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BORON–NITROGEN COMPOUNDS
XLIII.* THE INTERACTION OF HYDRAZINE-1,2-BIS(DIPHENYLBORANE) WITH ALDEHYDES, KETONES AND NITRILES

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SUMMARY

The reaction of hydrazine-1,2-bis(diphenylborane) with nitriles yields azines of borylamino ketones, $(C_6H_5)_2B{-}NH{-}CR{=}N{-}N{=}CR{-}NH{-}B(C_6H_5)_2$, which probably exist as coordinated bicyclic species. The interaction of the cited hydrazineborane with aldehydes and ketones appears to follow the same reaction path; however, due to the great affinity between boron and oxygen, derivatives of a $C_6H_5{-}BO$ species and azines of the carbonyl compounds are formed.

Hydrazine-1,2-bis(diorganoboranes), $R_2B{-}NH{-}NH{-}BR_2$, were first described in 1960[2], but little work has been done to explore their chemistry[3]. In the present study reactions of hydrazine-1,2-bis (diphenylborane) with carbonyl compounds (aldehydes, ketones) and nitriles are described.

Hydrazine-1,2,-bis(diphenylborane) was first reported by Mikhailov and Bubnov[4]. These authors refluxed (diethylamino)diphenylborane and hydrazine at temperatures as high as 200° and obtained a material, m.p. 135–137°. We have prepared the same hydrazineborane by refluxing (dimethylamino)diphenylborane and anhydrous hydrazine in ether. After recrystallization of the resultant hydrazine-1,2-bis-(diphenylborane) the compound had a m.p. 164–169°. On the basis of infrared spectral data the material was slightly contaminated with hydrazinodiphenylborane, $(C_6H_5)_2B{-}NH{-}NH_2$. On melting in vacuum slight decomposition seems to occur; surprisingly, the resolidified material had a new m.p. 135–145° in fair agreement with the previously described material[3,4].

The interaction of hydrazine-1,2-bis(diphenylborane) with an excess of aldehydes or ketones can be described by eqn. (1). The azines are obtained in excellent

$$6\,RR''CO + 3\,R'_2B{-}NH{-}NH{-}BR'_2 \rightarrow 2\,({-}BR'{-}O{-})_3 + 6\,R'H + 3RR''C{=}N{-}N{=}CCR'' \qquad (1)$$

$R = H$, alkyl, aryl; $R' = C_6H_5$; $R'' =$ alkyl, aryl

yield. In one case (*i.e.*, reaction with acetone) diphenylborinic acid was obtained rather than *B*-triphenylboroxine; this event may be due to the lower reaction temperature.

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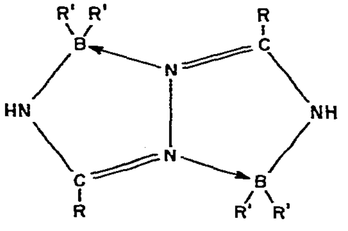
* For Part XLII see ref. 1.

The interaction of the hydrazineborane with nitriles also occurs in a 1/2 molar ratio. However, in this case it is possible to isolate a material containing both of the original reactants in the product. The reaction can be described by eqn. (2).

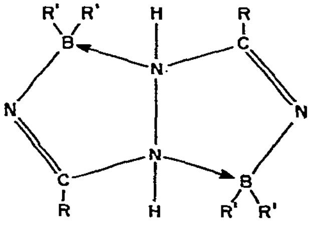
$$2\,\mathrm{RCN} + \mathrm{R'_2B{-}NH{-}NH{-}BR'_2} \rightarrow \mathrm{(I)} \qquad (2)$$

$\mathrm{R} = $ alkyl, aryl; $\mathrm{R'} = \mathrm{C_6H_5}$

The hydrolytic stability of compound (I) suggests the presence of four-coordinated boron in the molecule and either of the two structures (Ia) or (Ib) seems to be consistent with this observation. The symmetrical structure of (I) is substantiated by the proton magnetic resonance spectrum of the material which can be considered as azine of a (diphenylboryl)amino ketone.



