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Organoboron Compounds. XVII. Preparation and Hydrolytic Properties of Some Substituted Borazines Containing Fluorescent Groups[1]

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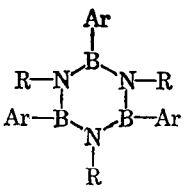
For the detection of neutrons by means of scintillation counters, compounds which have both high neutron cross sections and are strongly fluorescent are desirable. Interesting examples of such types of compounds can be obtained by introducing polyphenyl groups into the borazine molecule. In the present paper the preparation of four such compounds, B-tris(diphenylyl)-N-trimethylborazine (I), B-tris(diphenylyl)-N-triphenylborazine (II), B-tris(α-naphthyl)-N-trimethylborazine (III), and B-tris(p-terphenylyl)-N-trimethylborazine (IV), is described and their rates of hydrolysis are compared. The structural formulation of the compounds is given in Chart I.

CHART I



I, Ar = $C_6H_5C_6H_4$; R = CH_3
II, Ar = $C_6H_5C_6H_4$; R = C_6H_5
III, Ar = α-$C_{10}H_7$; R = CH_3
IV, Ar = p-$C_6H_5C_6H_4C_6H_4$; R = CH_3

Among the several methods reported for the preparation of borazine derivatives,[4] the more generally

(1) Previous paper: P. A. McCusker and J. H. Bright, *J. Org. Chem.* **29**, 2093 (1964).

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(4) J. C. Sheldon and B. C. Smith, *Quart. Rev.* (London), **14**, 201 (1960).

used are the method of Ruigh[5] which involves the reaction of organodichloroboranes with amines and the method of Harris, Ryschkewitsch, and Sisler[6] and Groszos and Stafiej[7] which consist of the reaction of Grignard reagents with substituted B-trichloroborazines. The availability of a convenient method for the preparation of the required B-trichloro-N-substituted borazines dictated our choice of the latter method for the preparation of the desired compounds.

Three of the four compounds to be prepared contain methyl groups attached to nitrogen and compounds of this type have been reported[7] to be readily hydrolyzed in contact with water. Completely anhydrous procedures were therefore used. It was found that much better results were obtained when lithium aryls were used rather than Grignard reagents. The yield of I was increased from 33 to 61% by using lithium aryl rather than Grignard reagent. In the case of IV the required Grignard is obtainable only with difficulty, while the lithium aryl was prepared conveniently by halogen exchange. The principal advantage of lithium aryls over Grignard reagents in these preparations lies in the relative ease of separation of lithium chloride from ether solutions compared to the separation of magnesium salts. The elimination of lithium chloride or its etherate from the residue, obtained by removal of most of the ether by distillation, was readily accomplished by successive treatments with dry benzene at reflux temperature, removal of ether by distillation, and separation of precipitated lithium chloride by filtration under anhydrous conditions.

No significant differences in the rates of reaction of the N-trimethyltrichloroborazine with the three different lithium aryls was observed, indicating that steric effects arising from the size of the aryl group did not seriously affect the reaction. The variation in the yields obtained is probably due to differences in the losses during crystallizations.

The products, obtained by recrystallization from a variety of solvents, were in the form of small white needles. Their identification was based on the reactions used and on elemental analysis. The infrared spectra all showed strong absorption in the B–N ring stretching region (1370–1410 cm.$^{-1}$) as well as the characteristic frequencies corresponding to the aryl groups.

The substituted borazines prepared in this work, although less sensitive to moisture than borazine itself, were found to undergo significant hydrolysis on storage as the result of occasional exposure to normal atmosphere. Elemental analysis of samples, stored for several months with occasional short exposure to the atmosphere, gave evidence of about 5% hydrolytic decomposition in the case of III and IV, and of about 15% decomposition in the case of I, accompanied by loss of volatile amine.

