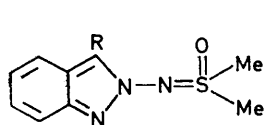
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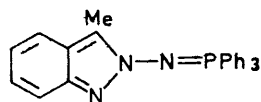
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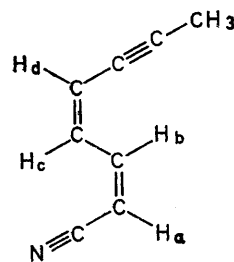
(21)



(22)

It was apparent, therefore, that the precursors of the carbononitrene (11) would have to be produced under conditions where more extensive fragmentation was facilitated. For example, the nitrenes derived from 1- and 2-aminoindazoles could well break down further at high temperature. In other systems we have shown that high temperature, low-pressure, vapour-phase pyrolysis of sulphoximides is a convenient source of 'hot' heterocyclic *N*-nitrenes.¹⁴ The sulphoximides (21; R = H or Me) were obtained in 10 and 50% yield, respectively, by oxidation of the 2-aminoindazoles (19; R = H and Me) with lead tetra-acetate in dimethyl sulphoxide (DMSO). None of the analogous indazol-1-ylsulphoximides were obtained since competing ring expansion to give 1,2,3-benzotriazines occurred exclusively with the 1-aminoindazoles.

Pyrolysis of the sulphoximide (21; R = Me) by sublimation through an oven maintained at 450° and 0.01 Torr gave a mixture of DMSO, biphenylene, and the cyano-acetylene (12; R = Me) on the solid CO₂-acetone-cooled receiver. The cyano-acetylene (12; R = Me) was a stable, colourless oil; its *cis,cis*-configuration was



(12; R = Me)

indicated by the presence of an intense i.r. absorption at 745 cm⁻¹ and the absence of appreciable absorption in the vicinity of 990 cm⁻¹. The n.m.r. spectrum (solvent carbon tetrachloride) was complex but first-order analysis gave values of 11.0—11.5 Hz for *J*_{a,b} and *J*_{c,d}. These values are consistent with a *cis,cis*-configuration and compare favourably with *J*_{a,b} (11.2 Hz) observed for the corresponding *cis,cis*-dicyanide.¹⁵ Similar pyrolysis of the sulphoximide (21; R = H) gave DMSO, biphenylene in lower yield, and the cyano-acetylene (12; R = H). This cyanoacetylene was isolated as an unstable oil which crystallised as yellow needles, m.p. 60—63°, but slowly polymerised. I.r. and n.m.r. spectroscopy again indicated a *cis,cis*-configuration.

The biphenylene formed in these two pyrolyses was unexpected, and was presumably formed by dimerisation of benzyne. The latter probably originates from competitive ring expansion of the indazole nitrenes, even at this high temperature, to give vibrationally excited benzotriazine which then undergoes complete fragmentation (see later). Significantly no benzotriazines were observed in either pyrolysis. A second, though perhaps less likely possibility is that the nitrene extrudes nitrogen and collapses to the benzazete which then undergoes fragmentation.

Iminophosphoranes, *e.g.* (22), were also considered as a further high temperature source of indazolynitrenes. The iminophosphorane from 2-amino-3-methylindazole was prepared by the general method of Bestmann¹⁶ (treatment of the amino-compound with triphenylphosphine dibromide in the presence of triethylamine). Vacuum pyrolysis at 700° gave triphenylphosphine and the cyano-acetylene (12; R = Me). While this route to

nitrenes requires higher temperatures and has not yet been further explored, it holds considerable potential for those cases where sulphoximides are not available from oxidation of the *N*-amines in DMSO.

Despite considerable effort no evidence was obtained for the isomerisation of the cyano-acetylenes to benzazetes. The methyl-substituted cyanoacetylene (12; R = Me) was recovered after heating overnight in refluxing benzene. Heating in the presence of reagents such as tetraphenylcyclopentadienone, water, and phenylhydrazone produced none of the products expected from

¹² R. G. Bergman, *Accounts Chem. Res.*, 1973, **6**, 25.

¹³ B. M. Adger, S. Bradbury, M. Keating, C. W. Rees, R. C. Storr, and M. T. Williams, preceding paper.

