Tetrahedron Letters No. 23, pp. 8-10, 1960. Pergamon Press Ltd. Printed in Great Britain

NEW HETERAROMATIC COMPOUNDS CONTAINING TWO BORON ATOMS

S. S. Chissick, M. J. S. Dewar[1] and P. M. Maitlis[2]

Department of Chemistry, Queen Mary College,

Mile End Road, London, E.1.

(Received 22 September 1960)

THE preparation of 10:9-borazarophenanthrene and of 10:9 boroxarophenanthrene by Friedel-Crafts cyclizations of 2-biphenylylaminoboron dichlorides and of 2-biphenylyloxyboron dichloride in presence of aluminium chloride, and of 2:1-borazaronaphthalenes by condensation of *o*-aminostyrene with boron trichloride or phenylboron dichloride have been described.[3,4,5] We wish to report the first two examples of analogous *bis*-borazaro compounds formed by analogous double cyclizations from diamines.

Phenylboron dichloride (6 g) in dry benzene (20 ml) was added to 2:6-diaminodiphenyl (2.5 g) in dry benzene (250 ml) over 45 min at room temperature. A white precipitate of the complex separated which redissolved on heating. After boiling under reflux for 1 hr, almost two moles of hydrogen chloride

---

[1] Present address: Department of Chemistry, University of Chicago, Chicago 37, Illinois.

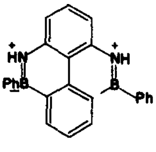
[2] Present address: Department of Chemistry, Cornell University, Ithaca, New York.

[3] M. J. S. Dewar, Ved P. Kubba and R. Pettit, *J. Chem. Soc.* 3073 (1958).

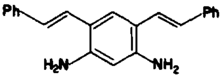
[4] M. J. S. Dewar and R. Dietz, *J. Chem. Soc.* 1344 (1960).

[5] M. J. S. Dewar and R. Dietz, *J. Chem. Soc.* 2728 (1959).

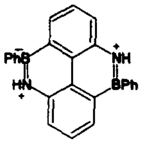
had been evolved. The solution was evaporated and the residue heated for 1 hr at 170° with a catalytic amount of aluminum chloride. The cold reaction product was hydrolyzed with wet benzene and chromatographed from ether on alumina. This gave 4:10-diphenyl-4:10-dibora-5:9-diazapyrene (I) (1.0 g, 21%), m.p. 200-2° (Found: C, 81.2; H, 5.4; N, 7.9; B, 6.0; M.W. (Rast) 348. $C_{24}H_{18}N_2B_2$ requires C, 80.9; H, 5.1; N, 7.9; B. 6.0; M.W. 356). The I.R. spectrum showed only a single NH peak, indicating that cyclization had occurred. The U.V. spectrum in ethanol was quite unlike that of the parent diphenyl, showing peaks at 258 mμ (log ε, 4.5) and 277 mμ (log ε, 4.0) and a broad shoulder at 335 mμ (log ε, 3.7).



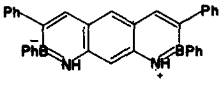
I



II



IV



III

When 1:3-diamino-4:6-<u>bis</u>(8-styryl)benzene (II) was heated with two moles of phenylboron dichloride in benzene, two moles of hydrogen chloride were evolved but no further reaction took place and no boron-containing product could be isolated. (These conditions sufficed for the synthesis of 2-phenyl-2:1-borazaronaphthalene from o-aminostyrene).[5] However use of tetralin led to evolution of almost four moles of hydrogen chloride during 2 hr reflux and formation of 2:3:6:7-tetraphenyl-2:7-dibora-1:8-diazaanthracene (III), m.p. 270°, which was isolated in 94% yield by removing the tetralin under reduced pressure and crystallizing the residue first from moist benzene and then from dry benzene (Found: C, 84.1; H, 5.4; N, 6.0; B, 4.4. $C_{34}H_{28}N_2B_2$

requires: C, 84.1; H, 5.8; N, 5.8; B, 4.5%). The molecular weight could not be measured either in camphor or in naphthalene. The I.R. and U.V. spectra were consistent with the structure (III).

We also tried to make the isomer (IV) of (I) by reacting 2:2'-diaminodiphenyl with boron trichloride or phenylboron dichloride and treating the condensation products with aluminum chloride; in this case no cyclization took place. Presumably the positively charged nitrogen in an arylaminoboron dichloride deactivates the adjacent ring; consequently both rings are deactivated in the bis-aminoboron dichloride derived from 2:2'-diaminophenyl and cyclization cannot therefore take place.

The authors wish to thank British Petroleum Ltd. for the award of a Fellowship (to P.M.M.) and the Department of Scientific and Industrial Research for the award of a Studentship (to S.S.C.).