On contact with liquid water, there was extensive hydrolysis in a period of 30 min. in the case of B-tris-(diphenylyl)-N-trimethylborazine (I), while the corresponding N-phenylborazine was only slightly hydrolyzed in the same period. This observation is in agreement with that of Groszos and Stafiej[7] on the relative rates of hydrolysis of N-methyl- and N-phenyl-substituted borazines. Two of the N-methyl-substituted borazines prepared in this work, III and IV, however, did not exhibit the property of ready hydrolysis on contact with liquid water. These latter two compounds were quite resistant to hydrolytic attack by liquid water and were comparable in this respect to the N-phenyl compound. It would appear that the large α-naphthyl and p-terphenylyl groups on the boron exert a steric effect which slows the attack by water.

More quantitative studies on relative hydrolysis rates were carried out on solutions containing 1.12 mg./ml. of the compounds in 22.5 wt. % dioxane in water. The rates of hydrolysis were followed by measurements of the conductivity of the solutions *vs.* time. The required relationships between conductivity and concentrations were obtained by measurements of the conductivities of various solutions of methylamine–phenylboronic acid in dioxane–water and of similar solutions of aniline–phenylboronic acid. Within a period of 2 min. at 25° I underwent 82% hydrolysis, while, in a 3-min. period, II was only 11% hydrolyzed. Slow hydrolysis of II proceeded, however, and reached 34% in about 18.5 hr. The data obtained on the rates of hydrolysis could not be fitted to any simple rate law. Since I and II have the same groups on boron and different groups on nitrogen, it would appear that, in this case, the nature of the group attached to nitrogen is a controlling factor in the rate of hydrolysis. The reduced rate of hydrolysis of an N-methylborazine when a diphenylyl group on boron is replaced by an α-naphthyl group, however, indicates that steric protection of boron can also reduce the rate of hydrolysis.

Experimental

Preparation of the Substituted Borazines.—The procedures used for the preparation of the several substituted borazines were, in general, quite similar. One of the preparations will be described in detail as typical of the general method used.

All operations, including filtrations, were carried out without exposure to air or moisture. Closed apparatus, using dry-nitrogen pressure, or a dry-nitrogen filled drybox was used. All solvents were thoroughly dried.

Preparation of B-Tris(diphenylyl)-N-trimethylborazine (I).—B-Trichloro-N-trimethylborazine was prepared by the method of Brown and Laubengayer.[8] A solution of 4.65 g. of B-trichloro-N-trimethylborazine in 100 ml. of dry ether was added dropwise with stirring to 90 ml. of a 0.685 *M* solution of diphenyllithium[9] in ethyl ether. A rapid exothermic reaction occurred and a white precipitate separated. The addition was complete in 20 min. and stirring and refluxing were continued for an additional hour. The ether was distilled off until a thick paste remained. Dry benzene (200 ml.) was then added and the solvent was distilled to near dryness. Additional benzene was added and the resulting suspension was filtered while hot and washed with hot benzene. These operations were repeated until a filtrate free of chloride was obtained. The solid remaining after evaporation of benzene was recrystallized from ethyl ether solution (saturated at reflux temperature and slowly cooled to −78°) giving 7.2 g. of crude product (yield, 61%), m.p. 214–219°. Several additional recrystallizations from ethyl ether gave white needles, m.p. 222–223°.

(5) W. L. Ruigh, Research on Boron Polymers, WADC Report 55-26, part I–III (1955–1956).

(6) J. J. Harris, C. E. Ryschkewitsch, and H. H. Sisler, Abstracts, 132nd National Meeting of the American Chemical Society, New York, N. Y., Sept., 1957, 9S; *J. Am. Chem. Soc.*, **80**, 4515 (1958).

(7) S. J. Groszos and S. F. Stafiej, Abstracts, 131st National Meeting of the American Chemical Society, Miami, Fla., April 1957, 53-O; *J. Am. Chem. Soc.*, **80**, 1359 (1958).

(8) C. A. Brown and A. W. Laubengayer, *ibid.*, **77**, 3699 (1955).

(9) H. Gilman, E. H. Zoellner, and W. M. Selby, *ibid.*, **54**, 1957 (1932).

Anal. Calcd. for $C_{39}H_{36}B_3N_3$: C, 80.81; H, 6.21; B, 5.61; N, 7.21. Found: C, 78.11; H, 6.41; B, 5.81; N, 7.31.

