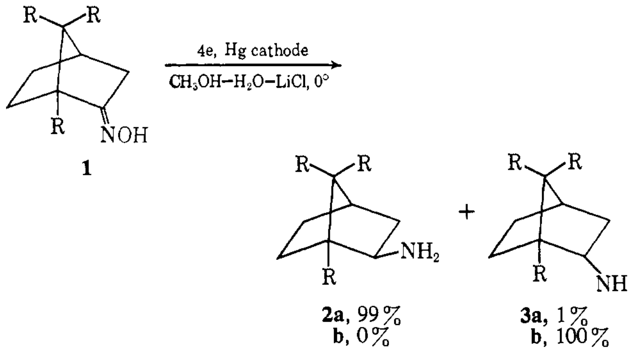
Stereoselective Electrochemical Reductions of Camphor Oxime and Norcamphor Oxime

Sir:

Despite increasing interest in synthetic organic electrochemistry,[1–3] little is known concerning the stereochemistry obtained in organic electrochemical reactions.[4] A working hypothesis has been advanced[4b] that, at least in reductions of alkyl halides, the electrode reactions resemble those in dissolving metal reductions.[5] We now report that (a) electrochemical reductions of camphor oxime (**1a**) and norcamphor oxime (**1b**) at a mercury cathode proceed with a high degree of stereoselectivity, and that (b) the products are in fact of *opposite* stereochemistry to those formed in dissolving metal (sodium–alcohol) reductions of **1a** and **1b** (Table I).



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2a, 99%
b, 0%

3a, 1%
b, 100%

a, R = CH_3; **b**, R = H

Table I. Stereochemistry in Reductions of Bicyclic Oximes[a]

Substrate	Reducing agent	—Relative % products— *exo*-Amine	*endo*-Amine
1a	Mercury cathode	99	1
1a	$LiAlH_4$	99	1
1a	Na-EtOH	4	96
1b	Mercury cathode	0	100
1b	$LiAlH_4$	0	100
1b	Na-EtOH[b]	75	25

[a] Analyses by vpc on a 4-ft column packed with 8% Dowfax 9N9 on Fluoropak 80 at 130° and 180°. [b] K. Alder, G. Stein, and H. Rickert, *Ann.*, **525**, 221 (1936), suggested, from melting behavior of the hydrochlorides, that this reaction gives a mixture predominating in the *endo*-amine. That this is not so is shown by the identity of the major product with a known sample of *exo*-amine prepared by the method of H. C. Brown, W. R. Heydkamp, E. Breuer, and W. S. Murphy, *J. Am. Chem. Soc.*, **86**, 3565 (1964).

The preponderance in these electrolyses of the *less stable* of each epimeric pair of amines imposes stringent stereochemical requirements on the nature of the processes occurring at the electrode. Specifically, no conformationally mobile intermediates can be involved. In view of the similarity between the lithium aluminum hydride and electrochemical reductions, we suggest that the electrolyses proceed by kinetically controlled attack by the electrode upon each oxime from the less hindered side (*endo* attack on **1a** and *exo* attack on **1b**), very possibly with formation of an alkylmercuric species at the electrode surface,[6] followed by protonolysis with retention of configuration, by analogy to a number of other electrophilic aliphatic substitutions.[7]

Electrolyses were carried out at a mercury pool cathode in a divided cell of conventional design.[8] The anolyte was a 1 *M* solution of lithium chloride in 75% methanol–20% water–5% hydrazine; the catholyte was a solution of 2.0–3.0 g of the oxime dissolved in 100 ml of a 1 *M* solution of lithium chloride in 80% methanol–20% water;[9] both controlled-potential[10] reductions (−2.0 v *vs.* Ag-AgCl reference)[11] and constant-current electrolyses were carried out, at initial currents in the range 0.3–0.5 amp, with identical results. Yields of amines were in the range 50–70%; they were accompanied by small amounts of unreacted oxime and ketone formed by hydrolysis of the oxime.

Acknowledgment. Financial support by the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged.

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[3] J. P. Petrovich, J. D. Anderson, and M. M. Baizer, *J. Org. Chem.*, 31, 3897 (1966).

[4] However, see (a) R. Annino, R. E. Erickson, J. Michalovic, and B. McKay, *J. Am. Chem. Soc*, **88**, 4424 (1966); (b) C. K. Mann, J. L. Webb, and H. M. Walborsky, *Tetrahedron Letters*, 2249 (1966).

[5] See also J. H. Brewster, *J. Am. Chem. Soc.*, **76**, 6361 (1954).

