

The reductions of Ia and Ib in the potential region of the first polarographic wave also were investigated using triangular wave cyclic voltammetry at a hanging mercury drop electrode. Scan rates ranging from 33.3 mv./sec. to 500 v./sec. (300 c.p.s.) were used. The reduction of Ia was reversible, giving a single cathodic and a single anodic peak under all conditions. Results obtained for the reduction of Ib depended on the rate of voltage scan. At the lower rates of scan (below 1 c.p.s.) five species were detected: Ib and Ib radical, Ia and Ia radical, and cyanide ion. The presence of Ib radical was detected easily at the lowest rates of voltage scan used, indicating that the dimerization reaction is relatively slow. At higher rates of voltage scan (>100 c.p.s.) only Ib and Ib radical were detected.

Polarographically, Ic and Id showed single,  $pH$  dependent waves. Attempts to produce one electron reductions at high  $pH$  values were not successful. At  $pH$  12 the free base completely destroyed the material within an hour.

**Tetra-*n*-butylammonium Perchlorate Solutions in Acetonitrile.**—The reduction of each of these salts also was investigated polarographically in acetonitrile and in each case the first wave corresponded to a reversible one electron reduction. The half wave potentials for Ia, Ib, Ic, and Id, were  $-0.57$ ,  $-0.79$ ,  $-0.93$ , and  $-1.06$  v., respectively. These values indicate that pyridinium ions are more easily reduced as the electron withdrawing power of the 4-substituent increases. In this aprotic solvent system further reduction was not observed for Ib, Ic, or Id. In the case of Ia, a second wave appeared at  $-1.06$  v., since here the two electron reduction does not involve hydrogen.

Controlled potential electrolyses were carried out to generate macro amounts of the free radical species. The electrolysis potentials were in the diffusion current region of each salt. The coulometric current efficiencies indicated that some minor side reactions accompanied the reduction of Ic and Id. The reduction of Ia proceeded very cleanly to give the expected blue free radical. As in the aqueous reductions, Ib radical dimerized to give the radical derived from Ia. This material was identified by its polarographic behavior and visible spectrum.

The electrode reactions in acetonitrile also were investigated using cyclic triangular wave voltammetry with a hanging mercury drop electrode. In each case the waves were reversible and only a single cathodic peak and a single anodic peak were observed over the entire range of voltage scan rates. For Ib, this indicates that the dimerization of the initially formed radical is much slower in acetonitrile than in water.

The formation of stable free radicals on reduction of Ia, Ic, and Id was proved conclusively by e.p.r. spectroscopy, although quantitative comparisons of the resonance spectra were not possible.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF WISCONSIN  
MADISON 6, WISCONSIN

W. M. SCHWARZ  
EDWARD M. KOSOWER  
IRVING SHAIN

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## RHODIUM HEXAFLUORIDE<sup>1</sup>

Sir:

Recently ruthenium hexafluoride was prepared by burning ruthenium metal in a fluorine atmosphere in a liquid nitrogen cooled quartz reactor.<sup>2</sup> The same method now has been applied successfully to the preparation of rhodium hexafluoride, the next member of this transition series. Under similar conditions it was not possible to make the last member of the series, palladium hexafluoride.

Ruff and Ascher<sup>3</sup> were the first to report studies of the reaction between rhodium and fluorine. At 500–600° their main product was the trifluoride. They also reported the formation of a small amount of a red-brown sublimate which they presumed to be either RhF<sub>4</sub> or RhF<sub>5</sub>. The highest rhodium fluoride that Sharpe<sup>4</sup> reported in his studies using bromine trifluoride as a fluorinating agent was the tetrafluoride. Prior to the preparation of RhF<sub>6</sub> no hexavalent rhodium compound had been prepared.

Solid rhodium hexafluoride, in bulk, is black in color; the gas is a deep red-brown, resembling ruthenium hexafluoride. Chemical analyses on different samples indicate a formula RhF<sub>6</sub> (calcd. for RhF<sub>6</sub>: F, 52.6; Rh, 47.4. Found: F, 51.8 ± 2.4; Rh, 47.8 ± 0.4.) Vapor density measurements at 50 mm. pressure give a molecular weight of 219 ± 4 compared with a formula weight of 216.9 for RhF<sub>6</sub>. X-Ray diffraction patterns show the solid to have a pseudo-orthorhombic structure at  $-23^\circ$ , and a cubic structure at room temperature.<sup>5</sup> Preliminary vapor pressure measurements with the solid gave the results:

$t$ , °C.	0	5	11	16	20
$p$ , mm.	15	19	29	40	49.5

Rhodium hexafluoride, unlike the other transition metal hexafluorides, appears to decompose into fluorine and a lower fluoride at room temperature. Preliminary investigations of the rate of this decomposition show it to be negligible at 0°. A sample of vapor kept at 50° was found to be 15% decomposed after three hours. The amount of fluorine produced in this experiment was equivalent to one half a mole per mole of hexafluoride decomposed.

