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Formation of Biphenylenes by Thermal Extrusion of Molecular Nitrogen from Benzo[c]cinnolines

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Summary Vacuum pyrolysis of benzo[c]cinnoline or its octachloro-derivative gives the corresponding biphenylene in high yield.

THERMAL and photochemical extrusion of molecular nitrogen from alicyclic azo-compounds, giving products derived from the resulting diradicals, is well documented.¹ The isolation of simple products from extrusion of the nitrogen atoms of an aromatic 1,2-diazine system, has not, however, been reported. Although this fragmentation mode has attracted considerable interest in the mass spectra of pyridazines,² thermal or photochemical excitation of pyridazine derivatives has led, hitherto, to rearrangement³ rather than extrusion of nitrogen.



Vacuum pyrolysis of (1; X = H) through a silica tube at ca. 870°, 0.2 torr, gives (3; X = H) in 70% yield (allowing for unchanged material, conversion ca. 60%). Similarly (1; X = Cl), † m.p. 293–295°, obtained by chlorination of (1; X = H) in the presence of aluminium trichloride, gives (3; X = Cl)[†] in high yield (> 80% with complete conversion) at ca. 700°, 0.2 torr.

Biphenylene (3; X = H), m.p. 110-111.5°, was readily identified from published spectra.4,5 Octachlorobiphenylene (3; X = Cl) was obtained as yellow needles (from

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benzene) m.p. 312-313.5° (with sublimation but not decomposition); lit.^{6,7} "yellowish-green," m.p. $292-294^{\circ}$ (decomp.) and $296-298^{\circ}$. The u.v. spectrum of (3; X = Cl) is similar to that published^{6,7} but bands reported at 428 and 452 nm are absent. The initial product of pyrolysis of (1; X = Cl) darkens during a more prolonged experiment (apparently due to heat from the furnace) and acquires a green tinge which could not be removed by recrystallisation or t.l.c. on silica; physical data for this impure material are in close agreement with the literature^{6,7} (u.v.) and with those of a sample of (3; X = Cl) prepared by pyrolysis⁷ of tetrachlorophthalic anhydride (i.r.).

The high yields of biphenylenes, and relative absence of by-products, observed in the pyrolysis of (1; X = H or Cl)suggest that these reactions occur via the diradicals (2: X = H or Cl) and not by fragmentation to benzynes (5: X = H or Cl), followed by recombination. In contrast the formation of biphenylenes by pyrolysis of the corresponding phthalic anhydrides $(4)^{6,7}$ or of indanetrione $(6),^5$ involving bimolecular reactions of the benzynes, give at best 40% yield (at the same temperature and pressure in the case of the octachloro-compound and at considerably lower temperature for the parent compound).

The markedly lower temperature needed to extrude nitrogen from the octachloro-compound (1; X = Cl) compared with the parent compound (1; X = H) is consistent with the severe steric interaction between the chlorine atoms at positions 4 and 5 (phenanthrene numbering) which would be expected to twist the molecule out of plane and reduce the aromatic stabilisation energy of the heterocyclic ring.

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† Correct analyses and mass spectra have been obtained for these compounds; the author thanks the staff of the Chemistry Department, University of Durham, for the determinations.

¹ E. g. E. L. Allred and J. C. Hirsham, Tetrahedron Letters, 1972, 387, and references therein. ² M. H. Benn, T. S. Sorensen, and A. M. Hogg, Chem. Comm., 1967, 574; S. J. Weininger and E. R. Thornton, J. Amer. Chem. Soc., 1967, 89, 2050; J. R. Elkins and E. Y. Brown, J. Heterocyclic Chem., 1968, 639; J. H. Bowie, G. E. Lewis, and J. A. Reiss, Austral. J. Chem., 1968, 21, 1233.

⁸C. G. Allison, R. D. Chambers, Yu. A. Cheburkov, J. A. H. MacBride, and W. K. R. Musgrave, *Chem. Comm.*, 1969, 1200; R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, *ibid.*, 1970, 739; D. W. Johnson, V. Austel, R. S. Feld, and D. M. Lemal, *J. Amer. Chem. Soc.*, 1970, 92, 7505; R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, *J. Chem. Soc.* (C), 1971, 3384.
 ⁴C. G. Cannon and G. B. B. M. Sutherland, Spectrochim. Acta, 1951, 373.
 ⁵D. F. C. Drawn and B. W. Schler And L. Chem. 100(100), 100 (2010).

⁵ R. F. C. Brown and R. K. Solly, Austral. J. Chem., 1966, 19, 1045.
⁶ P. Cava, M. J. Mitchell, D. C. De Jongh, and R. Y. Van Fossen, Tetrahedron Letters, 1966, 2947.
⁷ R. F. C. Brown, D. V. Gardner, J. F. W. McOmie, and R. K. Solly, Austral. J. Chem., 1967, 20, 139.