ORGANOBORON COMPOUNDS

332. (DIALKYLBORYL)AMIDINES FROM N,N-DIALKYLAMIDINES

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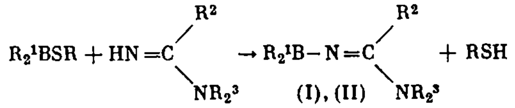
We have previously studied the structure and properties of complexes of trialkylboranes with amidines [1-3] and of cyclic coordination compounds of boron containing the amidine function [1,2,4]. Amidinetrialkylboranes that have only one hydrogen atom on the amine nitrogen of the amidine can eliminate alkanes on heating to form N-(dialkylboryl)amidines [1-3,5,6], compounds whose study impinges on several chemical problems. Particular interest surrounds the tendency of compounds of this type to self-association, internal coordination, and tautomeric rearrangement.

The key position in the study of the structure of amidines containing the dialkylboryl group is occupied by N^2-(dialkylboryl)-N^1,N^1- dialkylamidines (DABDAA) [6], which can be prepared from unsymmetrical N,N-dialkylamidines. We describe here the synthesis and some properties of several compounds of this type.

Unlike other (dialkylboryl)amidines, DABDAA cannot be prepared from trialkylboranes and free amidines. Thus, the reaction of N,N-dimethylbenzamidine with tripropylborane forms a complex that even at 130°C does not give the (dialkylboryl)amidine [3]. An intermediate six-membered cyclic state similar to that proposed for example for the reaction of trialkylboranes with 2-aminopyridine [7] does not seem to be possible in the reaction of trialkylboranes and N,N-dialkylamidines. Nor can DABDAA be prepared by the reaction of (dialkylamino)dialkylboranes with nitriles. To synthesize DABDAA we therefore used the general method for the synthesis of compounds with a B−N bond from (alkylthio)dialkylboranes [8]:

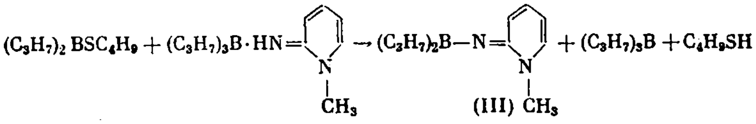


$$R_2^1BSR + HN{=}C(R^2)(NR_2^3) \rightarrow R_2^1B{-}N{=}C(R^2)(NR_2^3) + RSH$$

(I), (II)

$R^1 = R^2 = C_3H_7$, $R^3 = C_2H_5$ (I); $R^1 = i\text{-}C_3H_7$, $R^2 = C_6H_5$, $R^3 = CH_3$ (II)

The resulting N^2-(dipropylboryl)-N^1,N^1-diethylbutyramidine (I) and N^2-(diisopropylboryl)-N^1,N^1-dimethylbenzamidine (II) are liquids that can be vacuum-distilled without decomposing. Cryoscopic molecular weight measurements in benzene show that these compounds are monomeric and do not dimerize on standing. Another, related, (dialkylboryl)amidine − 2-(dipropylboryl)imino-1-methyl-1,2-dihydropyridine (III) − was synthesized by reaction of (butylthio)dipropylborane and the complex of tripropylborane with 2-imino-1-methyl-1,2-dihydropyridine:



(III)

Freshly distilled amidine (III), a yellowish oil, is also monomeric. The ^{11}B NMR spectra of compounds (I)-(III) show one signal at ~−40 ppm, which does not change when the temperature is increased to 100-120°C. Signals in the same region have been reported in monomeric aldiminodialkylboranes [9] and ketiminodialkylboranes [10], whereas the monomeric aminodialkylboranes [11], (acylamino)dialkylboranes [12], and 2-(pyridylamino)dialkylboranes [7] give signals slightly further downfield (~−46 to −54 ppm). This suggests that the signal in the ~−40 ppm region is a significant indication of a dialkylboryl group attached to imine nitrogen.

