Hexafluorocinnoline: Synthesis and Photochemical Isomerisation to Hexafluoroquinazoline

By R. D. CHAMBERS,* J. A. H. MACBRIDE, and W. K. R. MUSGRAVE
(*Department of Chemistry, The University, South Road, Durham*)

Summary Hexafluorocinnoline has been prepared from hexachlorocinnoline and isomerised to hexafluoroquinazoline by u.v. irradiation.

RECENTLY we showed[1] that tetrafluoropyridazine and its perfluoroalkyl derivatives isomerise thermally to pyrimidines and photochemically to pyrazines, and we have suggested the intermediacy of diaza-analogues of benzvalene and of prismane to account for these rearrangements. We now report the photochemical isomerisation of hexafluorocinnoline (**5**) to hexafluoroquinazoline (**3**; R=F), which probably involves the novel valence isomerisation of a benzodiazine.

Hexafluorocinnoline (**5**) has not been previously described while hexafluorophthalazine[2] and the potential re-arrangement products hexafluoroquinazoline[3] (**3**; R=F) and hexafluoroquinoxaline[4] have already been prepared in our laboratory. Hexafluorocinnoline (**5**) was obtained by the following sequence: the known 7,8-dichloro-4-hydroxycinnoline (**1**) X=OH, Y=H)[5,6] with sulphuryl chloride and acetic anhydride in acetic acid[7] gave 3,7,8-trichloro-4-hydroxycinnoline† (**1**; X=OH, Y=Cl), m.p. 323—325°, which was converted into 3,4,7,8-tetrachlorocinnoline (**1**; X=Y=Cl), m.p. 253—254·5°, with phosphorus pentachloride in phosphoryl chloride, and then into hexachlorocinnoline (**2**), m.p. 188—190°, λ_{max} (cyclohexane) 225, 260·5,

† Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds mentioned.

302 infl., 315·5, 327·5, 356, and 361 nm, with chlorine and aluminium trichloride. Fluorination of hexachlorocinnoline with potassium fluoride, under conditions similar to those used to obtain hexafluorophthalazine,[2] gave hexafluorocinnoline (**5**), m.p. 100—102°, λ_{max} (cyclohexane) 225, 274, 282, 294, and 330 nm. Hexafluorocinnoline reacted rapidly with atmospheric moisture giving 4-hydroxypentafluorocinnoline (**4**; R=OH), m.p. 226—228°, and with aqueous ammonia giving the 4-amino-derivative (**4**; R=NH_2), m.p. 179—181°. 5-Chloropentafluorocinnoline, m.p. 98—100°, λ_{max} (cyclohexane) 229, 273 infl., 286, 296·5, and 332·5 nm. was isolated by preparative g.l.c. as a by-product of fluorination.

Irradiation of hexafluorocinnoline at *ca.* 100° in an evacuated quartz tube with an unfiltered medium-pressure mercury lamp slowly produced a mixture of volatile products and an involatile black tar. The volatile material was treated with aqueous ammonia, the resulting mixture of amino-derivatives was analysed by t.l.c. on silica, and shown to contain 4-aminopentafluoroquinazoline (**3**; R =NH_2), 4-aminopentafluorocinnoline (**4**; R=NH_2), together with several minor, unidentified products. 4-Aminopentafluorophthalazine[2] was not present, while a tiny spot close to a marker of the amino-derivative of hexafluoroquinoxaline[4] was not identified. A sample of 4-aminopentafluoroquinazoline was isolated from the photolysis product by preparative t.l.c. and its identity with an authentic sample[3] was confirmed by i.r., m.p., and mixed m.p.; the yield of hexafluoroquinazoline, which was not optimised, was 5—10%. When hexafluoroquinazoline was irradiated under the same conditions, but for half the time of the cinnoline experiment, 80% was recovered unchanged together with an involatile tar; no other perfluorodiazine was detected. Preliminary results indicate that hexafluoroquinazoline is also produced by pyrolysis of hexafluorocinnoline.

It is probable that the isomerisation of hexafluorocinnoline to hexafluoroquinazoline occurs *via* the benzodiazabenzvalene (**6**), analogous to the diazabenzvalene postulated in the conversion of polyfluoropyridazines into polyfluoropyrimidines.[1] It is noteworthy that (**6**) is the only valence isomer of a benzopyridazine, capable of producing a ring shift of nitrogen by N–N fission, in which the carbocyclic ring remains aromatic. If this mechanism is correct, the corresponding isomerisation of hexafluorophthalazine would need a non-aromatic valence isomer intermediate of high energy and reactivity (as would the formation of hexafluoroquinoxaline from hexafluorocinnoline). It is consistent with this view that we have been unable to isomerise hexafluorophthalazine under conditions which convert hexafluorocinnoline into hexafluoroquinazoline.

(*Received, April 27th*, 1970; *Com.* 629.)

[1] C. G. Allison, R. D. Chambers, Yu. A. Cheburkov, J. A. H. MacBride, and W. K. R. Musgrave, *Chem. Comm.*, 1969, 1200.
[2] R. D. Chambers, J. A. H. MacBride, W. K. R. Musgrave, and I. S. Reilly, *Tetrahedron Letters*, 1970, 57.
[3] C. G. Allison, R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, *Tetrahedron Letters*, 1970, 1979.
[4] C. G. Allison, R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, *Chem. and Ind.*, 1968, 1402.
[5] H. J. Barber, K. R. Washbourn, W. R. Wragg, and E. Lunt, *J. Chem. Soc.*, 1961, 2828.
[6] J. R. Keneford and J. C. E. Simpson, *J. Chem. Soc.*, 1947, 227.
[7] K. Schofield and T. Swain, *J. Chem. Soc.*, 1950, 384.