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

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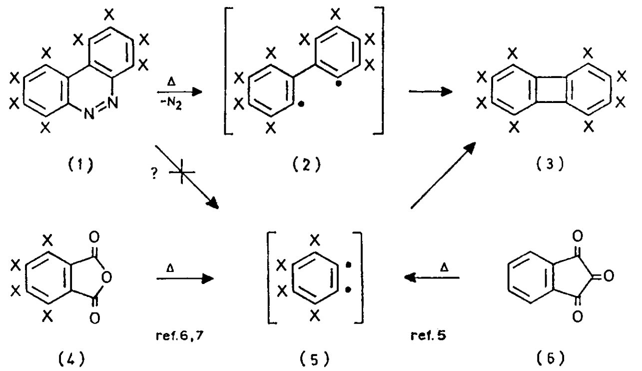
Summary Vacuum pyrolysis of benzo[*c*]cinnoline or its octachloro-derivative gives the corresponding biphenylene in high yield.

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 rearrangement[3] 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 benzene) m.p. 312—313·5° (with sublimation but not decomposition); lit.[6,7] "yellowish-green," m.p. 292—294° (decomp.) and 296—298°. 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 pyrolysis[7] 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.

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