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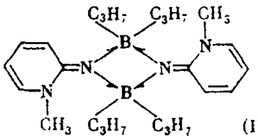
The IR spectra show intense bands at 1790 cm^{-1} [compounds (I) and (II)] and at 1765 cm^{-1} [amidine (III)]. Absorption in this region also typifies monomeric iminodialkylboranes [9, 13], and consequently is characteristic for nonassociated compounds containing the $R_2B{-}N{=}C\langle$ moiety. The IR and ^{11}B NMR spectra demonstrate that internal coordination and hence the formation of four-membered cyclic structures do not occur in amidines (I)-(III).

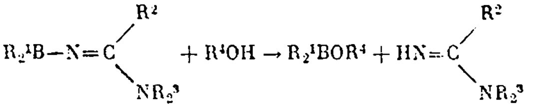
Unlike (I) and (II), amidine (III) crystallizes some time after distillation. Association here plainly results from donor–acceptor interaction between boron and nitrogen, since in the IR spectrum (in KBr) the band at 1765 cm^{-1} disappears and is replaced by a band at 1652 cm^{-1}. If the substance is melted the band at 1765 cm^{-1} replaces that at 1652 cm^{-1}. This has been reported more than once in studies of monomer-dimer equilibrium in iminodialkylboranes [9, 13]. Unfortunately, the poor solubility of the associate in organic solvents precluded measurement of its molecular weight (the IR spectrum shows that when warmed the compound passes into solution in the monomeric state). However, analogy with iminodialkylboranes suggests that the associate has the structure of dimer (IV):



(IV)

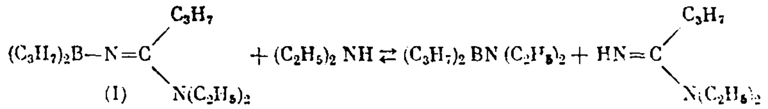
Nonetheless we cannot completely exclude the possibility of a higher degree of association in crystalline (III). The PMR spectrum of (II) at 30°C shows that the CH_3 groups on the amine nitrogen are equivalent, as in N,N-dimethylbenzamidine. Comparison of the PMR spectra of (dialkylboryl)amidine (III) and 2-(pyridylamino)-dialkylboranes [13] reveals that, as we would expect, the signals of the pyridine protons in the pyridon-2-imine structure (III) are at higher field than the signals of the corresponding protons in the aminopyridine compounds. We have demonstrated by ^{11}B NMR spectroscopy that amidines (I)-(III) are thermally stable up to 130-140°C. The spectrum of compound (I) shows plainly that it partially decomposes at 160°C.

Amidines (I)-(III) neither form complexes with pyridine nor give cyclic coordination compounds with aminodialkylboranes like that prepared from N-(dipropylboryl)acetamidine [2]. This is confirmed by the ^{11}B NMR spectra. Water or alcohols easily induce cleavage of the B–N bond in (I)-(III) to form the N,N-dialkylamidine:



$$R^1_2B{-}N{=}C\begin{matrix}R^2\\ NR^3_2\end{matrix} + R^4OH \rightarrow R^1_2BOR^4 + HN{=}C\begin{matrix}R^2\\ NR^3_2\end{matrix}$$

We decided to elucidate the response of DABDAA to amines. We found that even at room temperature diethylamine displaces N,N-diethylbutyramidine from (I) to form (diethylamino)dipropylborane. This we deduced from the disappearance from the IR spectrum of the reaction mixture of the band at 1790 cm^{-1} (B–N = C), and the appearance of the characteristic bands of N,N-diethylbutyramidine at 1595 (C = N) and 3327 cm^{-1} (NH) [3], together with the appearance in the ^{11}B NMR spectrum of a signal at ~ −50 instead of − 39 ppm. However, this process is reversible, and the equilibrium is displaced toward formation of (I) if heat is applied to remove the more volatile diethylamine:



$$\underset{(I)}{(C_3H_7)_2B{-}N{=}C\begin{matrix}C_3H_7\\ N(C_2H_5)_2\end{matrix}} + (C_2H_5)_2NH \rightleftarrows (C_3H_7)_2BN(C_2H_5)_2 + HN{=}C\begin{matrix}C_3H_7\\ N(C_2H_5)_2\end{matrix}$$

This means that transamination of aminodialkylboranes by N,N-dialkylamidines can be used for the synthesis of DABDAA.

