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SYNTHESIS OF THE MONOAZABIPHENYLENES

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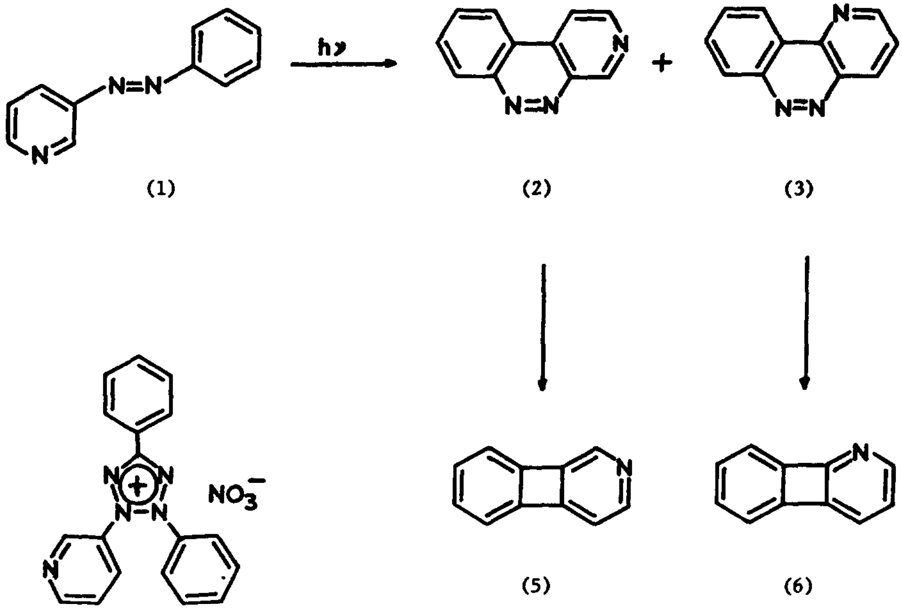
Few simple aza-analogues of biphenylene are known. Hünig and Putter[1] obtained a mixture of hexafluoro-2,6- and -2,7-diazabiphenylenes by pyrolysis of the disilver salt of 2,5,6-trifluropyridine-3,4-dicarboxylic acid and an unsubstituted diazabiphenylene has been isolated as a product of dimerisation of 3,4-pyridyne in the gas phase;[2] this is known to be 2,6-diazabiphenylene as the 2,7-isomer has recently been prepared by thermal extrusion of nitrogen from 2,7,9,10-tetra-azaphenanthrene.[3] The latter report prompts us to communicate the results of our work on the synthesis of 1- and 2-azabiphenylene, (5) and (6), the chemistry of which we are currently studying. Previously there have been unsuccessful attempts to prepare monoazabiphenylenes by the reaction of 2,3- and 3,4-pyridynes with benzyne in solution,[4] and by the Lothrop-type cyclisation of o,o'-dihalogenophenylpyridines.[5]

As an approach to possible triazaphenanthrene precursors of (5) and (6) we investigated the oxidative photocyclisation of the monophenylazopyridines, analogous to the known photocyclisation of certain azobenzenes to benzo[c]cinnoline derivatives.[6] Irradiation of a 1% solution of 3-phenylazopyridine (1) in concentrated sulphuric acid at 400-450 nm for 72 hr gave, on neutralisation, 2,9,10-triazaphenanthrene (2) (19%), m.p. 213-214°C, together with the 4,9,10-isomer (3) (3%), m.p. 161-163°C. As far as we are aware this is the first example of the photocyclisation of a heterocyclic azocompound,[7] although recently it has been reported that phenylpyridylazomethines cyclise to diazaphenanthrenes under similar conditions.[8] These structural assignments, made on the basis of the ^{1}H N.M.R. spectra of



(1) (2) (3)

(4) (5) (6)

(2) and (3), are consistent with those of the derived thermal extrusion products (5) and (6) vide infra. The minor product (3) is identical with that previously obtained by oxidative photocyclisation and subsequent reductive scission of the tetrazolium salt (4);[9] re-investigation of this sequence has confirmed that (3) is the only triazaphenanthrene formed.