Preparation of B-Tris(diphenylyl)-N-triphenylborazine (II).—Following the general procedure described above, 44 g. of B-trichloro-N-triphenylborazine[7] reacted with 450 ml. of 0.725 *M* diphenyllithium in ethyl ether to give 38.2 g. of crude product (47% yield), m.p. 292–298°. The product was purified by several recrystallizations from a 1:6 by volume mixture of benzene and petroleum ether (b.p. 35–55°), saturating at reflux temperature and slowly cooling to −30°. The purified product was in the form of white needles, m.p. 222–223°.

Anal. Calcd. for $C_{54}H_{42}B_3N_3$: C, 84.7; H, 5.5; B, 4.2; N, 5.5. Found: C, 84.8; H, 5.6; B, 4.7; N, 5.4.

Preparation of B-Tris(α-naphthyl)-N-trimethylborazine (III).—B-Trichloro-N-trimethylborazine (22.5 g.) reacted with 215 ml. of 1.41 *M* α-naphthylmagnesium bromide in ethyl ether. The combined crude products from three crystallizations from benzene totaled 28.1 g. (66% yield), m.p. 290–292°. Recrystallizations from a 1:5 by volume mixture of benzene and petroleum ether gave white crystals, m.p. 291–292.

Anal. Calcd. for $C_{33}H_{30}B_3N_3$: C, 79.1; H, 6.0; B, 6.5; N, 8.4. Found: C, 80.6; H, 5.9; B, 6.1; N, 7.7.

Preparation of B-Tris(*p*-terphenylyl)-N-trimethylborazine (IV).—Attempts to prepare *p*-terphenyllithium by direct reaction of *p*-terphenyl bromide with lithium gave very low yields. Better results were obtained when the *p*-terphenyllithium was prepared by a displacement reaction between *n*-butyllithium and *p*-terphenyl bromide.

B-Trichloro-N-trimethylborazine (22.7 g.) reacted as above with 0.3 mole of *p*-terphenyllithium. An 11-g. yield of crude product was obtained (15% yield based on *p*-terphenyl bromide), m.p. 245–250°. Recrystallizations from a 1:4 by volume mixture of benzene and petroleum ether gave a product, m.p. 255–256°.

Anal. Calcd. for $C_{57}H_{48}B_3N_3$: C, 84.8; H, 6.0; B, 4.0; N, 5.2. Found: C, 82.8; H, 5.9; B, 3.9; N, 5.0.

Hydrolysis Studies.—For the qualitative hydrolysis experiments, weighed samples (50–100 mg.) were treated with 20 ml. of water in a small flask at room temperature and in one case at reflux temperature. After various time intervals, the suspensions were filtered through sintered glass crucibles and the insoluble materials dried under vacuum, weighed, and their identity checked by melting point. The filtrates were analyzed for boron. The results of these experiments are given in Table I. In addition, samples of I and II were treated for several hours with hot concentrated KOH and hydrolysis was found to be complete. Similar treatment of III resulted in only 30% hydrolysis.

TABLE I

HYDROLYSIS OF SUBSTITUTED BORAZINES

Compound	Time, hr.	% recovery	B analysis of filtrate	M.p., °C., of recovered solid
I	0.5	52	Pos.	199–202
II	0.5	95	Neg.	Unchanged
II	0.5[a]	91	Pos.	Unchanged
III	24	95	Neg.	Unchanged

[a] At reflux temperature.

The data obtained on the rates of hydrolysis of I and II in dioxane–water solutions are listed in Table II. Less complete studies on the hydrolysis of III under comparable conditions indicated that the rate of hydrolysis of III was roughly comparable to that of II.

TABLE II

RATES OF HYDROLYSIS IN DIOXANE–WATER SOLUTIONS AT 25°

Compound I		Compound II	
Time, min.	% hydrolysis	Time, min.	% hydrolysis
2	82	3	11
8	87	5	13
27	90	15	16
157	93	53	20
1013	97	83	22
		1112	34