

methanol,⁶ where the non-gel forming salts may possibly have two or more molecules in their aggregates and the gel-forming ones a larger number. A still greater number would be required to produce a colloidal solution or a gel, and this would be more easily attained by those solutions having aggregates ready formed as nuclei.

If the gel-producing solutions are visualized as consisting of a comparatively small number of ions, together with some single and some aggregates of molecules, each surrounded by solvent molecules, then a larger number of these latter would find steric possibilities of attachment round

(6) The conception of solutes forming aggregates of molecules is not new; it appears in widely differing textbooks. "Indeed, with most solutes and with most solvents, too, there is a certain degree of molecular association, as it is called." Jerome Alexander, "Colloid Chemistry," Lancaster Press, Lancaster, Pa., 1929, p. 32. Also in a paragraph on Solubility Product, "when a nearly saturated solution of sodium chloride is treated with alcohol, or with hydrogen chloride, the solvent combines with the added material, and less is available for the solution of the salt in question; the solute may form polymerized molecules in the solution." J. W. Mellor, "Modern Inorganic Chemistry," Longmans, Green, London, England, 1917, p. 320.

the large volumes of the atoms of the alkali metals and calcium than round the atoms of metals of smaller atomic volume, with the consequence that these three metals would produce larger aggregates of solute and solvent molecules, from which to form gel micellae with dispersion media.

This is being investigated further.

Summary

Gels are formed by some of the simpler organic acid salts of the alkali metals and of calcium, in methanol solution, on the addition of suitable organic liquids as dispersion media. The ultimate seat of gel formation will be the salt solutions, which have been investigated by means of adsorption experiments. The idea of molecular aggregation in varying degree is proposed as the reason for gelation, which is also partly due to the large atomic volume of the metals concerned.

EXMOUTH, DEVON, ENGLAND

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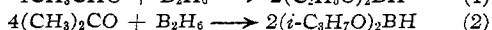
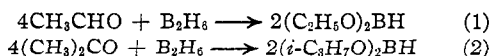
[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

Hydrides of Boron. XI. The Reaction of Diborane with Organic Compounds Containing a Carbonyl Group

BY HERBERT C. BROWN,¹ H. I. SCHLESINGER AND ANTON B. BURG

The investigation of the reaction of diborane with the carbonyl group in certain organic compounds was undertaken with two objectives in view. First, it was hoped that a knowledge of the mechanism of the reaction might shed light upon the electronic structure and modes of reaction of diborane; second, it seemed possible that results of significance to organic chemistry might be obtained.

Preliminary experiments showed that diborane (present in excess) reacts readily at room temperature with acetaldehyde and with acetone to yield the corresponding dialkoxy derivatives of borine



Attempts to isolate the mono-alkoxy derivatives have been unsuccessful. Conditions which would

be expected to yield these compounds have resulted in the production of unstable white crystalline substances² which were not investigated further because their volatility was too low. In the presence of an excess of the aldehyde or ketone, the trialkyl boric ester is formed.

An attempt to apply this reaction to other compounds containing a carbonyl group disclosed the fact that these substances could be classified into three groups, depending upon their rate of reaction with diborane, as follows:

I. **Rapid**—reaction complete within fifteen minutes, either at room temperature or at $\sim 80^\circ$. Examples: acetaldehyde, trimethylacetaldehyde, acetone.

II. **Slow**—several hours required to obtain measurable changes at room temperature; no reaction observed at low temperatures. Examples: methyl formate, ethyl acetate.

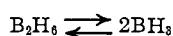
(2) These crystalline substances appear to be polymers of the mono-alkoxyborines in which oxygen in one molecule occupies the fourth position in the coordination sphere of boron in another. Compare Burg and Schlesinger, *THIS JOURNAL*, **55**, 4020 (1933).

(1) This paper is taken from a dissertation submitted by Herbert C. Brown to the Faculty of the Division of the Physical Sciences of the University of Chicago, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. It was presented before the Organic Division at the Milwaukee Meeting of the American Chemical Society, September 6, 1938.

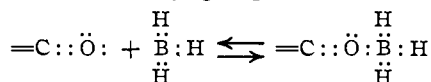
III. **No reaction** as yet observed. Examples: chloral, acetyl chloride, carbonyl chloride.

The fact that acetaldehyde and trimethylacetaldehyde react readily with diborane, while a compound structurally as similar to them as chloral does not, indicates that the cause of the variation lies in a difference in the chemical character of the carbonyl groups in these molecules. Another method of recognizing such differences was suggested by consideration of the following possible mechanism of the reaction.

