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HETERO ATOM DERIVATIVES OF AZIRIDINE.

III. Coordination Complexes of Ethyleneimine and Trimethyl and Triphenyl Borates*

L. A. Fedotova and M. G. Voronkov

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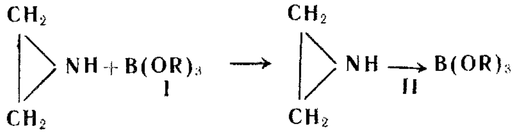
Labile equimolecular coordination complexes of ethyleneimine with trimethyl and triphenyl borates (N-ethylene-B-trimethoxyborazane and N-ethylene-B-triphenoxyborazane) are prepared for the first time and their properties investigated.

Aliphatic amines, piperidine, and ammonia readily form 1 : 1 coordination complexes with trimethyl borate [2-4]. In $B(OMe)_3$ the electron-accepting properties of the boron atom are comparatively weak, so that trimethyl borate does not form complexes with pyridine and quinoline, and in general the higher trialkyl borates do not react with amines [2, 3]. Triaryl borates are stronger Lewis acids. This is due partly to interaction of lone electron pairs of aroxy group oxygen atoms with the π electron cloud of the aromatic ring, weakened by their $p\pi$-$p\pi$ interaction with the 2p orbital of the boron, and to the polar factor of the phenoxy group, which is considerably higher than for methoxyl ($\sigma^* = 2.38$ and 1.45, respectively).

Consequently, triaryl borates from 1 : 1 complexes with methylamine, ethylamine, and diethylamine, piperazine, aniline, pyridine, 2-picoline, and quinoline [5-7].

The present work was undertaken with a view to determining the ability of ethyleneimine to form coordination complexes with trimethyl and triphenyl borate. Previously all that was known was that ethyleneimine formed rather stable 1 : 1 coordination complexes with borane [8] and trimethylborane [9].

The present authors have now found that ethyleneimine adds to trimethyl borate (Ia) at −78° in ether according to the equation:



(1)

a) $R = CH_3$; b) $R = C_6H_5$

In this way N-ethylene-B-trimethoxyborazane (IIa) is prepared. This substance, melting point 3-5°, is stable only below 0° and is readily hydrolyzed. On storage in a refrigerator at about −10°, IIa sublimes, and beautiful large crystals, sometimes attaining a length of 1-1.5 cm, grow on the walls of the vessel. The complex is soluble in water (alkaline reaction), ethanol and acetone, but insoluble in ether and hexane. In a sealed vessel at room temperature the complex dissociates into its initial components as it melts, frequently thereby passing into a transparent viscous polymer of the same composition. If this polymer is allowed to stand in an open vessel, it gradually changes into a solid glassy mass. At room temperature in the presence of atmospheric moisture dissociation of IIa is accompanied by hydrolysis of the trimethyl borate formed.

The structure assigned to IIa is supported by a study of its IR spectrum, which exhibits bands characteristic of the ethyleneimine ring (820, 868, 1210, 3070 cm^{-1}) and of BO_3 antisymmetric valence vibrations (1340 cm^{-1}).

A transparent viscous undistillable mass can be isolated from the mother liquors remaining after separating the complex. It has the same composition as IIa, with basic properties, but more resistant to hydrolysis. The same polymer is formed when the reaction between ethyleneimine and trimethyl borate is run at high temperature (40°). This product is readily soluble in water and ethanol, but insoluble in other organic solvents, so that its molecular weight was not determined. Ethyleneimine does not react with tributyl borate at −80° to +20°.

Ethyleneimine reacts readily with triphenyl borate (Ib) at room temperature in accordance with equation 1 to give a crystalline 1 : 1 complex, N-ethylene-B-triphenoxyborazane (IIb), melting at 63-65°. IIb is more stable in air than

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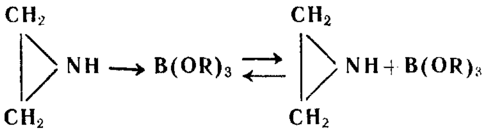
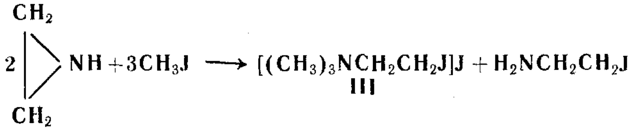
*For Part II see [1].

IIa. When heated it does not dissociate into its components, but splits off phenol. Ethyleneimine is formed on heating with aqueous alkali.

The failure of IIb to react even when refluxed with methyl iodide in ether indicates its considerable stability. Above −5°, IIa reacts with methyl iodide, first gradually dissociating into its components:


(2)



(3)

Ethyleneimine itself reacts with methyl iodide in accordance with equation 3, even at −15° [10].

Experimental

Starting materials. 98% commercial ethyleneimine was dried over sodium metal and distilled, bp 56-57°, n_D^{20} 1.4127. Trimethyl borate was used as its 68% azeotrope in methanol (bp 55°), prepared by distilling a mixture of boric acid and methanol containing a catalytic quantity of sulfuric acid through a suitable column. Triphenyl borate (mp 92°) was prepared from phenol and boric acid [6]. Tri-n-butyl borate was prepared by azeotropic distillation of water off from a mixture of boric acid and n-butanol; mp 79° (1 mm); n_D^{20} 1.4087 [11].

