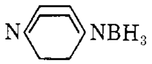
TABLE IV

INFRARED ABSORPTIONS (CM^{-1}) OF TEDA·2BH$_3$

2985 m	1460 s	996 m
2915 w	1328 s	873 m
2370 vs	1159 vs	851 s
2309 s	1071 s	841 sh
2273 s	1059 s	

Cooling this solution to room temperature produced a white, air-stable precipitate which could be purified by sublimation *in vacuo* at 100°. The sublimed material melted at 167–170° with decomposition as evidenced by rapid resolidification above the melting point. TEDA·BH$_3$, it may be noted, is the first monoborane adduct of a difunctional base to exhibit thermal stability at and above room temperature. Analysis gave a C:B ratio of 6.01 in good agreement with the value expected for the structure



A sample heated to 180° for several hours and then fractionally sublimed led to recovery of TEDA, TEDA·2BH$_3$, and the starting material, each identified by its infrared spectrum (the infrared absorptions are presented in Table V). The ratio of TEDA to TEDA·2BH$_3$ recovered was 0.95, which agrees with the value expected for the reaction

TABLE V

INFRARED ABSORPTIONS (CM^{-1}) OF TEDA·BH$_3$

2967 s	1477 m	1040 m
2898 m	1460 s	989 m
2358 s	1372 w	962 m
2315 s	1324 s	872 s
2273 s	1287 m	838 s
2203 m	1174 vs	804 m
2128 w	1063 s	790 m
2045 w	1048 s	669 m

$$2\text{TEDA}\cdot\text{BH}_3 \rightleftharpoons \text{TEDA} + \text{TEDA}\cdot 2\text{BH}_3$$

The proton nmr spectrum of a benzene solution of the monoborane adduct of TEDA revealed a single resonance which was identical in chemical shift with that of authentic TEDA. While the measurement was being made, a white precipitate assumed to be TEDA·2BH$_3$ appeared. Since, over a period of several months, the crystalline monoadduct has shown no evidence of such deterioration, we infer that the monoadduct is stable in the solid phase but unstable (with respect to disproportionation) in solution.

Experimental Section

All preparations and sublimations with the exception of those involving the monoborane adduct of TEDA were carried out in conventional Stock-type vacuum apparatus. The diadducts were made by vigorously stirring a cold ether solution of excess amine under a diborane atmosphere until no further pressure change occurred. DMP·2BH$_3$ was isolated by filtration under a nitrogen atmosphere and was returned to the vacuum apparatus for sublimation. TEDA·2BH$_3$ was crystallized by concentration of an acetonitrile solution in a nitrogen stream.

TEDA·BH$_3$ was prepared in air by heating TEDA·2BH$_3$ with excess TMED in a water bath at 70°, crystallized by cooling to room temperature, and isolated by suction filtration. The product was washed several times with hexane and purified by vacuum sublimation.

Proton nmr spectra were determined with a Varian A60 and a Varian HA100 spectrometer while B^{11} nmr spectra were obtained with a Varian 4300-2 12-Mc spectrometer.

Infrared spectra were run on mineral oil and perchlorobutadiene mulls using a Beckman IR 5A spectrophotometer.

Acknowledgment.—The authors are indebted to the National Science Foundation for providing much of the nuclear magnetic resonance instrumentation used in these studies.

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Boroxine: A Simplified Preparation[1]

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Received June 28, 1966

Methods presently available for the preparation of boroxine ($H_3B_3O_3$) are a high-temperature reaction of H_2O with elemental boron[2] and an explosive reaction of B_5H_9 and oxygen.[3] Gaseous $H_3B_3O_3$ is thermodynamically unstable with respect to B_2O_3(s) and B_2H_6(g) at ordinary temperatures.[4] However, under certain conditions, the decomposition reaction is not rapid and it is possible to isolate small quantities of this compound for chemical studies.[5,6] An alternative preparative procedure, starting with diborane and oxygen, offers certain advantages that are described in this paper.