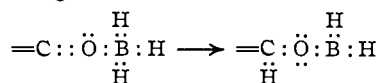
1. Either spontaneously, or under the influence of the reagent, the boron-boron link in diborane is broken



2. The resulting borine particles add to the oxygen of the carbonyl group

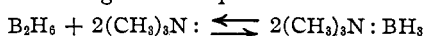


3. This complex compound then undergoes a rapid rearrangement

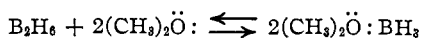


4. Finally, the labile mono-alkoxyborine undergoes further reaction, either to form a polymer, or to produce the dialkoxyborine, which is the product usually isolated.

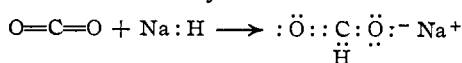
For the most part, this mechanism is based upon recognized reactions. Although free borine particles may not actually be required for the reaction, the formation of complex compounds of the postulated type certainly occurs when diborane reacts with trimethylamine and with methyl ether³ according to the equations



and



In the rearrangement of the complex addition product, it is postulated that a proton *with a pair of electrons* is transferred to carbon.⁴ Although uncommon, examples of such a transfer are recorded in the literature. For example, sodium formate has been isolated as a product of the reaction between sodium hydride and carbon dioxide⁵



(3) Schlesinger and Burg, *THIS JOURNAL*, **60**, 296 (1938).

(4) Although this transfer has been designated as an intramolecular process, the possibility that it occurs intermolecularly is not excluded.

(5) Moissan, *Ann. chim. phys.*, [8] **6**, 304 (1905).

Furthermore, it has been shown that trialkylborines undergo addition to the carbonyl group in a manner analogous to that suggested for borine. Thus



If this mechanism of the addition of diborane to the carbonyl group is correct, *the different reactivities of the carbonyl groups in various molecules should be related to the ability of the oxygen atom in these groups to share a pair of electrons*, completing the octet of the boron atom. This correlation has been demonstrated by the use of boron fluoride.

Boron fluoride adds to the carbonyl group of aldehydes, ketones, and acid halides to form complex compounds, the stabilities of which are of the relative magnitudes to be expected on the basis of the hypothesis outlined.⁷ Thus it was found that those aldehydes and ketones which react rapidly with diborane form relatively stable addition compounds by reaction with boron fluoride. On the other hand, those compounds which do not react with diborane react with boron fluoride only at very low temperatures to form unstable addition products.

According to this parallelism one might expect that the compounds which react slowly with diborane (Group II) would form addition compounds of intermediate stability with boron trifluoride. Instead the addition compounds are extraordinarily stable.⁸

Consideration of two points leads to a possible explanation of this discrepancy. The first is the fact that, whereas the more rapid reactions of compounds of Group I proceed with practically undiminished velocity at -80° , the reactions of compounds of Group II appear not to occur at all at the lower temperature. Since lowering of temperature should favor the formation of borine addition products, it may be that the rearrangement which follows addition, rather than the extent of formation of addition product, is the rate

(6) Gilman and Marble, *Rec. trav. chim.*, **55**, 76 (1936). The intermediate step is assumed by the present authors.

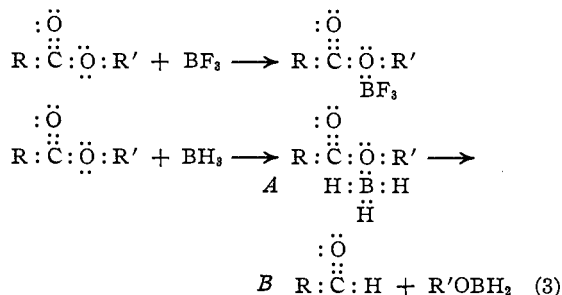
(7) The use of boron fluoride in this manner promises to become a valuable technique for studying the effects of substituents upon the chemical character of the carbonyl group. The dissociation pressures of these complex compounds and the application of the data to the interpretation of a number of addition reactions to the carbonyl group are being investigated further (Herbert C. Brown).

(8) Methyl formate-boron fluoride and ethyl acetate-boron fluoride can be distilled unchanged at atmospheric pressure: Bowlius and Nieuwland, *THIS JOURNAL*, **53**, 3835 (1931).

determining factor.⁹ According to this point of view the rate of rearrangement of addition compounds of Group I is rapid, of those of Group II, slow.

