

first direct chemical connection between a diterpene of the phyllocladene class and the diterpenoid alkaloids.<sup>12</sup> In view of the rigorous structure proof of the *Garrya* alkaloids,<sup>12</sup> this interconversion also represents a confirmation of Briggs' structure proposal<sup>10</sup> for kaurene (IX).

The absolute configuration of garryfoline (I) and the other diterpenoid alkaloids already has been settled<sup>2</sup> in terms of stereoformula I. The earlier rotatory dispersion arguments<sup>6</sup> in the steviol series applied only to the absolute stereochemistry of positions 8 and 13, but the present interconversion with garryfoline *via* II allows expansion to the absolute configurational representation VI. The only point still open for discussion is the absolute configuration at C-9. Several circumstantial arguments have been raised in favor of an *anti*-backbone, *i.e.*, Ia (and hence VIa) with a 9 $\beta$ -hydrogen atom, among them the very great steric hindrance of C-20 substituted derivatives<sup>2</sup> of garryfoline (I)<sup>13</sup> which is also reflected in the preference<sup>14</sup> of various methine double bonds toward termination at C-20 (establishment of trigonal center) rather than C-19, as well as certain rotational shifts<sup>15</sup> in the related alkaloid ajaconine. If these arguments are accepted, then (-)-kaurene must have absolute configuration IXa rather than IXb.<sup>11</sup> This, in turn, requires that (+)-mirene be represented by VIIIa, since the earlier suggested<sup>11</sup> absolute configuration VIIIb would then imply that kaurene and mirene are antipodes, which is not the case.<sup>11</sup>

Except for this possible uncertainty relating to the stereochemistry of C-9, all structural features as well as the relative and absolute configuration of steviol, mirene, kaurene and the diterpene alkaloids (of the *Garrya* and atisine groups) are now settled.

(12) Garryfoline (I) already has been related (ref. 3) to garryine and veatchine (see K. Wiesner and Z. Valenta in L. Zechmeister's "Progress in the Chemistry of Organic Natural Products," Springer, Vienna, 1958, Vol. XVI, pp. 26-89) as well as to the atisine group (S. W. Pelletier, *J. Am. Chem. Soc.*, **82**, 2398 (1960)).

(13) Stereochemistry Ib requires that ring B be a boat and this presumably reduces steric hindrance to an appreciable extent.

(14) See K. Wiesner and J. A. Edwards, *Experientia*, **11**, 255 (1955); D. Dvornik and O. E. Edwards, *Can. J. Chem.*, **35**, 860 (1957).

(15) D. Dvornik and O. E. Edwards, *Proc. Chem. Soc.*, 305 (1958); A. J. Solo and S. W. Pelletier, *Chem. & Ind.*, 1108 (1960).

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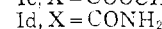
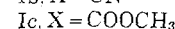
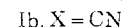
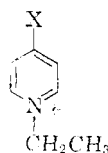
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#### FORMATION OF STABLE FREE RADICALS ON ELECTROREDUCTION OF N-ALKYLPYRIDINIUM SALTS

Sir:

The intensely colored free radical species formed by the one electron reduction of 1,1'-dialkyl-4,4'-dipyridinium salts were characterized by Weitz

and co-workers.<sup>1</sup> Recently Wallenfels and Gellrich<sup>2</sup> reported that colored radicals are formed by chemical reduction of N-dichlorobenzylpyridinium salts in which thiazole or thiazolium substituents are in the 4-position of the ring. In addition, it was reported that free radicals are obtained by chemical reduction of the N-dichlorobenzyl analog of Id. We have investigated the electrochemical reduction of the N-ethylpyridinium salts Ib, Ic, and Id, where the substituents are electron withdrawing, and have detected the presence of stable free radical species. The reduction of Ia was used as a "standard" of behavior for the simple pyridinium salts. The reductions of 10<sup>-3</sup> and 10<sup>-4</sup> M solutions of the various pyridinium salts were carried out in both aqueous and acetonitrile solutions.



#### Buffered Aqueous Potassium Chloride Solution.

—Polarographically, Ia gave two waves: a reversible one electron reduction at -0.71 v. and an irreversible two electron reduction at -1.09 v.<sup>3</sup> In general, the results are comparable to those obtained for similar 4,4'-dipyridinium salts.<sup>4</sup> A controlled potential coulometric reduction of Ia at -0.85 v. yielded the expected blue dipyridinium ion radical with nearly a 100% current efficiency.

In basic solution, Ib also gave two polarographic waves: a reversible one electron reduction at -0.87 v., and a pH dependent second wave at -1.16 v. (pH 8.5). In neutral or acidic solution the second wave is shifted to less negative potentials, obscuring the first wave. In solutions more basic than pH 8.5, the rate of the base catalyzed hydrolysis of the cyano group is increased markedly.<sup>5</sup>

Macroscopic constant potential coulometric reductions of Ib were carried out in buffered solution (pH 8.5) at a potential of -0.93 v., corresponding to the diffusion current region of the first wave. After a short induction period the solutions gradually turned deep blue. Spectroscopic and polarographic measurements showed that the main reduction product was the same radical which was formed from Ia.<sup>6</sup> Apparently the initially formed Ib radical slowly dimerizes with the elimination of two cyanides to produce Ia. Since Ia is more easily reducible than Ib, however, it immediately adds another electron to produce Ia radical. Current efficiencies based on an over-all 1.5 electron reduction of Ib were high, indicating some side reactions were taking place.

(1) See E. Weitz, *Angew. Chem.*, **66**, 658 (1959), and references therein.

(2) K. Wallenfels and M. Gellrich, *Ann.*, **621**, 198 (1959).

(3) All potentials are referred to the aqueous saturated calomel electrode.

(4) R. Elofson and R. Edsberg, *Can. J. Chem.*, **35**, 646 (1957).

(5) J. W. Patton, Ph.D. Thesis, University of Wisconsin, 1961.

(6) Reduction of Ib with sodium dithionite in buffered aqueous solution led to the same radical: J. L. Cotter and E. M. Kosower, unpublished results.

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.

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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).