The main features of the infrared spectrum are very similar to those of molybdenum hexafluoride<sup>6</sup>; this suggests that rhodium hexafluoride is similar in structure to the other hexafluorides and has the symmetry of a regular octahedron. Two very intense bands, presumably  $\nu_3$  and  $\nu_4$ , have been observed, one at 722 and the other at 283.5  $\text{cm.}^{-1}$ . Evidence for a dynamic Jahn-Teller coupling such as that found in ruthenium hexafluoride<sup>2</sup> has not been found. These observations parallel those made for the corresponding iso-electronic compounds

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) H. H. Claassen, H. Selig, J. G. Malm, C. L. Chernick and B. Weinstock, *J. Am. Chem. Soc.*, **83**, 2390 (1961).

(3) O. Ruff and E. Ascher, *Z. anorg. Chem.*, **183**, 206 (1929).

(4) A. G. Sharpe, *J. Chem. Soc.*, 3444 (1950).

(5) D. Northrop and S. Siegel, unpublished results.

(6) T. G. Burke, D. F. Smith and A. H. Nielsen, *J. Chem. Phys.*, **20**, 447 (1952).

osmium hexafluoride and iridium hexafluoride.<sup>7</sup>

Table I summarizes some of the properties of the 4d series hexafluorides. The volatility decreases rapidly in going across the series, although each compound is less volatile than its counterpart in the 5d transition series. The solid-solid transition temperatures and the triple points increase regularly; the values given in the table for RhF<sub>6</sub> are approximate extrapolations and have not been observed directly. An attempt to measure the triple point by warming the solid in a glass capillary was unsuccessful because of rapid decomposition of the sample. The infrared active fundamentals  $\nu_3$  and  $\nu_4$  observed in this series are of the same magnitude as those in the 5d series.<sup>8</sup> Although the metal to fluorine distances are not known for the 4d series, the fact that the infrared frequencies do not vary greatly from molybdenum to rhodium indicates that the metal to fluorine bond lengths also do not vary, as has been found for the 5d series.<sup>8</sup>

TABLE I

	MoF <sub>6</sub>	TcF <sub>6</sub>	RuF <sub>6</sub>	RhF <sub>6</sub>
Vapor pressure at 15°	361 <sup>a</sup>	135 <sup>d</sup>	58 <sup>f</sup>	38
Solid-solid transition temp.	-9.55 <sup>b</sup>	-5.3 <sup>e</sup>	+2.5 <sup>f</sup>	(+7)
Triple point	17.45 <sup>b</sup>	37 <sup>e</sup>	54 <sup>f</sup>	(70)
Infrared active fundamental $\nu_3$ <sup>c</sup>	741	745	735	722
fundamental $\nu_4$ <sup>c</sup>	264	265	275	283.5

<sup>a</sup> O. Ruff and E. Ascher, *Z. anorg. Chem.*, **196**, 419 (1931).

<sup>b</sup> A. P. Brady, O. E. Myers and J. D. Clauss, *J. Phys. Chem.*, **64**, 588 (1960).

<sup>c</sup> Unpublished results from this laboratory.

<sup>d</sup> H. Selig, C. L. Chernick and J. G. Malm, *J. Inorg. Nucl. Chem.*, in press.

<sup>e</sup> J. G. Malm and H. Selig, to be published.

<sup>f</sup> Ref. 2.

(7) H. H. Claassen and B. Weinstock, *J. Chem. Phys.*, **33**, 436 (1960).

(8) H. H. Claassen, *ibid.*, **30**, 968 (1959).

ARGONNE NATIONAL LABORATORY  
 ARGONNE, ILLINOIS  
 FORD MOTOR COMPANY  
 SCIENTIFIC RESEARCH LABORATORY  
 DEARBORN, MICHIGAN

CEDRIC L. CHERNICK  
 HOWARD H. CLAASSEN  
 BERNARD WEINSTOCK

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## STEREOCHEMICAL CONSEQUENCES OF KETONE REDUCTIONS BY DIBORANE AND SUBSTITUTED BORANES

Sir:

We wish to report the achievement of steric control of the reduction of cyclanones by the use of dialkylboranes containing bulky substituents, such as disiamylborane and diisopinocampheylborane, as well as the applicability of the latter reagent for the asymmetric reduction of ketones.