The second factor to consider is that compounds of Group I have only the carbonyl oxygen atom at which addition can occur, whereas in compounds of Group II there are two oxygen atoms, that of the carbonyl group and that of the ether linkage. If borine may be assumed to form addition compounds analogous to those of boron fluoride, it would probably add to the ether rather than to the carbonyl oxygen atom. This statement is made because addition compounds of boron trifluoride with esters resemble more closely the stable addition products with ethers than the much less stable addition products of boron trifluoride with aldehydes, ketones, and acid halides.

It is, therefore, appropriate to suggest that with compounds of Group II the reaction proceeds through addition of borine to the ether oxygen atom, and that this step is followed by rearrangement and fission of the carbon-oxygen linkage, as represented by the equations



In accordance with this interpretation we find that the products of the reaction are of such character that they could be formed only by cleavage of a carbon-oxygen bond. Furthermore, the slight difference in mechanisms postulated for reactions of Group I and of Group II can theoretically account for a considerable difference in speed of reaction. The mechanism for Group I involves only addition and wandering of a hydrogen atom (with an electron pair), whereas the mechanism for compounds of Group II involves the breaking

(9) That the decrease in speed of reaction of Group II compounds is not caused by decrease in rate of addition is shown by the lack of this temperature effect in the case of Group I compounds. Another interpretation—that the slowness with which the final reaction products of Group II are formed is due to an extraordinary stability of an intermediate borine addition product—is also not sound. If this interpretation were correct this intermediate could be detected, but no direct evidence of its existence was obtained. Irrespective of its nature, the hypothetical addition product must be quite unstable and its rate of formation must be determined by the rate of its rearrangement to the stable end-products.

of the carbon-oxygen link, a reaction undoubtedly involving a high energy of activation.

Other factors beside the stability and nature of the hypothetical borine addition products are probably involved. The specific chemical properties of the individual organic compounds under discussion cannot be without considerable influence. Furthermore, parallelisms other than that with the character and stability of the boron fluoride addition products can be drawn. Thus the compounds of Group I are, in general, the most readily reduced, and the reactions under discussion are reductions. But this fact need not be considered an objection to the hypothesis herein advanced; on the contrary, it is quite conceivable that the ease of reduction of the types of compounds under discussion is in many cases related to their ability to form addition compounds with the reducing agent.

Another interesting fact was discovered in this investigation. In previous researches in the chemistry of diborane, the usual procedure in carrying out reactions has been to condense the diborane and the other reactant in a reaction flask, and then permit them to vaporize. It was assumed that most reactions took place in the gas phase. But an experiment in which acetone vapor was mixed with diborane, without condensation, showed that the reaction in the gas phase is extremely slow compared with that between diborane and liquid acetone. The slight reaction which did occur was wall-catalyzed.

Experimental Part

Apparatus and Technique.—The apparatus and technical methods used in this investigation have been described by Stock¹⁰ and in earlier papers of this series.¹¹ However, the use of three types of reaction flasks must be mentioned. The flask having an inner cup, as shown in Fig. 1, was used in the earlier part of the work. Measured samples of the reactants were condensed by means of liquid nitrogen contained in the in-sealed cup and, after the connection to the apparatus had been closed, the liquid nitrogen was removed by a blast of air. The diborane evaporated first, and then the heavier vapor of the organic substance could mix with it rather effectively. When it was discovered that the reaction took place mainly in the liquid phase before the organic compound had vaporized completely, the use of this type of reaction vessel was discontinued.

The flask shown in Fig. 2 was used in some of the attempts to follow the rate of the reaction between diborane

(10) Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933; *Ber.*, **54A**, 142 (1921).

(11) Schlesinger and Walker, *THIS JOURNAL*, **57**, 622 (1935); Burg, *ibid.*, **56**, 499 (1934), and earlier publications.

and acetone in the gas phase. The quantities of the reactants were such that the total pressure remained small enough to permit the acetone to evaporate rapidly and completely. Nevertheless, the reaction in the liquid phase was so rapid that it was necessary to devise a method of mixing the diborane with acetone vapor in the absence of any liquid phase.

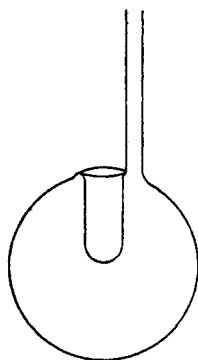


Fig. 1.

This elimination of the liquid phase was accomplished by the use of the apparatus shown in Fig. 3. The organic compound was condensed in the flask and its vapor imprisoned, thereby allowing the mercury to rise into the adjacent manometer. After complete evaporation, the vapor was mixed with diborane by allowing the latter to evaporate from the U-tube and bubble through the mercury in the manometer. Since the diborane

entered at the bottom of the flask, the mixing with the heavier vapors was very effective.