Experimental Section

Diborane was obtained from the reaction of stannous chloride with potassium borohydride *in vacuo* at 250°.[7] Oxygen, research grade, was obtained from the Matheson Co. and used without further purification. The reaction was carried out in a 350-ml Pyrex vessel illustrated in Figure 1. Reaction mixtures were prepared by first adding B_2H_6 and then slowly adding O_2 from a reservoir at pressures high enough to prevent backflow of B_2H_6. The reaction was initiated by applying an electrical discharge from a Tesla coil to a piece of Kovar wire sealed through the neck of the reaction vessel. For these experiments it is imperative that the reaction vessels be taped and placed behind a safety shield. The total pressure of the reaction mixtures never exceeded 40 mm. Under these conditions, initiation of the reaction was noted by a flash of light. It should be cautioned, however, that at higher pressures the explosive reaction may be intense enough to fragment the reaction vessel. Mass spectrometric analyses indicated that the gaseous products were mainly H_2(g) and $B_3O_3H_3$(g). Deuterated boroxine was obtained by substituting B_2D_6 for normal diborane in the reaction. Infrared spectra of $H_3B_3O_3$(g) and $D_3B_3O_3$(g) are shown in Figure

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[1] Work supported by the U. S. Army Research Office (Durham) and the Advanced Research Projects Agency.

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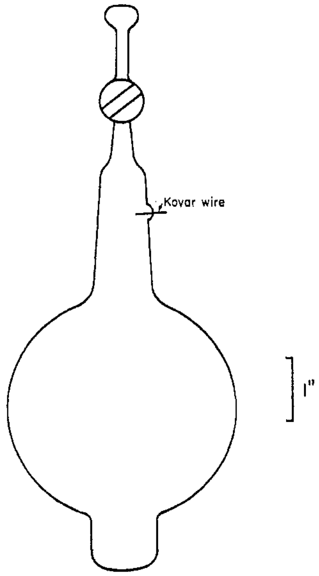

Figure 1.—Reaction vessel.

2. The yield of boroxine was determined by noting the decrease in total pressure of the products as $H_3B_3O_3(g)$ decomposed according to the reaction[4]

$$H_3B_3O_3(g) \longrightarrow 1/2\ B_2H_6(g) + B_2O_3(s) \qquad (1)$$

The pressure of B_2H_6 produced by complete decomposition was obtained from infrared absorbance measurements. The initial pressures of $H_3B_3O_3$ calculated from the B_2H_6 pressure agreed within 5% of the values obtained from the decrease in total pressure. Results for a series of runs are shown in Table I.