[6] M. D. Morris, P. S. McKinney, and E. C. Woodbury, *J. Electroanal. Chem.*, 10, 85 (1965).

[7] *E.g.*, F. R. Jensen and K. L. Nakamaye, *J. Am. Chem. Soc.*, **88**, 3437 (1966).

[8] L. Meites in "Technique of Organic Chemistry," Vol. 1, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 3300.

[9] A referee has suggested that the sodium–alcohol reductions proceed by initial base-catalyzed formation of the equilibrium mixtures of epimeric 2-nitrosobornanes and norbornanes, that the composition of this mixture determines the *exo*:*endo* ratio of amines in the product, and that this epimerization pathway is not available in the electrolysis media. In fact, the solutions become quite basic during electrolysis, due both to accompanying solvent discharge[11] and to protonation of intermediates in the oxime reduction, so that the differences in product ratios cannot be due simply to basicity differences.

[10] M. J. Allen, "Organic Electrode Processes," Reinhold Publishing Corp., New York, N. Y., 1958.

[11] At this potential about 20% of the electrolysis current was involved in solvent discharge at the cathode; coulometry was not carried out, but there is in the literature a considerable amount of coulometric evidence that reductions of oximes indeed consume four electrons/molecule, *e.g.*, H. Lund, *Acta Chem. Scand.*, 13, 249 (1959).

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The Preparation and Configuration of the $[Re_4(CO)_{16}]^{2-}$ Anion. A Planar, Triangulated, Rhenium Carbonyl Cluster[1]

Sir:

In tetrahydrofuran, the reduction of $Re_2(CO)_{10}$ with sodium amalgam at room temperature yields[2] the pale yellow salt $Na^+Re(CO)_5^-\cdot 0.5C_4H_8O$. At reflux temperatures, or with other reducing agents such as sodium borohydride,[3] carbon monoxide is evolved and the solution acquires the intense red coloration typical of polynuclear carbonyl metallates.[4]

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[1] Work supported by NSF Grant GP-6720 (H. D. K.) and ARPA Grant SD-88 (M. R. C.).

[2] W. Beck, W. Hieber, and G. Braun, *Z. Anorg. Chem.*, **308**, 24 (1961).

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[4] See $HFe_3(CO)_{11}$ [J. R. Case, and M. C. Whiting, *J. Chem. Soc.*, 4632 (1960)] or $Ni_4(CO)_9^{2-}$ [cited in the review article by W. Hieber, *Angew. Chem.*, 72, 795 (1960); *Angew. Chem. Intern. Ed. Engl.*, 72, 65 (1961)] or, more recently, $Co_6(CO)_{14}^{4-}$ [P. Chini, *Chem. Commun.*, 440 (1967)].

The complex pattern of infrared absorptions in the carbonyl stretching region and the results of acid hydrolysis (which yields, in varying amounts, $HRe(CO)_5$, $Re_2(CO)_{10}$, and the polynuclear carbonyl hydrides $H_3Re_3(CO)_{12}$[3] and $HRe_3(CO)_{14}$[5]) suggest that this deep red solution contains several different species. We wish now to report some preliminary results of our investigations into the polynuclear metallate solutions of rhenium.

Dirhenium decacarbonyl (5 g, 7.7 mmoles) was stirred with sodium borohydride (1.25 g, 33 mmoles) in tetrahydrofuran (75 ml) for 5 hr at reflux. The solution was decanted from excess solid $NaBH_4$ and evaporated. The dry salts were dissolved in acetone (37 ml) and a saturated solution of tetra-*n*-butylammonium iodide (4.42 g, 12 mmoles) in ethanol was added. More ethanol was added dropwise until some cloudiness was observed; the solution was then titrated with acetone until just clear. On standing overnight at −5°, $[(n\text{-}C_4H_9)_4N^+]_2[Re_4(CO)_{16}{}^{2-}]$ was isolated in about 20% yield (1.5 g) based on total content of rhenium.

Anal. Calcd for $C_{48}H_{72}N_2O_{16}Re_4$: Re, 44.5; C, 34.4; H, 4.30; O, 15.3. Found: Re, 44.43; C, 34.2; H, 4.35; O, 16.5.

Crystals of $[(C_4H_9)_4N^+]_2[Re_4(CO)_{16}{}^{2-}]$ are obtained as dark red plate-like parallelepipeds, crystallizing in the monoclinic spacegroup C2/c ($C_{2h}{}^6$; no. 15) with a = 24.65 A, b = 12.93 A, c = 19.49 A, β = 107.7°, V = 5918 A^3, Z = 4. Observed and calculated densities are respectively 1.89 ± 0.01 and 1.883 g cm^{-3} (M = 1678).