The Reaction of Diborane with Acetaldehyde.—In the reaction of acetaldehyde with diborane good yields of the new compound diethoxyborine are obtained. This substance, like its previously discovered homolog dimethoxyborine,¹² decomposes on standing to produce diborane and the corresponding trialkyl borate. Also like dimethoxyborine, it is hydrolyzed rapidly to produce one mole of boric acid, one mole of hydrogen, and two moles of alcohol per mole of compound.

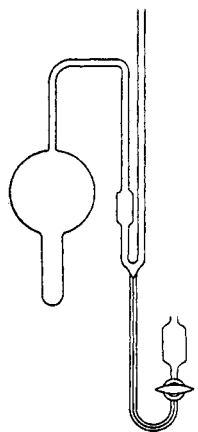


Fig. 2.

The production of diethoxyborine is not quantitative because of side reactions. A certain amount of solid material which appears to be a polymer of monoethoxyborine is formed.

The question whether triethyl borate is produced could not be decided because of the formation of considerable quantities of paraldehyde; these compounds are almost equally volatile.

In a typical experiment, 52.3 cc. of pure diborane¹³ (vapor tension 225 mm. at -111.8°) and 200 cc. of acetaldehyde (vapor tension 331 mm. at 0°) were condensed together in a reaction flask of the first type. After five minutes at room temperature, the residual reactants were passed through a U-tube at -80° (in which all of the reaction products condensed completely) and returned to the reaction chamber. After four repetitions of this process,

(12) Burg and Schlesinger, *THIS JOURNAL*, **55**, 4021 (1933).

(13) All volumes given in this paper refer to gases at standard conditions.

there remained 19.5 cc. of diborane and 6.0 cc. of acetaldehyde; hence 32.8 cc. of diborane and 194 cc. of acetaldehyde had reacted to produce less volatile material. Unexplained side reactions produced 2.6 cc. of hydrogen. The main product was diethoxyborine, contaminated with material whose vapor tension was 3.5 mm. at 0° (probably a mixture of paraldehyde and ethyl borate). The diethoxyborine was purified by fractional condensation: it passed through a U-tube at -65° , but it was trapped completely at -80° . The vapor tension of the pure material at 0° is 37.5 mm. The yield from the experiment was 52 cc., representing nearly 80% of the diborane used by the reaction.

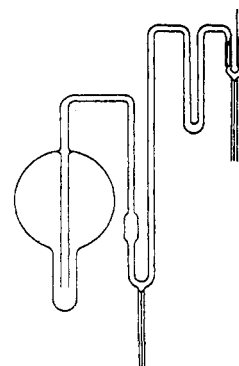


Fig. 3.

The molecular weight of diethoxyborine was determined to be 103 (24.6 cc. weighed 0.1132 g.); the calculated value is 101.9.

The analysis of diethoxyborine was carried out in two ways: by the nitric oxide catalyzed combustion with oxygen in a sealed bulb, and by hydrolysis.

A 7.65-cc. sample of the material was condensed in a 250-cc. bulb, and then 10 cc. of nitric oxide and 180 cc. of pure oxygen were added. The sealed bulb was heated for two hours at 400° ; then it was opened by a tube opener and the volatile contents pumped off through a red-hot tube packed with copper gauze, followed by a trap at -155° . This trap condensed the carbon dioxide and water, but not the nitric oxide nor the oxygen. The metaboric acid remaining in the bulb was heated to convert it to boric anhydride and water, a reaction which occurs easily *in vacuo*. The water was separated from the carbon dioxide by fractional condensation (water was trapped at -80°); the former was weighed and the latter measured as a gas. The boric anhydride was dissolved in water and titrated. The results were 7.7 "cc." of boron¹⁴ (calcd. 7.65), 33.5 mg. of water (that is, 40.7 cc.; calcd. 42.1), and 30.5 cc. of carbon dioxide (calcd. 30.6). The data obtained for hydrogen by this method are never very dependable since a small quantity of water usually clings to the glass walls of the originally dry apparatus.

A 5.90-cc. sample of the material was hydrolyzed in a sealed bulb containing a small excess of water. The resulting hydrogen was measured; the alcohol was separated from the water by repeated fractional condensation, and measured as a vapor; the boric acid was titrated. The results were 5.94 cc. of hydrogen (calcd. 5.90), 11.4 cc. of alcohol (calcd. 11.8), and 5.8 "cc." of boric acid (calcd. 5.9).

