TABLE I

CHROMATOGRAPHIC DATA FOR ADSORPTION AND ELUTION OF COMPOUND I

			Active eluted fractions			
Solute adsorbed, g.	Chromatographic conditions	Quantity recovered, g.[a]	Concn., 10^2 *M*	Specific rotation, $[\alpha]_{5983}$[b]	Max. mol. rotation, $[M]_{5983}$[c]	Racemization constant, 10^2k, hr.$^{-1}$
0.0490	Column: 13 drops/min.	0.0460	1.044	−6.63	−20.11	
	Breakthrough: 9.25 hr.					3.2
	Total time: 12.00 hr.		1.102	+6.89	+20.89	
0.0569	Column: 12 drops/min.	0.0530	0.664	−12.43	−37.69	
	Breakthrough: 8.0 hr.					3.9
	Total time: 11.0 hr.		0.711	+11.59	+35.15	

[a] Determined spectrophotometrically. [b] Readings determined using a Bendix Ericsson ELT-NPL automatic polarimeter, Type 143A, and a 4.0-cm. cell (precision = ±0.0004°). [c] $[M]_{5983} = [\alpha]_{5983} \times$ molecular weight $\times 10^{-2}$.

also have a square pyramidal structure and would exhibit stereoisomerism. Compounds of type A should exist as optical enantiomers. Compounds of type B should exhibit both geometrical and optical isomerism; the *trans* forms should be susceptible to resolution into optical enantiomers.

A compound of type A, bisacetylacetonepropylenediiminooxovanadium(IV), compound I, was prepared by heating the ligand[2] (0.012 mole) and bis-(2,4-pentanediono)oxovanadium(IV) hydrate (0.01 mole) at 230–250° for 2.5 hr.; acetylacetone distilled, and the product was isolated from the residue by crystallization from toluene: dark blue crystals, m.p. 199–200° (24% yield). *Anal.* Calcd. for $C_{13}H_{20}O_3N_2V$: C, 51.48; H, 6.60; N, 9.24. Found: C, 51.56; H, 6.54; N, 9.09.[3]

Compound I was resolved by means of a chromatographic technique[4] which consisted of adsorption on a column of D-lactose, followed by elution with toluene. Prior to adsorption, there was no indication of optical activity of compound I in toluene. Typical resolution data are summarized in Table I. Concentrations of the eluted fractions were determined spectrophotometrically, and it was found that the spectra of the eluted fractions corresponded to those of compound I.

Compound I should exist as two pairs of optical enantiomers inasmuch as the ligand itself contains an asymmetric carbon atom. In each trial only two fractions having maximum dextro and levo rotation were observed. However, it has been found that either fraction undergoes slow mutarotation, reaches a maximum value, and then racemization apparently occurs. This is a stereospecific change, and it is provisionally interpreted as being due to conversion of a less stable enantiomorphic form to the more stable, followed by racemization. However, because of the low magnitude of the specific rotation, it has not been possible to determine the rotatory dispersion curves.

It should be noted that compound I could be a six-coordinate complex in solution with a molecule of toluene occupying the sixth coordination position. It has not been possible to detect the formation of a toluene adduct in carbon tetrachloride solution as determined by Job's method[5] using absorption spectra (380–720 mμ).

Investigation of the optical activity of compounds of type A and B is in progress.

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[2] P. J. McCarthy, R. J. Hovey, K. Ueno, and A. E. Martell, *J. Am. Chem. Soc.*, **77**, 5820 (1955).

[3] A second sample was prepared by heating the ligand[2] (0.01 mole) and vanadium pentoxide (0.014 mole) at 240° for 1.2 hr.; dark blue crystals, m.p. 202–204°. *Anal.* Found: C, 51.39; H, 6.66; N, 8.98.

[4] T. Moeller and E. Gulyas, *J. Inorg. Nucl. Chem.*, **5**, 245 (1958).

[5] *Cf.* W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).

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The Preparation of Hexaborane

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Hexaborane has long been one of the least accessible of the boron hydrides, being first isolated by Stock[2] in poor yield by the hydrolysis of magnesium boride, and more recently by Kotlensky and Schaeffer,[3] by the action of an electrical discharge on diborane, and by Boone and Burg[4] in good yield by treating unstable pentaborane B_5H_{11} with bases.

We have hydrolyzed magnesium boride prepared from technical amorphous boron and magnesium powder and have found the yields of hexaborane to be at least ten times as high as reported by Stock or by the Russian workers Markina and Mikheeva.[5] The mixture of hydrides obtained by the hydrolysis was separated by gas–liquid chromatography, and the individual hydrides were trapped and weighed to determine the yields. The hexaborane was identified by its molecular weight[6] (found 75.5, correct 74.9),

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[2] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

[3] W. V. Kotlensky and R. Schaeffer, *J. Am. Chem. Soc.*, **80**, 4517 (1958).

[4] J. L. Boone and A. B. Burg, *ibid.*, **80**, 1519 (1958); **81**, 1766 (1959).

[5] V. I. Mikheeva and V. Yu. Markina, *Zh. Neorgan. Khim.*, **1**, 619 (1956).

[6] C. S. G. Phillips and P. L. Timms, *J. Chromatog.*, **5**, 131 (1961).