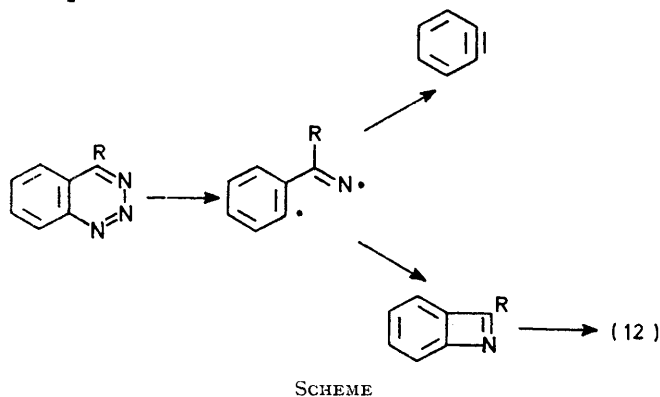
¹⁴ D. J. Anderson, T. L. Gilchrist, D. C. Horwell, C. W. Rees, and E. Stanton, *J.C.S. Perkin I*, 1972, 1317.

¹⁵ J. A. Elvidge and P. D. Ralph, *J. Chem. Soc. (C)*, 1966, 387; J. H. Hall and E. Patterson, *J. Amer. Chem. Soc.*, 1967, **89**, 5856.

¹⁶ H. J. Bestmann and H. Fritzsche, *Chem. Ber.*, 1961, **94**, 2477.

a benzazete, which should be a reactive dienophile and a reactive imine. Although the unsubstituted cyanoacetylene was less stable and polymerised, similar trapping experiments gave no evidence for benzazete formation.

In view of our failure to obtain benzazetes *via* cyanoacetylenes (12) and/or carbeno-nitrenes (11) we next turned our attention to 1,2,3-benzotriazines as precursors. In this case, the most likely mode for loss of nitrogen would lead to a species which could only fragment further or collapse to the stable cyanoacetylene (12) *via* a benzazete (Scheme). The mass spectra of 1,2,3-benzotriazines showed intense peaks corresponding to losses of N₂ and RCN.



Complete fragmentation of the triazine ring to give benzyne occurs above the relatively low temperature of 500° and provides a route to biphenylene. This is illustrated in the Table, which also summarises our

Vapour-phase flash pyrolyses^a

	Oven temp (°C)	% Bi-phenylene
1,2,3-Benzotriazine	500	42
4-Methyl-1,2,3-benzotriazine ^b	420–450	60
4-Phenyl-1,2,3-benzotriazine ^c	500	55
6-Chloro-4-phenyl-1,2,3-benzotriazine	420–450	40 ^d
1,2,4-Benzotriazine	850	20
3-Methyl-1,2,4-benzotriazine	870	45
3-Phenyl-1,2,4-benzotriazine	870	40

^a Quinazoline, phthalazine, and 2,3-diphenylquinoxaline were recovered unchanged from pyrolysis at 800°. 2-Methyl-3,1-benzoxazin-4-one was recovered unchanged at 800° and gave a complex mixture at 1000°; similar results have been reported by other workers who found that the isomeric 4-substituted 2,3-benzoxazin-1-ones did give biphenylene: M. P. David and J. F. W. McOmie, *Tetrahedron Letters*, 1973, 1361. 6-Methylpyrido[3,2-*d*][1,2,3]triazine gave 6-methylpyridine-2-carbonitrile. ^b Recovered triazine (30%). ^c For other products formed in this pyrolysis see ref. 22. ^d A mixture of 2,6- and 2,7-dichlorobiphenylene.

vacuum pyrolysis studies of other aza-heterocycles; the superiority of 1,2,3-benzotriazines is obvious. This is particularly apparent on comparison with the isomeric 1,2,4-benzotriazines.

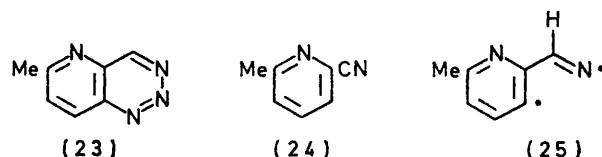
The first indications that one molecule of nitrogen could be selectively extruded from a 1,2,3-benzotriazine

¹⁷ J. M. Kramer and R. S. Berry, *J. Amer. Chem. Soc.*, 1971, **93**, 1303.

¹⁸ J. A. H. MacBride, *J.C.S. Chem. Comm.*, 1974, 359.