The Reaction of Diborane with Acetone.—The main product of the reaction of diborane with acetone (equation 2) was identified as diisopropoxyborine by a determination of its molecular

(14) Calculated as a monoatomic gas.

weight and by hydrolytic analysis. The chemical behavior of this new compound is like that of its lighter homologs.

A 236-cc. sample of diborane was treated at room temperature with a total of 108 cc. of pure acetone (vapor tension 67.5 mm. at 0°) in four separate portions, each acting for five minutes. The excess diborane was recovered by trapping all of the other material in a U-tube at -130°; the unchanged acetone was recovered by slow passage through a U-tube at -60°, in which the products of the reaction were condensed completely. It was thus learned that 20 cc. of the diborane had reacted with 80.3 cc. of acetone. The main product was purified by passing it through a U-tube at -40° and trapping it at -60°. The yield was 36.9 cc. of a substance having a vapor tension of 10 mm. at 0° (a 92% yield based on the quantity of diborane used).

The molecular weight was determined as 131.2 (36.9 cc. weighed 0.2121 g.); the calculated value is 129.9.

Hydrolysis of 28.3 cc. of the product formed 28.4 cc. of hydrogen, 28.3 "cc." of boron, and 55.0 cc. of isopropyl alcohol; these results correspond closely with the assigned formula.

The alcohol was separated from the excess water used in the hydrolysis by repeated passage of the mixture through a tube containing calcium carbide. Its identity was indicated by its vapor tensions: 8.6 mm. at 0° and 32.5 mm. at 20°. This identification was verified by preparing from the sample the isopropyl ester of 3-nitrophthalic acid (m. p. 154-154.5°).¹⁶

The Reaction of Diborane with Trimethylacetaldehyde.—The study of the reaction of diborane with trimethylacetaldehyde was undertaken primarily to discover whether enolization played any necessary part in the addition of diborane to the carbonyl group. It was found that diborane reacts readily with this non-enolizing aldehyde in a manner quite analogous to its reaction with acetone or acetaldehyde.

The reactants, 221 cc. of diborane and 21.7 cc. of trimethylacetaldehyde,¹⁷ were condensed in the reaction flask and allowed to react during ten minutes at room temperature. There remained 217 cc. of diborane and 5.5 cc. of trimethylacetaldehyde; the latter was recovered by several distillations through a trap at -50°. Thus 4.0 cc. of diborane had reacted with 16.2 cc. of the aldehyde, indicating a process which may be represented by the equation

(15) Compare Parks and Barton, *THIS JOURNAL*, **50**, 24 (1928).

(16) Nicolet and Sachs, *ibid.*, **47**, 2348 (1925); Dickinson, Crosson and Copenhaver, *ibid.*, **59**, 1094 (1937).

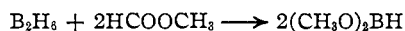
(17) The preparation of trimethylacetaldehyde was originally attempted by the action of *t*-butylmagnesium chloride upon ethyl orthoformate, according to the general procedure suggested by Wood and Comley, *J. Soc. Chem. Ind.*, **42**, 429 (1923). A product was obtained in moderate yield, but investigation disclosed that it was not trimethylacetaldehyde, b. p. 74-76°, but *t*-butyl ethyl ether, b. p. 73.1°. The preparation of the aldehyde was then accomplished by the addition of *t*-butylmagnesium chloride to an excess of ethyl formate at -80°; cf. Whitmore, "Organic Chemistry," D. Van Nostrand Company, New York, N. Y., 1937, p. 246.



The reaction product was purified by passage through a U-tube at 8°. Only one substance seemed to be present; its vapor tension was 3 mm. at 25°.

Because of its low volatility and its instability, this product was not investigated beyond the demonstration of the presence of a boron-hydrogen bond (by hydrolysis). There is no reason to doubt that the compound is the neopentyl homolog of the dialkoxyborines previously described. The ease of its formation discredits the idea that enolization is required for the reaction here studied.

The Reaction of Diborane with Methyl Formate.—Methyl formate reacts with diborane in such a manner that the only products which can be isolated are dimethoxyborine and methyl borate. The addition of diborane to the carbonyl group of acetaldehyde or acetone is far more rapid than the present reaction, which nevertheless is completed during eleven hours at room temperature. The total result may be expressed by the equation



followed by the previously observed reversible disproportionation of dimethoxyborine into diborane and methyl borate.¹²

A 47.9-cc. sample of methyl formate (vapor tension 203 mm. at 0°) and 431 cc. of pure diborane were condensed into the reaction flask. After ten minutes at room temperature, the two were separated; no apparent reaction had occurred. The reactants were remixed and allowed to remain at room temperature for eleven hours. The residual diborane was purified by passage through a U-tube at -140°. Since 410 cc. of diborane was recovered, 21 cc. had been used in the reaction. The products were 6.4 cc. of methyl borate (identified by its vapor tension of 35 mm. at 0° and melting point of -29°) and 35.0 cc. of dimethoxyborine (vapor tension 275 mm. at 0°).