TABLE I

YIELDS OF BORANES FROM VARIOUS MAGNESIUM BORIDE SAMPLES

Expt.	Type of boron	Comp. of mixture	Temp. of heating, °C.	Time of heating, min.	% yield of hydrides (based on boron)			
					B_4H_{10}	B_5H_9	B_6H_{10}	Total
1	Tech. amorph.	Mg_3B_2	640	120	5.0	0.4	4.5	9.9
2	Tech. amorph.	Mg_3B_2	770	30	4.7	0.4	5.5	10.6
3	Tech. amorph.	Mg_3B_2	770	240	3.4	0.7	6.0	10.1
4	Tech. amorph.	MgB_2	770	30	1.1	0.4	2.7	4.2
5	Tech. amorph.	Mg_3B	770	30	6.6	0.3	5.5	12.4
6	99.5% pure cryst.	Mg_3B_2	770	40	1.8	0.2	2.2	4.2

its melting point (found −62.2°, reported −65°,[2] −63.4°,[7] −62.3°[8]), and its vapor pressure at 0° (found 7.2 mm., lit.[2,8] 7.2 mm.).

When a 3:1 by weight mixture of 98% pure magnesium powder and about 80% pure technical amorphous boron was heated to 780° for 30 min. in a covered alumina boat in a stream of pure hydrogen, a boride was formed which yielded 5.5% of its boron content as hexaborane on hydrolysis with 8 *M* phosphoric acid.[9] The total yield of hydrides was about 11% based on the boron. Table I shows the yields of tetraborane, pentaborane B_5H_9, and hexaborane from samples of magnesium boride prepared under different conditions. Appreciable amounts of decaborane were also formed but were not estimated in the total hydride yield. Trace amounts of unstable pentaborane B_5H_{11} were obtained from borides prepared at the higher temperatures.

The hydrolysis reaction was carried out in a 1-l. flask. In a typical experiment 5 g. of the powdered boride was tamped into five or six 1-cm. bore cylinders of very thin aluminum foil and these were added to 200 ml. of acid over a period of about 15 min. The foil dissolved away quickly, liberating the boride into the acid at a convenient rate. A flow of 600 ml./min. of hydrogen was passed for 1 hr. through the acid to carry the hydrides through a phosphorus pentoxide drying tube into a trap cooled in liquid oxygen.

The yields of hexaborane were reduced if the temperature of the phosphoric acid rose above about 80° during the hydrolysis. Temperature control was facilitated and the yields of hexaborane improved by using the high ratio of acid volume to boride weight of 200 ml.:5 g. Where the cost of boron is not limiting, the alloy of composition MgB_2 can be used to advantage (see experiment 4, Table I). It gives more hexaborane per weight of boride than Mg_3B_2 and evolves much less heat in reaction with the acid, so that larger samples of hexaborane can be made at one time. It is interesting that the relative yields of hydrides are the same from borides made with amorphous and crystalline boron (compare experiments 2 and 6, Table I) although the total hydride yield is much lower from the latter.

In our system the trapped hydrides were separated by injection onto a 12 ft. × 1 cm. column packed with 10% tritolyl phosphate on Celite. The detector was a katharometer (Pretzel Cell, Gow-Mac Instrument Co.) and the column flow was 600 ml./min. of oxygen-free hydrogen. Relative to *n*-hexane the retention times for tetraborane, pentaborane, and hexaborane on tritolyl phosphate at 20° are approximately 0.5, 3.7, and 49.5. At room temperature on our column the start of the peak from a 250-mg. sample of hexaborane emerged 2.5 hr. after the other boron hydrides and possible silane and phosphine impurities. This suggests that a 3 ft. × 1 cm. column would probably adequately purify samples of up to 250 mg. of hexaborane.

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(7) S. G. Gibbins and I. Shapiro, *J. Chem. Phys.*, **30**, 1483 (1959).

(8) A. B. Burg and R. Kratzer, *Inorg. Chem.*, **1**, 725 (1962).

(9) B. D. Steele and J. E. Mills, *J. Chem. Soc.*, **74** (1930).

CONTRIBUTION FROM THE RESEARCH LABORATORIES
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Tetracarbonylcyclopentadienyl Compounds of the Group V Transition Metals

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Although several organometallic compounds belonging to the classes of "double sandwich" and "half-sandwich" π-complexes of vanadium are known,[2] very few fully characterized organometallic[3] complexes of tantalum and niobium have been reported. The latter group is represented by the tetracyclopentadienyl complexes of niobium and tantalum,[4a] bis-cyclopentadienyltantalum trihydride,[4b] and the recently reported tetracarbonylcyclopentadienylniobium.[5] We now wish to report the preparation and properties of tetracarbonylcyclopentadienyltantalum, as well as a new and more efficient procedure for the vanadium and niobium homologs.

The reductive carbonylation of group V metal chlorides has previously been shown to furnish the

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[1] To whom all communications should be addressed.

[2] (a) E. O. Fischer and W. Hafner, *Z. Naturforsch.*, **9b**, 503 (1954); (b) R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **81**, 5263 (1959); (c) R. P. M. Werner and S. A. Manastyrskyj, *ibid.*, **83**, 2023 (1961); (d) E. O. Fischer and H. P. Kögler, *Chem. Ber.*, **90**, 250 (1957); (e) R. L. Pruett, J. E. Wyman, D. R. Rink, and L. Parts, U. S. Patent 3,007,954 (Nov. 7, 1961).

[3] Defined here as those complexes which do not contain metal–oxygen or metal–halogen bonds.

[4] (a) E. O. Fischer and A. Treiber, *Chem. Ber.*, **94**, 2193 (1961); (b) M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4854 (1961).

[5] R. B. King, *Z. Naturforsch.*, **18b**, 157 (1963).