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Note

Thin-layer chromatographic behavior of some aminodichloroboranes

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Although much research has been done involving the preparation of aminoboranes and aminohalogenoboranes, no systematic studies have been made of their separation. Rapid, reproducible methods for the separation and identification of compounds in these classes could be of great use to synthetic inorganic chemists in the area. This report contains the results of our preliminary work on the chromatographic behavior of aminohalogenoboranes.

Aminodihalogenoboranes, R_2N-BX_2 , have been known since they were first prepared by Michaelis¹. Commonly existing as liquids at room temperature, they are purified *in vacuo* by fractional distillation. Storage under an inert atmosphere is required in order to prevent hydrolysis to boric acid.



As in the case of the related aminoboranes, R_2N-BR_2 , the boron-nitrogen bond exhibits a "double-bond" character. Although, the double bond is not nearly so strong as that of an analogous alkene^{2,3}. Surveying the literature one can find virtually nothing concerning the use of chromatographic methods to separate halogenoaminoboranes. The 'double-bond' character of these compounds suggests that either liquid-solid or gas-solid chromatography might provide a solution. However, any solvent used would have to be very dry to prevent hydrolysis and, unfortunately, these compounds tend to decompose at high temperature.

Thin-layer chromatography (TLC) has the advantage that development of the chromatogram requires only small amounts of solvent. It is possible to detect compounds containing B-N bonds by spraying with silver nitrate solution. This was shown by Hermanek *et al.*⁴ in their successful separation of a number of amineboranes by TLC. Amineboranes, R_3N-BX_3 , are compounds in which nitrogen shares its free pair of electrons with boron. These compounds are considerably more stable than aminoboranes and hydrolyze less rapidly and therefore it was found⁴ that satisfactory results could be obtained using common organic developing solvents on silica and alumina plates. Hermanek *et al.*⁴ were able to make several correlations between structure and retention of species. Compounds containing the highest number of alkyl groups and the most branched alkyl groups attached to nitrogen had the highest R_F values. This is not surprising since alkyl groups would increase the affinity of the compounds for the organic solvents used. If the proper conditions for separation could be established, such correlations should be possible

for aminohalogenoboranes and aminoboranes. This study reports the behavior of three model aminohalogenoborane compounds: I, diethyl aminodichloroborane; II, methyl phenyl aminodichloroborane; and III, ethyl phenyl aminodichloroborane.

EXPERIMENTAL

Thin-layer media

A silica gel impregnated fibrous support system (ITLC, Gelman, U.S.A.) was selected for this work. It was felt that for these initial studies the thin-layer media should not contain a binder but should be dimensionally stable. This latter restriction results from the need to work in a stringently inert atmosphere and from the design of the apparatus used. The ITLC strips were heated in an oven at 100° for several hours to remove surface water. Silanized ITLC (SITLC) strips were prepared by reacting oven-dried 25 × 125 mm strips with the vapors of a 1:2 hexamethyldisilazane-trimethylsilyl chloride mixture in a sealed flask at 50°. It was observed that the surface of the support was sufficiently altered so that it could no longer be wetted when dipped in water.

Reagents

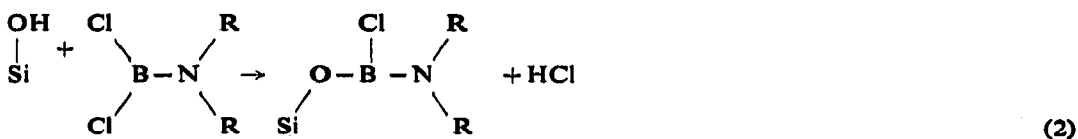
The halogenoaminoboranes I, II and III were prepared and purified by standard methods by fractional distillation *in vacuo*. After distillation, the compounds were stored under dry nitrogen. For the purpose of these experiments 1% solutions of each compound in anhydrous *n*-hexane were prepared and similarly stored. All solvents used were carefully dried by conventional means and distilled on to molecular sieve pellets for storage. All other reagents were used as received.