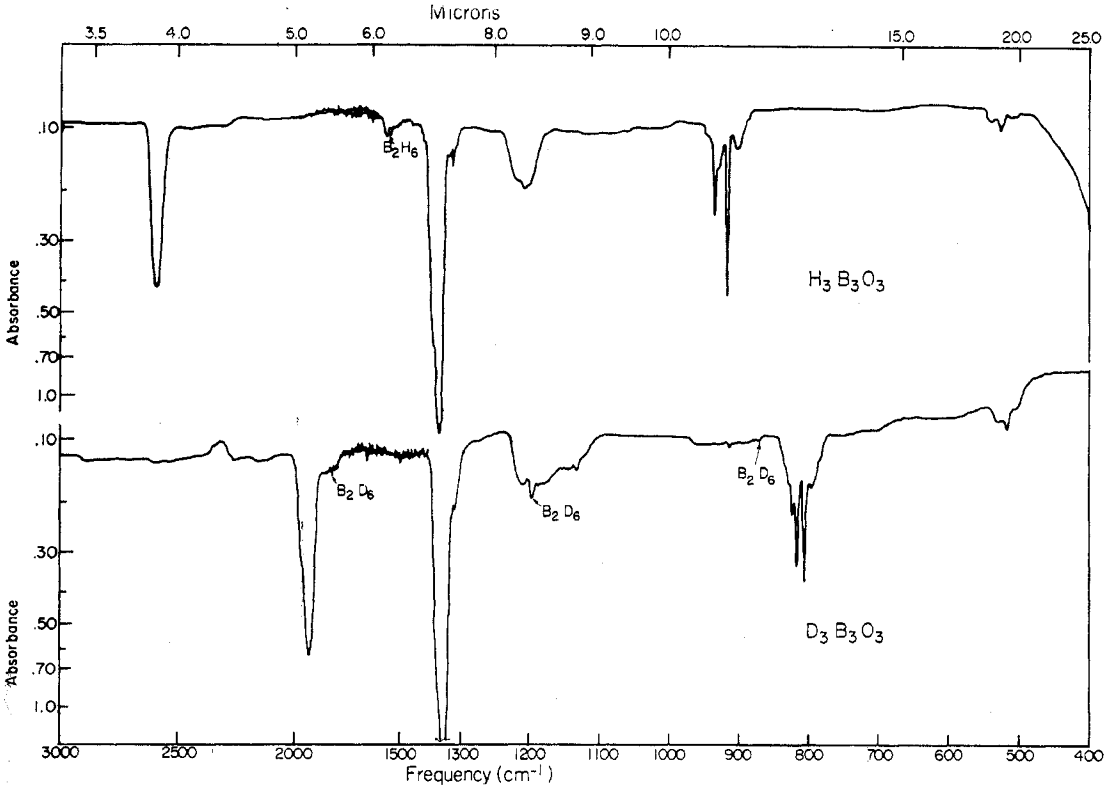

Figure 2.—Infrared spectra of $H_3B_3O_3(g)$ (KBr cell) and $D_3B_3O_3(g)$ (CsBr cell).

Results and Discussion

Examination of the data in Table I indicated that the highest yields of boroxine were obtained with a $B_2H_6:O_2$ ratio of about unity and a total pressure between 20 and 25 mm. Under these conditions, O_2 was entirely consumed and the amount of residual B_2H_6 was less than 5% of the original. The white solid formed in the reaction was mostly B_2O_3. This was determined from its infrared spectrum[8] and from considerations of the material balance with respect to H_2 produced. An approximate stoichiometric equation can be written as in eq 2.

TABLE I

DATA FOR B_2H_6–O_2 EXPLOSION REACTION

Initial B_2H_6 pressure, mm	Initial O_2 pressure, mm	Final $B_3O_3H_3$ pressure, mm	Final H_2 pressure, mm
11.2	11.1[b]	4.6	26.9
13.1[a]	11.9[b]	3.5	37.7
11.6	20.2[b]	Present in very low yield	26.8
11.8[a]	20.4[b]	Present in very low yield	32.5
24.0	10.4	Present in very low yield	72.7
24.7[a]	11.5	0.5[c]	75.4

[a] Reaction vessel coated with products of the preceding run. [b] Oxygen completely consumed in the reaction (shown by mass spectrometric measurements). [c] Small amount of $H_2B_2O_3$ produced after initial explosion.

$$B_2H_6(g) + O_2(g) \longrightarrow 0.32H_3B_3O_3(g) + 2.8H_2(g) + 0.4B_2O_3(s) \qquad (2)$$

Results of experiments using either excess O_2 or B_2H_6 indicated that there were two competing proc-

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(8) T. A. Sidorov and N. N. Sobolev, *Opt. i Spektroskopiya*, **3**, 9 (1958).

esses. When O_2 was in excess, oxidation to B_2O_3 and H_2 occurred, but when B_2H_6 was in excess, decomposition of B_2H_6 became important. Pyrolysis must become more rapid than the oxidation process under these conditions since some O_2 remained after the explosion. This type of decomposition of B_2H_6, initiated by another exothermic reaction, in this case the explosive oxidation of B_2H_6, has been observed previously. Gunn and Green[9] noted that the decomposition B_2H_6 was initiated by the explosive decomposition of stibine. The $H_2B_2O_3$ observed must arise from a reaction of O_2 with boroxine[10]

$$H_3B_3O_3(g) + {}^1/_2O_2(g) \longrightarrow H_2B_2O_3(g) + {}^1/_6B_2H_6(g) + {}^1/_3B_2O_3(s) \quad (3)$$

In most cases it was found that the presence of solid deposits produced on the wall of the reaction vessel did not notably affect the yield of $H_3B_3O_3$ obtained in a subsequent run in the same vessel. However, it was noted that a buildup of these deposits tended to inhibit initiation of the reaction by the electrical discharge.