¹⁹ E.-G. Bartsch, A. Golloch, and P. Sartori, *Chem. Ber.*, 1972, **105**, 3463.

molecule came from studies of the pyrolysis of pyridotriazines as a possible route to azabiphenylenes *via* the gas-phase dimerisation of didehydropyridines. At the outset of this work no azabiphenylenes had been reported but since then examples have been produced by the vapour-phase photolysis of pyridinediazonium-carboxylate,¹⁷ by the high-temperature vapour-phase pyrolysis of 2,7,9,10-tetra-azaphenanthrene,¹⁸ and by pyrolysis of the silver salt of 2,5,6-trifluoropyridine-3,4-dicarboxylic acid.¹⁹ At high temperature the pyridine ring undergoes fragmentation²⁰ and at low temperature in solution pyridynes are so reactive towards nucleophiles that dimerisation is not observed.²¹ The moderate temperatures required for decomposition of benzotriazines therefore seemed ideal. The pyridotriazine (23) was the only such derivative that we were able to obtain, for reasons outlined in the preceding paper. On vapour-phase pyrolysis, no trace of a diazabiphenylene was obtained and the cyanopyridine (24), formed by loss of nitrogen only, was the sole product isolated over a wide range of temperatures (350–700°). This can be rationalised in terms of hydrogen migration in an intermediate such as (25) although collapse to a pyridozete followed by re-arrangement cannot be entirely discounted.



Pyrolysis of a 4-substituted benzotriazine would lead to an intermediate in which collapse to a nitrile is not possible and benzazete formation is therefore more likely. This hope was successfully realised with 4-phenylbenzotriazine. Pyrolysis above 450° gave only benzyne and thence biphenylene by complete fragmentation of the triazine ring. However when the pyrolysis was carried out at 420–450° a dark red deposit was observed on the cold finger at –80°. The major component of this deposit was 2-phenylbenzazete. Evidence for its structure, and a detailed description of the chemistry of this, the first heterocyclic derivative of cyclobutadiene,¹ is presented in the following paper.²²

EXPERIMENTAL

For general comments see preceding paper. Vapour-phase pyrolyses were carried out using the apparatus described in detail previously.¹⁴

SS-Dimethyl-N-(3-methylindazol-2-yl)sulphoximide (21; R = Me).—2-Amino-3-methylindazole (2.25 g, 15 mmol) in dry dimethyl sulphoxide (10 ml) was added dropwise to a stirred solution of lead tetra-acetate (7.5 g, 17 mmol) in dry dimethyl sulphoxide (50 ml). The solution was stirred vigorously for 0.75 h, then poured into water (250 ml) and extracted with ethyl acetate (3 × 75 ml). The combined extracts were washed thoroughly with water (4 × 200 ml),

²⁰ M. P. Cava, M. J. Mitchell, D. G. DeJongh, and R. Y. Van Fossen, *Tetrahedron Letters*, 1966, 2947.

²¹ G. W. J. Fleet and I. Fleming, *J. Chem. Soc. (C)*, 1969, 1758; G. W. J. Fleet, I. Fleming, and D. Philippides, *ibid.*, 1971, 3948.

²² B. M. Adger, C. W. Rees, and R. C. Storr, following paper.

dried (Na_2SO_4), and evaporated, and the residue was chromatographed on silica gel. Elution with 10% ethanol-ether gave the *sulphoximide* (1.7 g, 50%) which crystallised from cyclohexane as needles, m.p. 107–108° (Found: C, 53.6; H, 5.8; N, 18.6. $\text{C}_{10}\text{H}_{13}\text{N}_3\text{OS}$ requires C, 53.8; H, 5.9; N, 18.8%), ν_{max} 1218, 1198, 1025, and 740 cm^{-1} , λ_{max} 228 (log ϵ 4.26), 284 (3.95), 306 (3.88), and 322sh nm, τ (CDCl_3) 2.35–3.05 (4H, m, aromatic), 6.64 (6H, s, SMe), and 7.42 (3H, s, CMe), *m/e* 223 (M^+).

