brucine. After discarding small batches of yellow gummy material obtained during the concentration of the solution, the residue was taken up in ethanol and the solution diluted with chloroform, then made cloudy with ether. A gelatinous precipitate, 1.66 g., was finally obtained and air dried. Some of this was subjected to hydrogenolysis followed by ion exchange and fresh brucine. The product thus obtained was found to be brucinium sulfate by its x-ray diffraction pattern and a sulfate test. Another sample was dissolved in a minimum of hot water, the solution diluted with ethanol, and finally made cloudy with ether. A crystalline product resulted. This was recrystallized for analysis. Its melting point was 197.5–200.5° dec. It gave negative sulfate and nitrate tests.

Anal. Found: C, 57.01, 56.97; H, 5.95, 6.01; N, 5.61; S, 6.04; O (by difference), 25.38.

These data indicate a molecular formula of $C_{50}H_{64}N_4O_{17}S_2$. Of the possible compounds it might be, brucinium methyl α-D-glucopyranoside disulfate comes closest to this: $C_{53}H_{66}N_4O_{20}S_2$, Calcd.: C, 55.68; H, 5.82; N, 4.90; S, 5.61. Per cent brucinium ion was determined by ion exchange[2] to the free acid followed by titration with standard base. As with the elemental analysis, the results were indicative of a disulfate but did not prove it: Calcd.: brucinium methylglucoside monosulfate, 59.1% brucinium ion; brucinium methyl glucoside disulfate, 69.2% brucinium ion. Found: 74% brucinium ion.

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Addition of Iodine Monochloride to Chlorotrifluoroethylene[1]

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The recent publication of Haptschein, Braid, and Fainberg[3] on the addition of iodine monochloride to chlorotrifluoroethylene has prompted us to submit the following confirmatory and supplementary data from our own independent investigation. We have confirmed the formation of two isomers and have successfully separated them by vapor-liquid partition chromatography (VPC). The addition was carried out on a one-mole scale in a Parr low pressure hydrogenation apparatus and yielded 69% (based on iodine monochloride) of crude haloethanes consisting of roughly equal amounts of 1,2-dichloro-1-iodo-1,2,2-trifluoroethane (I) and 2,2-dichloro-1-iodo-1,1,2-trifluoroethane (II) with a small amount of 1,1,2-trichloro-1,2,2-trifluoroethane (III).

Pure I and II were obtained from the crude mixture by VPC in 1-ml. portions on an 18 mm. i.d. by 4-m. column of nonylphenoxy(polyethoxy)ethanol on 42–60 mesh C-22 firebrick (25/100) at 100°. Helium at an inlet pressure of 24 p.s.i.g. was used as the carrier gas.

The identity of the individual isomers follows from the behavior of the corresponding dichlorotrifluoro-1-butenes derived from them by reaction with ethylene followed by dehydroiodination.[4] The butene derived from II [4,4-dichloro-3,3,4-trifluorobutene-1 (IV)] was recovered unchanged on treatment with zinc and isopropyl alcohol under conditions which converted that from I [3,4-dichloro-3,4,4-trifluorobutene-1 (V)] to 1,1,2 trifluorobutadiene.[5]

IV and V were purified by VPC on the nonylphenoxy(polyethoxy)ethanol column at 55°. V contained 1% of an unidentified impurity which was not separated on the nonylphenoxy(polyethoxy)ethanol column but was readily removed on a similar column of Zonyl E-91[6] at 55°. The molecular weight of IV as determined by PVT measurements was 180.0, that of V, 178.7 (Calcd. for $C_4H_3Cl_2F_3$, 179.0).

Physical properties of the two haloethanes and the two halobutenes are listed in Table I. The major infrared absorption bands for I in the vapor state were at 8.45, 9.10, 9.70, 11.50, 12.00, 12.50, 12.50, and 13.50 μ. Those for II were at 8.45, 8.60, 9.00, 9.85, 11.05, 11.80, and 13.3μ. Those for IV were at 7.10, 8.05, 8.40, 8.80, 9.25, 9.85, 10.20, 10.40, 11.05, 11.50, and 13.70 μ. Those for V were at 7.10, 8.20, 8.60, 9.20, 9.50, 9.80, 10.25, 10.45, 11.30, and 12.00 μ. A C=C stretching frequency was ob-

TABLE I

PHYSICAL PROPERTIES OF HALOETHANES AND HALOBUTENES

	I	II	IV	V
A[a]	7.5257	7.5089	7.5538	7.5394
B[a]	1751.8	1741.4	1632.0	1641.1
nbp. °C	103.9	103.1	76.0	79.1
$\Delta H_{vap.}$ cal./mole	7569	7506	7002	7045
Trouton ratio	20.1	19.9	20.0	20.0
$n^{25.2}D$	1.44816	1.44512	1.37382	1.37364
d_{23}	2.20	2.19	1.39	1.33
t_c/t_{CCl_4}[b]	3.12	2.69	0.95 (2.02)	0.73 (1.70)

[a] A and B are the constants for the vapor pressure equation $\log P_{(mm.\ Hg)} = A - B/T_{(°K)}$ in the range 300 to 800 mm. The vapor pressure curve and constants derived therefrom were obtained as previously described.[9] [b] Elution time ratios as defined in ref. 3 for a nonylphenoxy(polyethoxy)ethanol column at 100° for I and II and at 55° for IV and V. Figures in parentheses are for the Zonyl E-91 column at 55°.