The reduction of norcamphor by lithium aluminum hydride and by sodium borohydride yields *endo*-norborneol predominantly, evidently produced via a hydride transfer from the reagent to the carbonyl group from the less hindered direction. Similar results are observed in related rigid bicyclic systems.<sup>1</sup> On the other hand, the reduction of 2-methylcyclopentanone and 2-methylcyclohexanone by these reagents gives predominantly

(69–75%) of the more stable *trans* alcohol.<sup>2</sup> These phenomena have been discussed by Dauben and his co-workers<sup>2c</sup> in terms of "steric approach control" and "product development control."

Diborane is an interesting reducing agent with reducing capabilities quite different from those of the basic complex hydrides.<sup>3</sup> However, in the present instance it yields predominantly *trans*-2-methylcyclopentanol (69%) and *trans*-2-methylcyclohexanol (65%). The introduction of bulky substituents, as in disiamylborane, markedly modifies the hydroborating<sup>4</sup> and reducing<sup>5</sup> action of the reagent. This reagent led to the predominant formation of the *cis* alcohols: 78% *cis*-2-methylcyclopentanol and 77% *cis*-2-methylcyclohexanol.

In seeking to enhance the steric requirements of the reagents, we had recourse to diisopinocampheylborane, previously utilized for the asymmetric hydroboration of olefins.<sup>6</sup> With this reagent we realized the formation of 94% *cis*-2-methylcyclopentanol and 92% of *cis*-2-methylcyclohexanol. Thus, it has been possible to achieve a shift from predominant *trans* to nearly complete *cis* formation by the use of boranes with high steric requirements.

Diisopinocampheylborane had led previously to the asymmetric synthesis of alcohols *via* the hydroboration of olefins in optical purities of 80–90%.<sup>6</sup> It was of interest to examine the optical purities of the products resulting from the reduction of ketones with this reagent.

The mixture of 2-methylcyclohexanols exhibited optical activity, but because of the difficulty in separating the two isomers we were unable to determine the optical purities of the individual compounds. Accordingly, we treated a series of methyl ketones, RCOCH<sub>3</sub>, with this reagent with these results ( $[\alpha]_D^{25}$ , optical purity in %, configuration): R = ethyl, -1.5°, 11%, R; isopropyl, -0.91°, 17%, R; *t*-butyl-, +2.3°, 30%, S<sup>7</sup>; phenyl, +6.0°, 14%, R.

Although the optical purities are far less than those realized in the earlier hydroboration of olefins,<sup>6</sup> they are comparable with those obtained by existing methods. A detailed study of the utility of diisopinocampheylborane for the prediction of absolute configuration is in process.<sup>8</sup>

In a typical reduction a solution of 11.2 g., 100 mmoles, of 2-methylcyclohexanone in 25 ml. of diglyme was added during 15 minutes to a stirred suspension of 100 mmoles of diisopinocampheylborane<sup>6</sup> in 200 ml. of diglyme. The reaction mixture was stirred at 0° for three hours and then left overnight at room temperature. Following oxida-

(2) (a) J. B. Umland and M. I. Jefraim, *J. Am. Chem. Soc.*, **78**, 2788 (1956); (b) J. B. Umland and B. W. Williams, *J. Org. Chem.*, **21**, 1302 (1956); (c) W. G. Dauben, G. J. Fonken and D. S. Noyce, *J. Am. Chem. Soc.*, **78**, 2579 (1956); (d) W. G. Dauben and R. E. Bozak, *J. Org. Chem.*, **24**, 1596 (1959).

(3) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **82**, 681 (1960).

(4) H. C. Brown and G. Zweifel, *ibid.*, **83**, 1241 (1961).

(5) H. C. Brown and D. B. Bigley, *ibid.*, **83**, 486 (1961).

(6) H. C. Brown and G. Zweifel, *ibid.*, **83**, 486 (1961).

(7) J. A. Mills and W. Klyne, "The Correlation of Configuration," Chapt. 5 in W. Klyne, ed., "Progress in Stereochemistry," Vol. 1, Butterworths Scientific Publications, London, 1954, p. 206, have indicated that the evidence for the assignment of configuration to pinaacetyl alcohol "is not entirely convincing."

(8) Research in progress with G. Zweifel and N. R. Ayyangar.

(1) S. Beckmann and R. Mezger, *Ber.*, **89**, 2738 (1956).