N-(*Indazol-2-yl*)-*SS*-*dimethylsulphoximide* (21; R = H).—Oxidation of 2-aminoindazole in dimethyl sulphoxide by the above procedure gave the *sulphoximide* (10%). This was eluted from the silica gel column with ether and crystallised from benzene-petroleum as pale yellow plates, m.p. 138–140° (Found: C, 51.5; H, 5.2; N, 19.7; S, 12.2. $\text{C}_8\text{H}_{11}\text{N}_3\text{OS}$ requires C, 51.7; H, 5.3; N, 20.1; S, 11.5%), ν_{max} 1625, 1195, 1010, and 745 cm^{-1} , τ (CDCl_3) 2.20 (1H, s, 3-H), 2.20–3.10 (4H, m, aromatic), and 6.70 (6H, s, SMe), *m/e* 209 (M^+).

All attempts to obtain sulphoximides from 1-amino-3-methyl- and -3-phenylindazoles failed: only the 1,2,3-benzotriazines were obtained.

Pyrolysis of the Sulphoximide (21; R = Me).—The sulphoximide was sublimed at 180° and 0.1 Torr through an oven maintained at 450° to give a pale yellow solid deposit on the solid CO_2 -acetone-cooled receiver. On warming to room temperature this deposit melted to give a red oil which was subjected to preparative t.l.c. on silica gel. Elution with petroleum-ether (3 : 1) gave (at R_F 0.8) biphenylene (4 mg, 16%), m.p. and mixed m.p. 110°, and (at R_F 0.6) *cis,cis*-*octa-2,4-dien-6-yne*nitrile (12; R = Me) (24 mg, 41%) as an oil, m.p. 15° (Found: C, 81.9; H, 6.4; N, 11.9. $\text{C}_8\text{H}_7\text{N}$ requires C, 81.2; H, 6.0; N, 11.9%), ν_{max} 2200 ($\text{C}\equiv\text{N}$), 1600 ($\text{C}=\text{C}$ stretch of diene), 1350, 1239, and 745 (*cis*-disubstituted alkene) cm^{-1} , τ (CCl_4) 2.73 [1H, t, J 11.5 Hz, C(3)H], 3.24br [1H, t, J 11.5 Hz, C(4)H], 4.22 [1H, dm, J 11 Hz, C(5)H], 4.78br (1H, d, J 11 Hz, C(2)H), and 7.96 (3H, d, J 2 Hz, CH_3), *m/e* 117 (M^+). Decoupled ^1H n.m.r. spectra indicate that the proton absorbing at τ 4.22 is coupled to the terminal methyl group, hence its assignment as C(5)H. The absorption at τ 3.24 is also broadened relative to that at τ 2.73 suggesting that the corresponding proton is also coupled to the terminal methyl group. It is therefore assigned to C(4)H.

Pyrolysis of the Sulphoximide (21; R = H).—Similar pyrolysis of this sulphoximide at 500° gave two products which were separated by preparative t.l.c. on silica gel. Elution with ether-petroleum (1 : 3) gave (at R_F 0.8) biphenylene (trace) and (at R_F 0.65) *cis,cis*-*hepta-2,4-dien-6-yne*nitrile (12; R = H) as an oil which crystallised to give pale yellow needles, m.p. 60–63°, ν_{max} 3200 (alkyne C–H stretch), 3050, 2200 ($\alpha\beta$ -unsaturated $\text{C}\equiv\text{N}$ stretch), 2080 (monosubstituted $\text{C}\equiv\text{C}$ stretch), 1600 ($\text{C}=\text{C}$ stretch of diene), 1350, 1235, 1195, 945, 750, 720 (*cis*-disubstituted alkene), and 680 cm^{-1} , τ (CCl_4) 2.80 [1H, t, J 11 Hz, C(3)H], 3.07 [1H, t, J 11 Hz, C(4)H], 4.18 [1H, dt, J 11 and 3 Hz, C(5)H], 4.66br [1H, d, J 11 Hz, C(2)H], and 6.66 (1H, d, J 3 Hz, C(7)H]. This compound decomposes to give a polymer at room temperature within 12 h.

Thermolysis of 1-(o-Azidophenyl)-1-diazoethane (16).—The diazo-azide (800 mg) in petroleum was added slowly to refluxing bis-(2-methoxyethyl)ether (20 ml). A violent reaction occurred with vigorous evolution of gas. The mixture was heated at 180° for 10 min, cooled, poured into water (200 ml), and extracted with ether (2 \times 25 ml). The extracts

were washed with water, dried (Na_2SO_4) and evaporated. The residue was subjected to preparative t.l.c. on silica gel with petroleum-ether (3 : 1) to give the nitrile (12; R = Me) (20 mg, 3%) identical with that obtained from the sulphoximide (21; R = Me).