This preparation of $H_3B_3O_3$ involving only the readily available B_2H_6 and O_2 as starting materials is more convenient than the high-temperature procedure or the use of B_5H_9 which is usually obtained by controlled pyrolysis of B_2H_6. Initiation of the reaction, using an electrical discharge rather than heat, avoids a complication due to the unpredictability of the explosion limits for these reactions. This method also affords an easy route to $H_2B_2O_3$ by reaction 3. Preferential isotopic labeling of the oxygen positions in $H_2B_2O_3$ is possible by using different isotopic species of oxygen in the initial preparation of $H_3B_3O_3$ and further reaction with labeled O_2 to obtain either $H_2B_2{}^{16}O^{18}O_2$ or $H_2B_2{}^{18}O^{16}O_2$.

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Electric Moments of Certain Substituted Tris(acetylacetonato)chromium(III) Compounds

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Received June 30, 1966

There has been considerable interest in recent years in the nature of the bonding in the chelate ring of β-diketones. Calvin and Wilson[2] explained the greater stability of Cu(II) chelates of β-diketones over those of salicylaldehydes in terms of the stabilizing influence of benzenoid resonance in the chelate ring. This view was strengthened by the determination, by X-ray crystallography,[3] of the planarity, C_{2v} symmetry, as well as of the 1.39-A distance of C–C atoms of the chelate ring of tris(acetylacetonato)iron(III). Cotton and Holm[4] have questioned the validity of the presence of "aromaticity" in these chelate rings on the basis of charge-transfer spectra and pmr measurements of a wide variety of acetylacetonates. Collman,[5] on the other hand, using arguments based on the chemical reactivity of acetylacetonates, considers that the term "quasiaromatic" applied to these chelate rings is important in the description of the chemical behavior of the acetylacetonate chelates.

Since the values of C–Cl and $C–NO_2$ group moments are sensitive to the nature of the carbon atom [C_{aliph}–Cl (μ = 1.93 D.), $C_{aliph}–NO_2$ (μ = 3.2 D.), C_{arom}–Cl (μ = 1.57 D.), $C_{arom}–NO_2$ (μ = 4.0 D.)],[6] this study was undertaken to shed further light on the nature of the chelate ring in tris(acetylacetonato)chromium(III).

In order to calculate the electric moment from dielectric polarization data obtained in solution, it is necessary to evaluate both the electronic and atomic polarizations. In most cases, where atomic polarization is relatively small, these two terms are combined and evaluated as the molar refraction at the Na D line.[7]

With compounds, such as the acetylacetone chelates, that have abnormally large atomic polarization values, solution measurements usually give meaningless results[8] when this procedure is followed.

In this work, we have attempted to overcome this problem in the following way. Reasoning that the atomic polarization of a closely related series of compounds would vary in a regular manner, we have assumed the induced polarization (the sum of electronic and atomic polarizations) values of the mono- and disubstituted chelates are evenly spaced between the values of the un- and trisubstituted chelates. Since the un- and trisubstituted chelates are symmetrical, their electric moments are considered to be zero so that their measured total dielectric polarizations are equal to their induced polarizations. Thus, with 6.5- and 25.0-cc/mole differences in total polarization between tris(acetylacetonato)chromium(III) and its trichloro and trinitro analogs, respectively, the induced polarizations of the mono- and disubstituted compounds are obtained by adding ${}^1/_3$ and ${}^2/_3$, respectively, of these differences to the induced polarization of the tris(acetylacetonato)chromium(III). Even in the case of the nitro series, where the increment is 8.25 cc/mole, the

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