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(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

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served at 5.30 μ in both butene isomers, but it was quite weak.

Ultraviolet irradiation of either I or II in the gas phase in a quartz vessel resulted in the formation of a mixture of I and II in a ratio of about 3:2, together with sizable amounts of iodine, III and chlorotrifluoroethylene[7]; no coupling[8] occurred. In the liquid phase in the presence of a halogen getter such as mercury, coupling[8] but not isomerization took place; and the formation of III and chlorotrifluoroethylene was very much reduced. Photochemical chlorination of either I or II in the gas phase produced III in high yield.

The observation by Hauptschein *et al.*[3] that I was more reactive than II was also confirmed. When either the addition to ethylene or the ultraviolet-light-promoted coupling reaction was carried out on a mixture of roughly equal amounts of I and II, recovered starting material was always over 99% II.

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(7) Hauptschein, (ref. 3) reported no isomerization occurred on heating either isomer at 40–50° with iodine monochloride in the presence of iron.

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The Preparation of Phosphite and Phosphinite Decaboranes

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In the course of some other work to be reported in detail in the near future, and encouraged by the work of Reetz[1] in preparing trialkyl phosphite boranes, we undertook the preparation of some phosphite and phosphinite derivatives of decaborane.

The reaction of decaborane with Lewis bases to produce $B_{10}H_{12}(Base)_2$ materials is well established[2] as is the replacement of the ligands with materials of higher base strengths in such molecules.[3] Accordingly it was found that organic phosphites would react with decaborane in refluxing benzene to produce the corresponding $B_{10}H_{12}$ derivatives as exemplified by the following equation. It was subsequently found that higher yields could be obtained when the replacement reaction with bis(acetonitrile)decaborane was employed, and the best yields were obtaned when bis(diethyl sulfide)[4] decaborane was used in a similar reaction.

$$B_{10}H_{14} + 2\,(C_2H_5O)_3P \longrightarrow H_2 + B_{10}H_{12}[(C_2H_5O)_3P]_2$$

$$B_{10}H_{12}[(C_2H_5)_2S]_2 + 2R_2R'P \longrightarrow B_{10}H_{12}[R_2R'P]_2 + 2\,(C_2H_5)_2S$$

I. $R = R' = OC_2H_5$
II. $R = R' = —OC_6H_5$
III. $R = —C_6H_5,\ R' = —OC_2H_5$

Although only compound I was prepared directly from decaborane it is thought that II and III[5] can likewise be prepared in this manner.

EXPERIMENTAL

Materials, Bis(acetonitrile)decaborane, bis(diethyl sulfide)decaborane, and ethyl diphenylphosphinite were prepared in these laboratories by established literature procedures. Decaborane was obtained from the Olin Mathieson Chemical Corp. and repurified by sublimation shortly before use. Other chemicals were used as received from suppliers.

Bis(triethyl phosphite)decaborane I. 1. To 5 g. (0.041 mole) of sublimed decaborane and 100 ml. of benzene in a 250-ml. three-necked flask was added 15 g. (0.09 mole) of triethyl phosphite. The reactants were refluxed for 20 hr. in an inert atmosphere, cooled, and the solution was washed with two 100-ml. portions of dilute (1:8) hydrochloric acid. The solvent was removed and the residue was sublimed to insure removal of any unchanged decaborane (no decaborane was recovered). The resultant viscous oil was dissolved in a minimum of methanol and cooled slowly to 0° The white crystalline product (6.8 g.) was isolated by filtration (37%; m.p. 90–91°)

Anal. Calcd. for $B_{10}C_{12}H_{42}P_2O_6$: C, 31.8; H, 9.3; P, 13.7; B, 24.1. Found: C, 31.8; H, 9.5; P, 13.3; B, 24.4.

2. To 10 g. (0.033 mole) of bis(diethyl sulfide)decaborane and 100 ml. of benzene in a 250-ml. three-necked flask was added 17 g. (0.1 mole) of triethyl phosphite. The reactants were refluxed for 10 hr. in an inert atmosphere, cooled, and washed with two 100-ml. portions of dilute (1:8) hydrochloric acid. Upon removal of the solvent layer, 20.5 g. of a light brown solid was recovered. When recrystallized from methanol, 12.8 g. of white crystalline product was isolated (85%; m.p. 90°) which was demonstrated to be identical to the material prepared from decaborane.

3. To 5 g. (0.025 mole) of bis(acetonitrile)decaborane and 100 ml. of benzene in a 250-ml. three-necked flask was added 10 g. (0.06 mole) of triethyl phosphite. The reactants were refluxed for 10 hr. in an inert atmosphere and washed with two 100-ml. portions of dilute (1:8) hydrochloric acid. After removal of solvent from the organic layer, 11.0 g. of crude product was isolated. Upon recrystallizing from methanol 8.0 g. of the product was recovered (72%; m.p. 90°).

Bis(triphenyl phosphite) decaborane II. To 5 g. (0.017 mole) of bis(diethyl sulfide)decaborane and 100 ml. of benzene in a 250-ml., three-necked flask was added 12 g. (0.039 mole) triphenyl phosphite. On cooling after refluxing for 6 hr. in an inert atmosphere, a white solid precipitated. The solid (10 g.) was removed and since it was found to be virtually insoluble in common organic solvents it was washed several times with benzene and then washed with hot methanol to purify (81%; m.p. 209–210°).

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(5) Substantiated later by Dr. H. A. Schroeder of these laboratories; to be published as part of a larger undertaking.