Vacuum thermolysis of (2) by slow sublimation through a 1 metre silica tube at 800°C, ∿0.05 torr gave, after preparative T.L.C. on silica gel in methylene chloride to remove unchanged (2), pale yellow 2-azabiphenylene (5) (58%), m.p. 88.5-89.5°C; M^+ 153; λ_{max}(EtOH)

241 (log ε 3.73), 248.5 (3.90), 318 (3.22), 331 (3.43) and 345.5 nm (3.49). Similarly, vacuum thermolysis of (3) gave colourless 1-azabiphenylene (6) (34%), m.p. 70-71°C; M^+ 153; λ_{max}(EtOH) 230 (log ε 4.27), 236 (4.29), 264 (3.84), 344 (3.66) and 358 nm (3.73). Both (5) and (6) exhibit characteristic biphenylene-type U.V. spectra; in their mass spectra the parent ions are the base peaks and prominent peaks at 126 indicate the loss of HCN, although in the case of (6) initial loss of C_2H_2 appears to be the major process. The ^1H N.M.R. spectrum of (5) in deuteriochloroform shows three resonances due to single protons of the pyridine ring at δ 8.16 (broad doublet, H_3), 7.75 (broad singlet, H_1) and 6.60 (doublet of doublets, H_4) with $J_{1,4}$ = 1.40 and $J_{3,4}$ = 4.50 cps, and a four-proton multiplet at δ 6.84 due to the ABCD system (H_{5-8}) of the benzene ring. The chemical shifts of the protons of the pyridine moiety show close correspondence with those reported for 2,7-diazabiphenylene.[3] The spectrum of (6) shows a four-proton multiplet at δ 6.87 (H_{5-8}) together with three single-proton doublets of doublets at δ 7.66 (H_2), 6.73 (H_4) and 6.51 (H_3), with $J_{2,3}$ = 5.9, $J_{3,4}$ = 6.9 and $J_{2,4}$ = 1.5 cps respectively. Irradiation of the lowfield signal at δ 7.66 causes collapse of the other two doublets of doublets to simple doublets having the same coupling constant (6.9 cps). For comparison purposes 1,8-diazabiphenylene, m.p. 156.5-158.5°C, was prepared (24% yield) by thermolysis of the known 1,5,6,10-tetra-azaphenanthrene[10] at 800°C; its ^1H N.M.R. spectrum consists of three doublets of doublets at δ 7.91 (H_2,H_7), 6.99 (H_4,H_5) and 6.68 (H_3,H_6), with $J_{2,3}$ = 5.9, $J_{3,4}$ = 7.0 and $J_{2,4}$ = 1.0 cps respectively.

Experiments are in progress to extend this route to the synthesis of other heterocyclic analogues of biphenylene.

References

1. S. Hünig and H. Putter, Angew. Chem. Intern. Edn., 1972, 11, 433.

2. J. Kramer and R.S. Berry, J. Amer. Chem. Soc., 1972, 94, 8336.

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

4. J.W. Barton and A.R. Grinham, unpublished results, c.f.
G.W.J. Fleet and I. Fleming, J. Chem. Soc. (C), 1969, 1758.

5. D.R. Preston, Ph.D. Thesis, University of Bristol, 1960.

6. N.C. Jamieson and G.E. Lewis, Austral. J. Chem., 1967, 20, 321, and earlier papers.

7. The photoreactions of 2- and 4-phenylazopyridines under these conditions will be described in a forthcoming paper.

8. H.H. Perkampus and B. Behjati, J. Heterocyclic Chem., 1974, 11, 511.

9. D. Jerchel and H. Fischer, Chem. Ber., 1956, 89, 563.

10. A. Etienne and J. Izoret, Fr. Pat. No. 1,369,401; Chem. Abs., 1965, 62, 570g.