obtained. The yield amounted to practically one-third the weight of chloro ester taken. Assuming that one molecule of the ester yields one third of a molecule of triethyl borate, the crude yield was 93%. Upon redistillation more than 75% of the product distilled between 112 and 114°, the boiling point of triethyl borate at 640 mm.' The residue was boric anhydride.

The Preparation of Diisoamyloxyboron Chloride.—Upon adding dry isoamyl alcohol to boron trichloride dissolved in dry chloroform and cooled to −20°, a yield of only 15% of diisoamyloxyboron chloride was obtained. On the other hand, by mixing triisoamyl borate with boron trichloride in the ratio of two moles to one, allowing the mixture to stand for twenty-four hours and then fractionating, a yield of 45% was obtained. The yield was not increased by allowing the mixture to stand for a longer time or by heating it in a sealed tube to 100° for eleven hours. The compound distilled at 110 to 115° at 14 mm. pressure. The substance was analyzed by decomposing a weighed sample with water and titrating the hydrochloric and boric acids produced, using methyl orange and phenolphthalein as indicators.

Anal. Calcd. for $(C_5H_{11}O)_2BCl$: Cl, 16.1; B, 4.9. Found: Cl, 15.9; B, 4.9.

The Reaction of Diisoamyloxyboron Chloride with Metals.—Diisoamyloxyboron chloride reacted vigorously with sodium or zinc dust when warmed. In order to avoid excessive decomposition the reaction was carried out in a dry benzene solution. Twenty-two grams (0.1 mole) of the chloride was dissolved in 75 cc. of benzene dried over sodium and 4.5 g. of sodium shavings added. The flask was equipped with a reflux condenser to which a tube was attached to carry the evolved gases through a wash bottle containing water and then through another bottle containing a carbon tetrachloride solution of bromine. Upon heating the flask to 70° the sodium reacted slowly and bubbles of gas were evolved. The gas turned the water acidic in the first bottle and a test for chloride ion with silver nitrate was positive. On the other hand, a test for borate ion with turmeric paper was negative. After passing through the water the gas had an odor similar to that of gasoline, burned with a sooty flame and when passed into the bromine solution rapidly decolorized it. The residual gas was odorless and burned with a pale blue flame similar to that of hydrogen.

The reaction mixture was heated until no chlorine could be detected in the benzene solution, a period of seven hours being required. The dark red solution was filtered from the solid residue which dissolved completely in water leaving no residue of amorphous boron. Thirty grams of the total of seventy-five grams of the solution was treated with water in an apparatus designed to detect the liberation of gas, but none was evolved. The remainder of the solution was fractionated twice and 6.6 g. of pure triisoamyl borate boiling at 245 to 250° at 640 mm. pressure and 2.0 g. of boric anhydride were obtained.

Summary

1. Diisoamyloxyboron chloride has been prepared.
2. Dialkoxyboron halides react with metals forming extensive decomposition products.

Salt Lake City, Utah

Received May 29, 1935

[Contribution from the Chemical Laboratory of the University of California]

The Thermal Equilibrium of the Cis–Trans Isomers of Dichloroethylene at High Temperatures

By William Maroney

In the investigation of the thermal and photochemical equilibria of the *cis–trans* isomers of dichloroethylene, Olson and Maroney[1] were limited by decomposition reactions to temperatures below 350°. In the present study, the temperature range has been extended to 975° by using a flow method and low pressures.

The method of preparing the materials and the method of analysis are the same as those described in the previous paper.

The experimental method consisted in passing mixtures of known composition of the gaseous isomers through a heated reaction tube, and finding the change in composition due to the thermal isomerization. The reaction tube used at 825° was a section of quartz tubing, 4.5 mm. inside diameter and the portion heated, 17 cm. long. The heating element was wound in five sections. The current through each section could be regulated separately. The temperature was measured by five thermocouples, one for each section. The reaction tube used at 975° was made in a similar manner. The inside diameter of the tubing was 2.5 mm., the heated portion, 12 cm. long. Three heating units and three thermocouples were used. It was found that the length and bore of the tubes employed could be changed without altering the values found for the equilibrium composition.

The pressure at each end of the reaction tube was measured by sulfuric acid manometers. Since the manometers were about 20 cm. from the

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(1) A. R. Olson and William Maroney, This Journal, **56**, 1320 (1934).

ends of the reaction tube, the pressure which they recorded was only approximately that at the ends of the tube.