From the ease with which the dimethoxyborine was purified, it was evident that no trace of methyl formate remained among the reaction products. In estimating the yields, it appeared that all of the boron from the diborane which underwent reaction reappeared as methyl borate and dimethoxyborine. On the other hand, there was some loss of carbon (approximately 6.6 "cc."), some loss of hydrogen (approximately 15 cc.), and some loss of oxygen (approximately 6.6 cc.). The proportions of these losses were near enough to the formula $(\text{CH}_2\text{O})_x$ to suggest the formation of a polymer of formaldehyde as a by-product. On the basis of the mechanism of the reaction suggested

in the introduction, the formation of formaldehyde would be expected.

The Reaction of Diborane with Ethyl Acetate.

—The study of the reaction of diborane with ethyl acetate was undertaken in order to establish the generality of the reaction of diborane with esters.

Diborane (153.5 cc.) and ethyl acetate (35.7 cc.; vapor tension 24.2 mm. at 0°), were left together for twenty-four hours in a one-liter reaction flask and permitted to stand at room temperature. As the reaction was then found to be only 25% complete, the mixture was returned to the reaction flask and permitted to stand at room temperature for three days longer. The residual diborane was then separated and measured; 9.5 cc. had reacted. The reaction product could not be purified completely, apparently because of a residual trace of the slightly less volatile ethyl acetate (the vapor tension of the exhaustively fractionated sample was only 34 mm. at 0°, whereas the value for pure diethoxyborine is 37.5 mm.). However, the reaction of this product with ethyl alcohol to form ethyl borate (vapor tension 3.0 mm. at 0°)¹⁸ and hydrogen clearly indicated that it was mainly diethoxyborine.

It is to be noted that the reaction products obtained by the interaction of diborane and esters are of such character that they could have been formed only by cleavage of a carbon-oxygen bond.

Diborane with Acid Chlorides.—All attempts to bring about a reaction between diborane and either acetyl chloride or phosgene, met with failure. In some cases the mixtures were heated enough to cause some decomposition of the diborane, but the acid chloride always could be recovered completely. At one time it was thought possible that these negative results might be due to an inactivating effect of the acid chlorides, similar to that discovered in the mutarotation of glucose.¹⁹ However, this idea was discarded when it was found that acetone reacts as readily with diborane in the presence of these acid chlorides as in their absence.

Diborane and Chloral.—The treatment of chloral with diborane also led to no reaction under any conditions tried. It now appeared that the inertness must be attributed to some fundamental difference in the properties of the carbonyl group in the different classes of compounds, and the investigation of the addition of boron fluoride to the carbonyl group was undertaken to test this conclusion.

Boron Fluoride-Carbonyl Complex Compounds.—Although a large number of boron

(18) Compare Webster and Dennis, *THIS JOURNAL*, **55**, 3234 (1933).

(19) Lowry and Magson, *J. Chem. Soc.*, **98**, 119 (1908).

fluoride addition products have been prepared during the past few years, the addition of boron fluoride to the carbonyl group has been almost entirely neglected. Gasselin²⁰ early reported that acetone forms a double compound with boron fluoride, melting at 35–40° and decomposing at 50°. The addition of boron fluoride to acetyl chloride at –80° has been reported by Meerwein.²¹ Quantitative data on the stabilities of these compounds were completely lacking. Since it seemed likely that such data would offer a convenient basis for comparing the electron donor properties of the carbonyl groups in various molecules, a number of the addition compounds were prepared and their decomposition pressures determined. It was found that the complex compounds formed by the addition of boron fluoride to the carbonyl groups of acetyl chloride and chloral are far less stable than those formed from boron fluoride with acetone, acetaldehyde, and trimethylacetaldehyde. The first group of compounds exist only at temperatures of –50° to –80°, while those of the second group are relatively stable at ordinary temperatures.