Analytical methods. Boron was determined as boric acid by titrating with 0.05 N NaOH in the presence of mannitol (phenolphthalein indicator).

Aziridine ring content was estimated by titrating with 0.1 N HCl using methyl orange. Carbon and hydrogen were determined as described in [12], nitrogen by the Dumas-Pregl method using nickel oxide as the catalyst.*

Ethyleneimine-trimethylborate complex, N-ethylene-B1trimethoxyborazane (IIa). A mixture of 30.2 g 68% methanol solution of Ia (0.2 mole) and 80 ml dry ether or dry petrol ether was cooled to −78° and stirred, and a solution of 8.6 g (0.2 mole) ethyleneimine in 20 ml ether added in 30 min, after which the reaction mixture was held at the same temperature for 2 hr longer. The white crystalline precipitate formed was filtered off, by suction-filtering off the liquid (without taking the flask out of the cooling mixture), washed with 2 lots of 40-50 ml cold ether, and dried in a stream of cold dry air. Yield of crystals of IIa mp 2-3°, 18.6 g (63.5%). The compound was readily soluble in water, alcohol, and chloroform, but insoluble in ether and hexane. Found: C 39.29; H 9.69; N 10.02; B 7.36; Az** 29.0%. Calculated for $C_5H_{14}BNO_3$; C 40.86; H 9.60; N 9.52; B 7.45; Az 29.3%.

When stored for 1-3 months in a sealed tube at −10°, the complex sublimed, beautiful colorless crystals which could attain a length of 1-1.5 cm, appearing on the walls of the vessel. IIa was readily hydrolyzed in air. On warming to room temperature crystals of IIa melted, and gradually dissociated into the components (the ethyleneimine formed was identified as its picrate mp 131°). Simultaneously there was formed a small quantity of viscous transparent substance, and this had the same composition as IIa, after completely removing volatile impurities. The yield of this material after distilling off solvent from the filtrate (obtained after separation of IIa crystals) amounted to 6-10 g (17.5-29.2%). Found: C 41.14; H 10.23; N 9.50; B 7.31%. Calculated for $C_5H_{14}BNO_3$: C 40.86; H 9.60; N 9.52; B 7.45%. The substance was soluble in ethanol and water, but insoluble in the usual organic solvents. It was more resistant to alkaline hydrolysis on standing than was IIa, and was readily titrated with 0.1 N HCl.

Reaction of ethyleneimine with trimethyl borate (same proportions) at room temperature followed by two hours heating on a water bath gave 12.0 g (40.9%) viscous colorless material similar to the above.

IIa did not react with methyl iodide in ether below −5°. However, at 0-5° there was a gradual dissociation. Crystals of β-iodoethyltrimethylammonium iodide (III) separated from the solution, mp 228° (ex water), mixed melting point with authentic material synthesized from ethyleneimine and methyl iodide undepressed. At room temperature this reaction was complete in two hours.

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*The authors wish to thank M. Purite for carrying out the C, H, and N analyses.

** Az - aziridine (ethyleneimine) ring content.

Reaction of ethyleneimine with tri-n-butyl borate. A solution of 2.15 g (0.05 mole) ethyleneimine in 20 ml ether was added with cooling to −78° to a solution of 11.5 g (0.05 mole) tri-n-butyl borate in twice its own volume of ether. No visible reaction was observed. The reaction mixture was allowed to warm up to room temperature, and held there for 6 hr. In the subsequent distillation all the ethyleneimine distilled over unchanged. There was also no reaction when the reaction mixture was heated for three hours on a water bath.

Ethyleneimine-triphenyl borate complex, N-ethylene-B-triphenoxyborazane (IIb). 4.3 g (0.1 mole) ethyleneimine, dissolved in 200 ml ether, was added to a stirred mixture of 29.0 g (0.1 mole) Ib in 200 ml ether. After two hours stirring at room temperature, the ether was distilled off, leaving 36.0 g of slightly colored, viscous material. It was kept for several days in a vacuum desiccator over phosphorus pentoxide till constant weight was reached, to completely remove volatile impurities. Then the material slowly changed into crystalline IIb, mp 60-65°. After treatment with hexane a crystalline material mp 63-65° was obtained. Found: C 70.46; H 5.85; N 3.56; B 3.33; Az 11.0%; Calculated for $C_{20}H_{20}BNO_3$: C 72.06; H 6.05; N 4.20; B 3.24; Az 12.60%.

The complex IIb was soluble in water, ethanol, acetone, and acetic acid, sparingly soluble in chloroform, and insoluble in dioxane, hexane, carbon tetrachloride, benzene, and nitrobenzene. It was not possible to recrystallize it. Ethyleneimine separated when it was heated with concentrated aqueous alkali. Methyl iodide does not react at its boiling point with IIb.

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Institute of Organic Synthesis AS Latvian SSR, Riga