Ia



Ib

The initial reaction of hydrazine-1,2-bis(diphenylborane) with nitriles can be

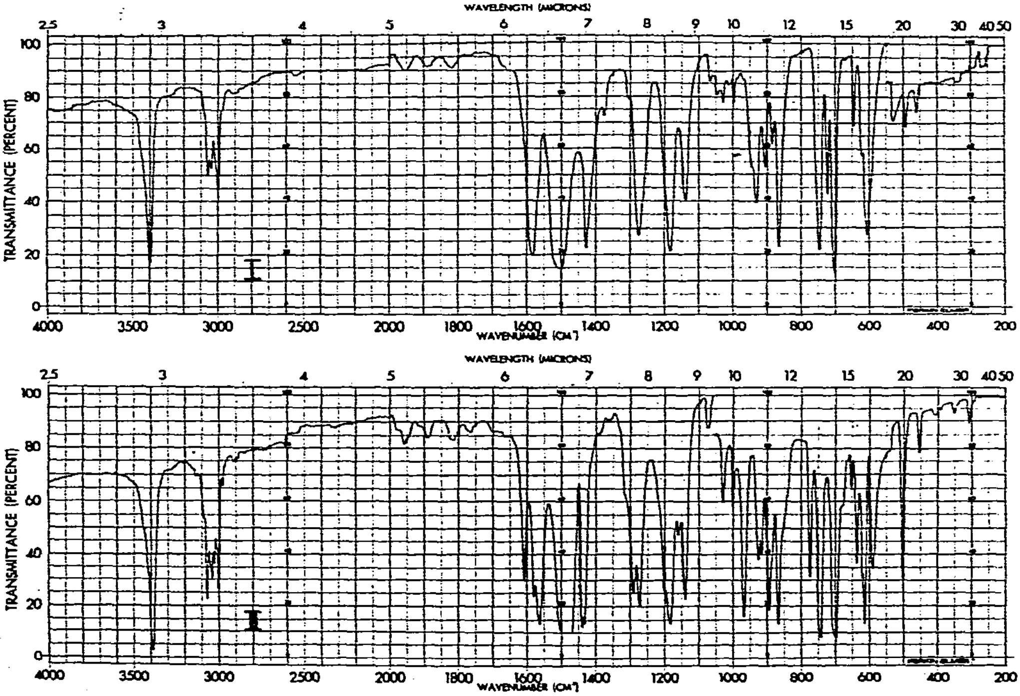


Fig. 1. Infrared spectra of the reaction products formed from hydrazine-1,2-bis(diphenylborane) and acetonitrile (I) or benzonitrile (II) (CsI pellets).

interpreted by an addition of each boron–nitrogen bond of the hydrazineborane across the C≡N triple bond of a nitrile or by reaction of the hydrazineborane as a 1,3-dipole. Similar reactions have been observed previously in organoboron chemistry[5,6]. In either case subsequent proton migration will provide the conjugate system (Ia).

Infrared spectra of compounds of type (I) do not provide conclusive evidence for their structure (see Fig. 1). However, absence of strong infrared absorptions in the 1600–1700 cm^{-1} region seems to exclude the presence of an isolated CN double bond as would be required for (Ib). Furthermore, structure (Ia) appears to be more in consonance with previously prepared compounds of similar type such as the $(C_6H_5)_2$-B–NH–N=$C(C_6H_5)_2$[3].

It is possible that aldehydes react with hydrazine-1,2-bis(diphenylborane) in similar fashion as described above. However, due to the great affinity between boron and oxygen, $(C_6H_5)_2BOH$ is formed which can trimerize under elimination of benzene to yield *B*-triphenylboroxine, an azine being the other reaction product.

EXPERIMENTAL

Melting points of the materials are uncorrected. All reactions were carried out in dry atmosphere. All reagents were dried and/or distilled before use. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Proton magnetic resonance spectra were recorded on Varian T-60 spectrometer; mass spectral data were obtained with a Perkin–Elmer Hitachi 6E mass spectrometer. Infrared spectra were (neat or CsI pellets) recorded on a Perkin–Elmer Model 621 spectrophotometer.

*Preparation of hydrazine-*1,2-*bis(diphenylborane)* (I)

A solution of 4.18 g (0.02 mole) of (dimethylamino)diphenylborane[7] in 30 ml of anhydrous ether was added dropwise to a vigorously stirred mixture of 0.30 g (ca. 0.01 mole) of anhydrous hydrazine in 15 ml ether of dry ice temperature. Some white precipitate was formed and the resultant mixture was warmed up to room temperature and was refluxed for 3 h. On filtration, 1.5 g (42%) of hydrazine-1,2-bis(diphenylborane) was collected and was recrystallized from benzene, m.p. 164–169°, mol. wt. (by mass spectroscopy) 360 (calcd. 360). The infrared spectrum of the material exhibited NH_2 absorptions indicating some minor contamination of the product with hydrazinodiphenylborane which could not be removed by repeated recrystallization. However, treatment with some additional (dimethylamino)diphenylborane provided a pure compound. (Found: C, 79.8; H, 6.2; B, 6.0; N, 7.7. $C_{24}H_{22}BN_2$ calcd.: C, 80.06; H, 6.16; B, 6.01; N, 7.78%.)