A 19.8-cc. sample of acetyl chloride was treated with 31.3 cc. of boron fluoride at –105° until absorption ceased. The excess boron fluoride was removed and measured as 12.0 cc. Hence 19.3 cc. of the boron fluoride had been absorbed by 19.8 cc. of acetyl chloride. The decomposition pressures of the complex compound at various temperatures were then determined.²² The data (Table I) are represented by the equation

$$\log p = -\frac{2877}{T} + 15.762$$

The addition of boron fluoride to chloral could be completed only by raising the temperature above the melting point of chloral (–57.5°) and maintaining a relatively high pressure of boron fluoride. After the maximum absorption had occurred, the tube was cooled to –100° and the excess boron fluoride removed. Since chloral is solid at the temperatures at which the decomposition pressures were observed, equilibrium was reached with greater difficulty than in the previous case. The data for the chloral compound (Table I) are represented by the equation

$$\log p = -\frac{2812}{T} + 15.000$$

No evidence for the formation of a complex compound between boron fluoride and carbonyl chloride could be observed even at temperatures as low as –120°. The additive property of the carbonyl group in this compound must be far less

(20) Gasselin, *Ann. chim. phys.*, [7] **3**, 58 (1894).

(21) Meerwein and Maier-Huser, *J. prakt. Chem.*, **134**, 51 (1932).

(22) Carbon dioxide and ammonia vapor tension thermometers were used to measure the temperatures.

TABLE I
EQUILIBRIUM PRESSURES OF BORON FLUORIDE ADDITION
COMPOUNDS

— With acetyl chloride —			— With chloral —		
<i>t</i> , °C.	<i>p</i> _{mm.} (obsd.)	<i>p</i> _{mm.} (calcd.)	<i>t</i> , °C.	<i>p</i> _{mm.} (obsd.)	<i>p</i> _{mm.} (calcd.)
-83.8	3.8	3.7	-78.2	4.0	3.8
-75.8	17.0	15.4	-75.5	6.0	6.0
-71.8	30.5	29.9	-71.9	11.0	10.7
-68.7	49.0	49.3	-68.3	18.0	18.7
-64.7	90.5	92.4	-65.7	27.8	26.7
-63.7	106	107	-59.2	74	72
-61.9	140	140	-58.0	91	85
-60.2	180	180	-53.7	150	154

pronounced even than that of chloral or acetyl chloride.

Both acetone and trimethylacetaldehyde readily add one equivalent of boron fluoride to form white solids stable at ordinary temperatures. The preparation of the boron fluoride-acetaldehyde compound is more difficult because the addition is accompanied by considerable polymerization of the aldehyde. These compounds were not studied beyond the observation of their relatively great stability.

The Reaction of Diborane with Acetone at -80°.—The existence of the borine-acetone addition compound could not be demonstrated by a study of the addition of diborane to acetone at -80°, evidently because the later steps of the reaction occur far too rapidly.

Thus 18.35 cc. of diborane was placed over 22.2 cc. of acetone kept at -80°. The pressure dropped very rapidly and soon became constant, as shown by the data in Table II.

TABLE II
ABSORPTION OF DIBORANE BY ACETONE AT -80°

Time, min.	0	3	10	60	120
Pressure, mm.	102 (calcd.)	81.0	76.5	76.0	76.0

The reaction was practically complete after ten minutes. Only 5.60 cc. of diborane was absorbed; this corresponds closely to the amount required (5.55 cc.) for the quantitative production of diisopropoxyborine from 22.2 cc. of acetone, while twice as much diborane would be required for the postulated complex compound. Actually, diisopropoxyborine was the only product isolated.

In a second attempt to demonstrate the borine-acetone intermediate, diborane was allowed to react with acetone at -80° for only three minutes; then the excess diborane was removed quickly and trimethylamine was added. If the borine-acetone complex compound had been present, the trimethylamine should have displaced the acetone to form the very stable compound, borine trimethylamine. However, the only product

which could be isolated was an unstable addition product of trimethylamine and diisopropoxyborine.²³ It therefore seems that any possible complex compound of borine with acetone is far too labile for a direct demonstration of its existence.

Further Studies on the Reaction of Diborane with Esters.—According to step B, equation 3, the interpretation advanced for the reactions of esters with diborane implies the intermediate formation of an aldehyde, which then reacts further with diborane. Since aldehydes react with diborane much faster than do esters, success in isolating the aldehyde seems very unlikely, but several reactions were carried out with this objective. Since the desired products were not obtained, the results are reported only very briefly.

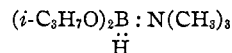
Formaldehyde is not obtained by the reaction of an excess of methyl formate with diborane, nor could methyl formate be obtained from a mixture of diborane and methyl carbonate. Methyl trichloroacetate,²⁴ which might have given the unreactive chloral with diborane, does not react with the latter in four days at room temperature or in four hours at 70-80°. Longer treatment was useless as decomposition of diborane sets in.

