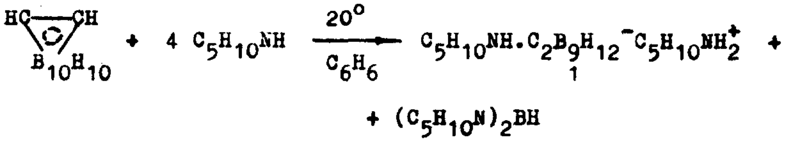
Tetrahedron Letters No.7, pp. 407-409, 1965. Pergamon Press Ltd.
Printed in Great Britain.

ON THE REACTION OF AMINES WITH BARENES

L.I. Zakharkin and V.N. Kalinin
Institute of Organo-Element Compounds, U.S.S.R. Academy of
Sciences, Moscow

(Received 28 December 1964)

Recently Grafstein and co-workers reported[1)] that barene and its derivatives give in benzene solution with certain amines stable (amine)$_2$-barenyl adducts.They point out that these adducts are coordinate-covalent compounds and not lower boron-containing species and that nitrogen donor atoms are bonded directly to boron.In contrast to american authors we have found that interaction of amines with barenes takes place with the degradation of a barenic molecule to the anions of dicarbaundecaboranes[a)].Thus, by the reaction of piperidine with barene in benzene solution at 20° the adduct of piperidine with piperidinium salt of dicarbaundecaborane(I) and bis-(piperidine)borine are rapidly formed:



$$\underset{B_{10}H_{10}}{HC{-}CH} + 4\ C_5H_{10}NH \xrightarrow[C_6H_6]{20^{\circ}} \underset{1}{C_5H_{10}NH.C_2B_9H_{12}{}^{-}C_5H_{10}NH_2^{+}} + (C_5H_{10}N)_2BH$$

I can be recrystallized from benzene or aqueous alcohol, m.p.

---

a) Previously the salts of dicarbaundecaboranes have been obtained by heating of barenes with hydrazine hydrate[1)].

169-170° a)(sealed tube),(Calc. for $C_{12}H_{35}B_9N_2$: C, 47.33; H, 11.50; B, 31.92; N, 9.21. Found: C, 47.19; H, 11.50; B, 32.00; N, 9.28). By heating in vacuum below melting point I easily splites off one molecule of piperidine and gives the piperidinium salt of dicarbaundecaborane, m.p. above 300° (Calc. for $C_7H_{24}B_9N$: N, 6.38. Found: N, 6.50)

$$C_5H_{10}NH\cdot C_2B_9H_{12}^{-}C_5H_{10}NH_2^{+} \xrightarrow{t} C_2B_9H_{12}^{-}C_5H_{10}NH_2^{+} + C_5H_{10}NH$$

This salt with piperidine in alcoholic solution forms again I. By the addition of aqueous solution of methylpyridinium iodide at 20° to aqueous-alcoholic solution of I the methylpyridinium salt of dicarbaundecaborane, m.p. above 300°(Calc. for $C_8H_{20}B_9N$: C, 42.40; H, 8.82; B, 42.80; N, 6.17. Found: C, 42.30; H, 8.98;B, 42.65; N, 6.21) is precipitated. These results show clearly that one molecule of piperidine in 1 is present in form of piperidinium cation and the other is bonded by means of a weak donor B-N linkage with the anion $C_2B_9H_{12}^-$. The formation of I shows that anions of the composition $C_2B_9H_{12}X^-$ to be capable of existence.

By interaction of piperidine or butyl amine with vinylbarene, phenylbarene, 1-chloro-2-phenylbarene and 2- propenyl 3,4- barenotetrahydrofurane in benzene or hexane solution at 20° we obtained also the corresponding derivatives of dicarbaundecaborane, isolated as methylpyridinium salts : from vinylbarene, m.p. above 300°(Calc. for $C_{10}H_{22}B_9N$: C,

---

a) Grafstein and co-workers report m.p.171-176°.

47.45; H, 8.70; B, 38.35; N, 5.53. Found: C, 47.38; H, 8.54; B, 38.49; N, 5.41), from phenylbarene, m.p.122-123°(Calc. for $C_{14}H_{24}B_9N$: C, 55.45; H, 7.92; B, 31.20; N, 4.63. Found: C, 55.08; H, 7.97; B, 32.18; N, 4.94), from 1-chloro-2-phenylbarene, m.p.126-128°(Calc. for $C_{14}H_{23}B_9ClN$: C, 49.86; H, 6.87; B, 28.82; N,4.20. Found: C, 50.35; H, 7.14; B, 29.03; N, 4.30), from 2-propenyl-3,4-barenotetrahydrofurane, m.p. 139-140°.

The facile degradation of barenic molecule in the above reaction is surprising (the reaction is completed in hydrocarbon solution at 20° in a few minutes), taking in consideration the stability of barenes towards another reagents. It is possible that by action of amine on barenic nucleus an instable $(amine)_2$-barenyl diadduct is first formed, which is rearranged then inthe presence of amine to the salt of dicarbaundecaborane. It is interesting to note that piperidine reacts with barene in alcoholic solution with the formation of I much slower than in benzene silution: the reaction proceeds by reflux in the course of four hours.

REFERENCES

1.D.Grafstein, J.Bobinski, J.Dvorak, H.Smith, N.Schwartz, M.S.Cohen and M.M.Fein, Inorg.Chem. 2, 1120 (1963).