Reaction of (*I*) *with benzaldehyde*

A 10-ml round-bottom flask equipped with a short condenser was charged with 4 ml of benzaldehyde and 300 mg of (I). The mixture was heated to 95–100° for 1 h and excess benzaldehyde was removed by vacuum distillation under 2 mm pressure. Repeated recrystallization of the residual pale yellow solid from hot n-hexane provided 200 mg (77%) of *B*-triphenylboroxine, m.p. 208°, which was identified by its mass and infrared spectrum as compared with that of an authentic sample of the compound.

Evaporation of the combined mother liquors afforded a yellow solid which was recrystallized from ethyl alcohol to yield 140 mg (83 %) of benzaldehyde azine, m.p. 91–93° (lit.[8] m.p. 93°); mol. wt. calcd. 208; found (by mass spectroscopy) 208.

Reaction of (I) with acetone

A quantity, 800 mg, of (I) was added to 10 ml of dry acetone and an exothermic reaction occurred. Excess acetone was removed by a flow of dry nitrogen and vacuum distillation of the residue provided 220 mg (88 %) of acetone azine exhibiting spectral features identical to those of an authentic sample of the compound[8].

The remaining white solid was dried at room temperature and under vacuum (700 mg, m.p. 105–130°). Sublimation yielded a solid of m.p. 115–130° and the mass spectrum showed a peak of highest mass number at m/e 182, indicative of $(C_6H_5)_2BOH$.

Reaction of (I) with acetophenone

A quantity, 280 mg, of (I) was dissolved in 15 ml of acetophenone and the solution was heated to 95–100° for 1½ h. Excess of acetophenone was removed by vacuum distillation and repeated recrystallization of the residue from hot n-hexane provided 170 mg (95 %) of acetophenone azine, m.p. 121–123° (lit.[8] m.p. 123–124°). White solid *B*-triphenylboroxine was collected as second crop from the same solution.

Reaction of (I) with benzophenone

A mixture of 200 mg of (I) and 880 mg of benzophenone was heated to 95–100° for 1½ h. After cooling to room temperature the melt solidified and was recrystallized from 30 ml of hot n-hexane to yield 180 mg (90 %) of benzophenone azine, m.p. 161–163° (lit.[8] 163–165°).

About 80 mg of fine needles precipitated from the mother liquor on prolonged standing. On the basis of the infrared spectrum they were identified to be primarily *B*-triphenylboroxine.

Reaction of (I) with acetonitrile

In a 100-ml round-bottom flask equipped with a condenser 800 mg of (I) was dissolved in 85 ml of acetonitrile by refluxing at 80° for 30 min; the reaction was continued for another hour. After cooling to room temperature 500 mg of white crystals were collected. An additional 300 mg of product were obtained on concentration of the mother liquor to provide a total yield of 75 %, m.p. 310° (dec.). Found: C, 76.1; H, 6.6; B, 4.7; N, 13.0; mol.wt. by mass spectroscopy, 442. $C_{28}H_{28}B_2N_4$ calcd.: C, 76.0; H, 6.4; B, 4.9; N, 12.7%; mol. wt., 442.)

The infrared spectrum of the compound is illustrated in Fig. 1 (spectrum 1). The proton magnetic resonance spectrum (in pyridine-d_5, tetramethylsilane as internal standard) exhibited a broad singlet at a τ value of 1.29 (2 H, bonded to nitrogen) and lines at 2.25 (multiplet, 8 H, aromatic *o*-hydrogen), 2.60 (multiplet, 12 H, aromatic *m*- and *p*-hydrogen) and 8.10 (singlet, 6 H, two methyl groups).

Reaction of (I) with benzonitrile

A mixture of 820 mg of (I) and 10 g of benzonitrile was added to 20 ml of chlorobenzene and was refluxed at 130° for 4½ h. Solvent and excess benzonitrile were removed in vacuum and the residue was dried at 100° (2 mm) for 2 h. It was treated with

30 ml of hot benzene and 860 mg of white solid was collected; concentration of the filtrate provided an additional 150 mg of the same product. After two recrystallizations from benzene the material had a m.p. 295° (dec.). (Found: C, 79.3; H, 5.8; N, 10.0; B, 3.8; $C_{38}H_{32}B_2N_4$ calcd.: C, 80.6; H, 5.7; B, 3.8; N, 9.9%.)

The infrared spectrum of the compound is illustrated in Fig. 1 (spectrum II). The proton magnetic resonance spectrum (in pyridine-d_5, tetramethylsilane as internal standard) exhibited a broad singlet at τ 0.64 (2 H) and a multiplet structure in the 2.00–3.00 area (30 aromatic H).

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