3-Methylindazol-2-ylimino(triphenyl)phosphorane (22).—A solution of bromine (800 mg, 5 mmol) in benzene was added to a stirred solution of triphenylphosphine (1.3 g, 5 mmol) in benzene, the temperature being maintained between 0 and 5°, to give a precipitate of triphenylphosphine dibromide. A solution of triethylamine (1.0 g, 10 mmol) and 2-amino-3-methylindazole (735 mg, 5 mmol) in benzene was then added and the mixture was stirred at 80° for 45 min, cooled, and filtered. The filtrate was evaporated, and the residue was chromatographed on silica gel. Elution with ether gave the *iminophosphorane* (1.5 g, 75%) as yellow needles (from cyclohexane), m.p. 116–117° (Found: C, 76.7; H, 5.4; N, 10.1. $\text{C}_{26}\text{H}_{22}\text{N}_3\text{P}$ requires C, 76.7; H, 5.4; N, 10.3%), ν_{max} 1200, 1100, 980, 815, 737, 700, and 680 cm^{-1} , λ_{max} 229 (log ϵ 4.55) and 299 nm (4.06), τ (CDCl_3) 2.0–3.1 (19H, m, aromatic) and 7.44 (3H, s, CH_3), *m/e* 407 (M^+).

Pyrolysis of the Iminophosphorane (22).—The iminophosphorane (250 mg) was sublimed at 220–230° and 0.01 Torr through an oven maintained at 700° to give a yellow solid on the solid CO_2 -acetone-cooled receiver. On warming to room temperature the pyrolysate melted to a pale yellow oil which was subjected to preparative t.l.c. on silica gel with petroleum-ether (3 : 1). This gave (at R_F 0.8) triphenylphosphine (50 mg, 32%), m.p. and mixed m.p. 80°, and (at R_F 0.6) the nitrile (12; R = Me) (25 mg, 32%), identical with that obtained from the sulphoximid (21; R = Me).

Attempted Isomerisation of the Cyano-acetylene (12; R = Me) to 2-Methylbenzazete.—(a) The cyano-acetylene was recovered unchanged from refluxing in benzene, or chlorobenzene, after 12 h.

(b) T.l.c. showed no evidence of reaction between the cyano-acetylene and 2,3,4,5-tetraphenylcyclopentadienone in refluxing benzene over 8 h. The reactants were recovered unchanged.

(c) The cyano-acetylene was recovered unchanged from its solution in bis-(2-methoxyethyl) ether (5 ml) containing water (0.5 ml) after refluxing for 12 h.

(d) The cyano-acetylene was recovered unchanged from refluxing in benzene containing phenylhydrazine.

A similar set of experiments was carried out with the nitrile (12; R = H). This compound was prone to polymerisation and no recognisable products were isolated.

Pyrolyses of 1,2,3-Benzotriazines and Related Heterocycles.—1,2,3-Benzotriazines were obtained as described in the preceding paper,¹³ 1,2,4-benzotriazines by oxidation of *N*-aminoquinoxalin-2-ones,²³ and other heterocycles by literature methods. Pyrolyses were carried out by sublimation (*ca.* 150 mg samples) under reduced pressure (*ca.* 10^{-1} Torr) through a hot oven. Products were collected on a solid CO_2 -acetone-cooled receiver. Biphenylene was isolated by column or preparative thin-layer chromatography and identified by comparison with an authentic specimen. Yields and oven temperatures are given in the Table.

Characterisation of other pyrolysis products from 4-phenyl- and 6-chloro-4-phenyl-benzotriazine is described in the following paper.²² 6-Methylpyrido[3,2-*a*][1,2,3]triazine²⁴ required a high sublimation temperature and considerable charring occurred. The pyrolysate was dissolved

²³ B. M. Adger, C. W. Rees, A. A. Sale, and R. C. Storr, *Chem. Comm.*, 1971, 695.

in ether and concentrated to give 6-methylpyridine-2-carbonitrile (37%), m.p. and mixed m.p. 72—73° (lit.,²⁴ 72—72.5°), identical with a sample obtained²⁵ from 2-amino-6-methylpyridine.

²⁴ R. F. Knott and J. G. Breckenridge, *Canad. J. Chem.*, 1954, **32**, 512.

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²⁵ F. H. Case and T. J. Kasper, *J. Amer. Chem. Soc.*, 1956, **78**, 5842.