Compounds (I)-(III) do not react with CH_3CN or benzonitrile, differing in this respect from (dialkylboryl)-amidines that have only one hydrogen atom in the amidine function.

The results of this study of these synthetic DABDAA could prove extremely useful in establishing the structure of (dialkylboryl)amidines prepared from N-monoalkylamidines [6].

EXPERIMENTAL

Operations were carried out in an atmosphere of dry argon. The ^{11}B and ^{1}H NMR spectra were recorded with RS-59/19 and Varian DA-IL instruments respectively and the IR spectra were recorded with a UR-20 instrument.

The starting amidines were synthesized by published methods (references can be found in [3]). The complex of tripropylborane with 2-imino-1-methyl-1,2-dihydropyridine was prepared by the procedure of [3].

N^2-(Dipropylboryl)-N^1,N^1-diethylbutyramidine (I). A mixture of (butylthio)dipropylborane (24.5 g) and N,N-diethylbutyramidine (15 g) was heated under vacuum (65-70 mm) on a boiling-water bath; the resulting butanethiol (11 ml) was distilled off. Distillation of the residue gave amidine (I) (20 g, 80%), bp 100-103°C (4 mm); n_D^{20} 1.4620. ^{11}B NMR spectrum (THF): −39 ppm. PMR spectrum (no solvent, δ, ppm): 3.16 q (NCH_2); 2.18 t ($=CCH_2$); 0.38-1.78 (other protons). Found: C 70.32; H 13.04; B 4.52; N 11.90%. mol. wt. 232. $C_{14}H_{31}BN_2$. Calculated: C 70.58; H 13.12; B 4.54; N 11.76%; mol. wt. 238.2.

N^2-(Diisopropylboryl)-N^1,N^1-dimethylbenzamidine (II). A mixture of triisopropylborane (12 g) and N,N-dimethylbenzamidine (10 g) was heated in the presence of propanethiol (3 ml) on an oil bath at 80-120°C until evolution of gas ceased. Distillation gave amidine (II) (14.4 g, 90%), bp 110-112°C (2.5 mm); n_D^{20} 1.5103. ^{11}B NMR spectrum (no solvent): −40 ppm. PMR spectrum (no solvent, δ, ppm): 6.95-7.43 m (C_6H_5); 2.59 s ($2CH_3$); 0.77-1.40 m ($2C_3H_7$). Found: C 73.65; H 10.28; B 4.29; N 11.25%. $C_{15}H_{25}BN_2$. Calculated: C 73.79; H 10.31; B 4.43; N 11.48%.

2-(Dipropylboryl)imino-1-methyl-1,2-dihydropyridine (III). A mixture of the complex (11.2 g) of tripropylborane with 2-imino-1-methyl-1,2-dihydropyridine and (butylthio)dipropylborane (10.0 g) was heated on a water bath in distillation apparatus arranged so that butanethiol and tripropylborane distilled over under vacuum (~20-25 mm). Distillation of the residue gave amidine (III) (8.6 g, 93%), bp 82-83°C (1 mm). ^{11}B NMR spectrum (THF): −41 ppm. PMR spectrum (CCl_4, δ, ppm): 6.48-6.90 m (pyridine $H_\alpha + H_\gamma$); 5.88 m ($H_{\beta'}$); 5.48 m (H_β); 3.07 s (NCH_3); 0.55-1.55 m ($2C_3H_7$). Found: C 69.80; H 10.07; B 5.39; N 14.00%. $C_{12}H_{21}BN_2$. Calculated: C 70.61; H 10.36; B 5.30; N 13.73%.

CONCLUSIONS

We have synthesized N^2-(dialkylboryl)-N^1,N^1-dialkylamidines by the reaction of N,N-dialkylamidines with (alkylthio)dialkylboranes and established the distinctive features of their IR and ^{11}B NMR spectra that characterize amidines with a dialkylboryl group on the imine nitrogen.

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