In making a run, the vapor from a mixture of the isomers in the liquid state contained in a glass storage bulb was allowed to flow through the reaction tube at a definite rate, controlled by a Fowler[2] gas leak and a streaming manometer. The reaction products were frozen out in a liquid air trap, from which they could be removed for analysis. The composition of the samples used in the runs was varied sufficiently so that the equilibrium was approached from both sides.

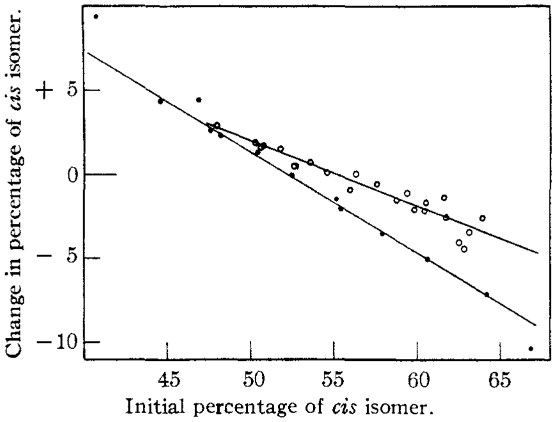

Fig. 1.—●, 975°; ○, 825°.

The two lines in Fig. 1 were obtained by plotting the change in the percentage of the *cis* isomer during a run against the initial percentage of that isomer. The composition corresponding to the point of zero change is the composition of the equilibrium mixture. The second and third columns of Table I give the average values of the pressures at the ends of the reaction tube as measured by the manometers. The values for the composition of the thermal equilibrium mixtures given in the next column are from Fig. 1.

Table I

Temp., °C.	Pressure, mm. Hg Input	Pressure, mm. Hg Output	% *cis* at equil.
975	7.5	0.30	52.3
825	11.2	.34	55.1

In calculating ΔH, the heat of transition, Olson and Maroney[1] used the approximate equation $N_{trans}/N_{cis} = e^{-\Delta H/RT}$ because the possible errors in the equilibrium constants were so large compared to the change in the equilibrium constant for the fifty-degree change in temperature. If we now combine the present equilibrium constants with those given by Olson and Maroney and use the exact equation

$$\Delta H = \log \frac{K_1}{K_2} \times 4.58 \frac{T_1 T_2}{\Delta T}, \text{ we get}$$

$$\Delta H_{300-975^\circ} = 725 \text{ cal.}, \quad \Delta H_{350-875^\circ} = 510 \text{ cal.}$$

the average of which agrees almost exactly with the value $\Delta H_{300^\circ} = 600$ cal. given by Ebert and Büll.[3]

Berkeley, California Received September 23, 1935

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[2] R. D. Fowler, *Rev. Sci. Inst.*, **6**, 26 (1935).

[3] Ebert and Büll, *Z. physik. Chem.*, **A152**, 451 (1931).

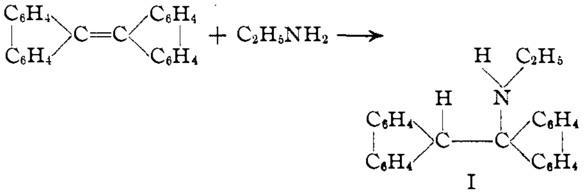
[Contribution from the Fertilizer Investigations Unit of the Bureau of Chemistry and Soils, U. S. Department of Agriculture]

Interaction of Amines and Ammonia with Dibiphenyleneethylene

By L. A. Pinck and Guido E. Hilbert

With the aim of obtaining more information that might aid in elucidating the mechanism of the interaction between 9-fluorylamine and dibiphenyleneethylene in liquid ammonia which gives as end-products 9-iminofluorene and dibiphenyleneethane,[1] and in order to test the suspected similarity of the double bond in dibiphenyleneethylene to an ethylenic linkage adjacent to an activating group, as carbonyl or cyano,[2] we have been led to investigate the action of amines on dibiphenyleneethylene.

It has now been found that dibiphenyleneethylene combines easily at room temperature with ethylamine, methylamine or dimethylamine to give 1-ethylamino (I), 1-methylamino (II) and 1-dimethylaminodibiphenyleneethane, respectively.



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[1] Pinck and Hilbert, This Journal, **54**, 710 (1932).

[2] Lapworth and McRae, *J. Chem. Soc.*, **121**, 2741 (1922), and Kolker and Lapworth, *ibid.*, **127**, 307 (1925), have suggested that the properties of an ethylenic linkage, which is in the α,β-position with respect to a carbonyl group, are intermediate to those of a normal ethylenic linkage and those of the carbonyl group.