The Relative Inertness of Diborane toward Acetone in the Gas Phase.—At one time an attempt was made to study the rate of reaction of diborane with acetone by following the decrease in the pressure of a reaction mixture containing the reactants entirely in the gas phase. The reaction was very slow, however, for it was only partially completed during twenty-four hours. Further investigation disclosed that even this slow reaction did not occur primarily in the vapor phase, for the reaction is catalyzed by glass.

In these experiments, the partial pressure of diborane was relatively low; hence it was considered possible that a certain critical pressure of diborane might be required for a rapid reaction. This idea was investigated and rejected; the rate in the gas phase is low even at high concentrations of diborane.

Into a 254-cc. flask of the type shown in Fig. 2, 10.4 cc. of diborane and 20.6 cc. of acetone were condensed. After

(23) This compound, whose structure evidently is to be represented as



is a white solid, melting between -19 and -10°. It appears to be completely dissociated at room temperature.

(24) This ester was conveniently prepared by the action of methyl alcohol on trichloroacetyl chloride, which was prepared by the method of Brown, *THIS JOURNAL*, **60**, 1325 (1938).

the mercury had been raised into the manometer, shutting off the flask from the rest of the apparatus, the condensed material was quickly vaporized by immersion in a bath of warm water. As shown in Table III, the pressure de-

TABLE III

REACTION OF DIBORANE WITH ACETONE (VAPOR)

Time, hours	0	1/60	1	10	30
Pressure, mm.	101 (calcd.)	95	94.7	88.7	78.3

creased very slowly. The discrepancy between the calculated pressure and the measured pressure at the end of one minute probably is due to reaction in the liquid phase, during the few seconds before the acetone was completely vaporized. The pressure calculated for complete reaction to form diisopropoxyborine is 51 mm.

In another experiment, the reaction vessel was packed with short lengths (average 15 mm.) of 4-mm. Pyrex tubing. Into this packed chamber were introduced 15.8 cc. of acetone and 9.7 cc. of diborane. The reactants were vaporized as before and the fall in pressure was observed. The results appear in Table IV. They leave no doubt that packing the reaction vessel increases the reaction rate.

TABLE IV

REACTION OF DIBORANE WITH ACETONE IN A PACKED CHAMBER

Time, hours	0	1/60	1/2	1	4
Pressure, mm.	104 (calcd.)	97	89	85.5	65.0

Into a reaction flask of the type shown in Fig. 3 were placed 148.1 cc. of diborane and 19.0 cc. of acetone. From the results (reaction at room temperature, as in the other experiments) given in Table V, it is seen that even at higher pressures the gas-phase reaction is very slow compared to that between diborane and liquid acetone. In this experiment, in which the reactants never were in contact with each other in a liquid phase, the first observed pressure agreed with the calculated initial value.

TABLE V

REACTION OF DIBORANE WITH ACETONE VAPOR IN A FLASK OF TYPE 3

Time, hours	0	1/30	1/6	1	8
Pressure, mm.	376 (calcd.)	375.8	375	368	351

Summary

1. The behavior of diborane toward organic compounds containing a carbonyl group is of

three types: (1) rapid addition to the carbonyl groups of simple aldehydes and ketones, such as acetone, acetaldehyde, and trimethylacetaldehyde, to form dialkoxyborines; (2) slow reaction with esters such as methyl formate and ethyl acetate, to yield similar products; (3) no reaction with acid chlorides or chloral.

2. Boron fluoride adds to the carbonyl groups of acetone, acetaldehyde, trimethylacetaldehyde, chloral and acetyl chloride to form complex compounds whose relative stabilities measure the electron donor properties of the carbonyl group in these substances. There exists a complete correlation between the ability of a carbonyl group to react with diborane and its ability to add boron fluoride.

3. This correlation is intelligible in terms of a mechanism for the addition of diborane to the carbonyl group, a mechanism involving (1) the intermediate formation of a complex compound of borine with the carbonyl group, followed by (2) the migration of a proton with a pair of electrons from the boron atom to the carbon atom of the carbonyl group. The reaction of diborane with esters, however, appears to proceed in another manner: by an attack upon the ether linkage in these molecules.

4. The reaction of diborane with acetone takes place primarily in the liquid phase; the reaction in the gas phase is extremely slow and is surface-catalyzed.

5. In the course of these studies, the following new compounds were prepared: diethoxyborine, diisopropoxyborine, dineopentoxyborine, and the one to one addition products of boron fluoride with chloral, acetaldehyde, and trimethylacetaldehyde. The decomposition pressures of the products of addition of boron fluoride to chloral and to acetyl chloride, were measured at various temperatures.

CHICAGO, ILLINOIS

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