The indicating reagent for the halogenoaminoboranes consisted of a saturated solution of silver nitrate in anhydrous methanol applied with a conventional sprayer. The reaction time was shortened significantly if the strips were exposed to shortwave length mercury lamp radiation after spraying.

Avoiding detail, the experimental conditions permitted spotting, development, spraying and UV irradiation of the thin-layer strips to be performed in a glove bag under a dry nitrogen atmosphere. Commercial dry nitrogen gas was further dried before entering the glove bag by passage through a molecular sieve-filled trap which was regenerated daily. The in-coming nitrogen was continuously removed along with any solvent vapors by means of the vacuum-line attachment.

RESULTS AND DISCUSSION

Initially, the three dialkylaminodichloroboranes were studied on the dried ITLC medium as received. It was observed that both benzene and hexane failed to elute the samples ($R_F=0$). Since the compounds are all soluble to some extent in both of these solvents, it was thought that the chemisorption might have taken place. Boron halides are known to be reactive toward hydroxyl groups and reaction 2 is a possibility.



Chemisorption to the silica would probably not inhibit aminohalogenoborane reduction of silver nitrate. If chemisorption does occur, it was hoped that altering the surface of the silica gel (*e.g.* silanization) might alleviate the problem.

Experiments with silanized strips indicated that in mixed binary solvents of gradually increasing solvent strength (calculated according to Snyder^{5,6}) an unexpected R_F value jump from 0 to 1 was observed on silanized ITLC strips at mole fraction benzene-hexane=0.7 and methylene chloride-hexane=0.35; *i.e.* at an eluent equal to 0.29 (ref. 6). The chromatographic behavior of fluorescein in propanol-hexane mixtures showed that the R_F value jump is not a characteristic of the silanized media (Table I). In addition, in the development of ethyl phenyl aminodichloroborane on silanized ITLC, an unidentified impurity in the sample also behaved normally (Table II). In view of its reactivity towards silver nitrate, the impurity was an aminoborane but not an aminohalogenoborane.

The R_F value jump from 0 to 1 would seem to indicate that the aminohalogenoboranes are very strongly, but reversibly, bound to the silanized substrate. The strong tailing observed could originate from strong reversible adsorption or a chemical reaction. Boron-halogen bonds are capable of cleaving silyl ethers⁷. Eqn. 3 illustrates this:



TABLE I

ELUTION BEHAVIOR OF DI-iodofluorescein ON SILANIZED AND UNSILANIZED MEDIA

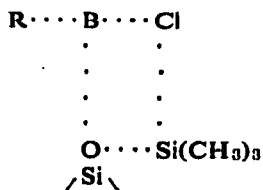
<i>Mole fraction 2-propanol in hexane</i>	R_F^{sil}	R_F
0.00	0.0	0.0
0.04	0.1	0.1
0.05	0.5	0.2
0.06	0.9	0.3
0.09	1.0	0.5
0.30	1.0	1.0
1.00	1.0	1.0

TABLE II

ELUTION BEHAVIOR OF AMINOBORANE IMPURITY ON SILANIZED MEDIA

<i>Mole fraction benzene in hexane</i>	R_F
0.00	0.3
0.59	0.5
0.83	0.7
1.00	0.8

If this was the predominant reaction, one might expect that the elution behavior of the aminohalogenoboranes would be the same on SITLC as on ITLC itself, since the final product, a >Si-O-B< ether, is the same in either case. A more reasonable reaction, considering the steric crowding at the silica gel surface is the formation of the intermediate:



which would account for the strong physicochemical adsorption and which could be reversed by increasing solvent eluent strength.

CONCLUSIONS

Aminohalogenoboranes are very reactive toward silica gel adsorption media presumably forming >Si-O-B< ethers. Silanization of the silica may prevent true chemisorption but very strong physicochemical adsorption does occur. These observations are relevant to the observed gas chromatographic behavior of aminohalogenoboranes⁸ and suggest that non-silicaceous supports such as graphitized carbon black might be more promising if the problem of thermal stability can be overcome. TLC of aminoalkylboranes should present fewer problems.

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