A single-crystal X-ray crystallographic analysis, based on complete three-dimensional data ($\sin \theta_{max}$ = 0.37, Mo Kα radiation) collected with a 0.01°-incrementing Buerger automated diffractometer, has led to the location of all atoms other than hydrogen. Data were corrected for absorption (μ = 87.1 cm^{-1} for Mo Kα radiation), the present discrepancy index, R_F, being 10.6% for the 2700 independent nonzero reflections.

The stereochemistry of the tetranuclear dianion is shown in Figure 1. The rhenium atom skeleton consists of two fused, approximately equilateral, triangles; a crystallographic twofold axis passing through Re_1 and Re_2 requires that the four rhenium atoms lie in a plane. The $Re_4(CO)_{16}{}^{2-}$ ion thus contains the first reported planar, triangulated, tetranuclear metal cluster. (A similar triangulation appears in the metal skeleton of $Co_4(CO)_{10}(C_2H_5C{\equiv}CC_2H_5)$,[6] but there is a dihedral angle of 118° between the three-membered rings in this complex.) The individual rhenium–rhenium distances (angstroms) in the $Re_4(CO)_{16}{}^{2-}$ ion are: Re_1–Re_2 = 2.96, Re_1–Re_3 = 2.98, Re_2–Re_3 = 3.02 (the nonbonding distance, $Re_3 \cdots Re_{3'}$, is 5.23 A). These distances are consistent with the rhenium–rhenium distance of ~3.02 A in $Re_2(CO)_{10}$,[7] and with the rhenium–manganese distance of 2.96 A in $HRe_2Mn(CO)_{14}$.[8] (It should be noted that the very much shorter rhenium–rhenium distances observed in a variety of halogenated trinuclear Re(III) complexes, Re–Re(av) ≃ 2.48 A,[9] correspond to a formal metal–metal bond order of 2.0[10].)

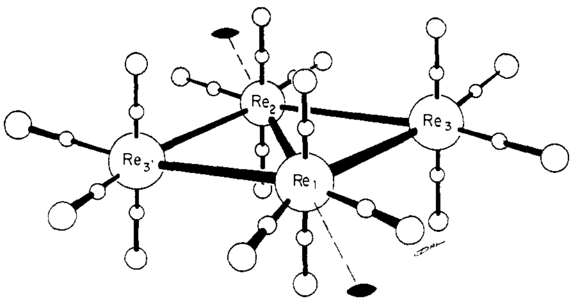

Figure 1. The stereochemistry of the $Re_4(CO)_{16}{}^{2-}$ anion.

As is customarily the case for third-row transition metals, the $Re_4(CO)_{16}{}^{2-}$ ion contains no bridging carbonyl groups. Each rhenium atom is associated with four carbonyl ligands, two of which are *axial* and two *equatorial.* The ion has approximate D_{2h} symmetry. All four rhenium atoms may be regarded as attaining the expected rare gas (Rn) configuration. The "bridgehead" rhenium atoms (Re_1 and Re_2) have a distorted pentagonal bipyramidal (*i.e.*, pseudo-D_{5h}) stereochemistry and may be assigned a formal zero-valent oxidation state. The "singly bridging" rhenium atoms (Re_3 and $Re_{3'}$) have a distorted octahedral stereochemistry and may be regarded formally as Re(−I) ions. It is probable, however, that delocalization of the net negative charge will tend to blur this formal distinction.

The compound is insoluble in ethanol but soluble in acetone or CH_2Cl_2. Four principal absorptions in the carbonyl stretching region of the infrared are observed in CH_2Cl_2: 2007 (s), 1985 (m), 1969 (s), and 1901 (m, very broad) cm^{-1}. This could only result from the anion $Re_4(CO)_{16}{}^{2-}$, of idealized symmetry D_{2h}, if the stretching force constants of the carbonyl groups (axial and equatorial) on atoms Re_3 and $Re_{3'}$ were very similar to those of the corresponding carbonyl groups on atoms Re_1 and Re_2. Such similarity in the carbonyl groups, in turn, could only come about from extensive delocalization of negative charge on all four Re atoms; otherwise, a larger number (up to eight) of resolvable infrared-active absorptions would be expected.

Treatment of the red crystals with phosphoric acid affords only trace quantities of cyclohexane-soluble materials; the residue gives three principal carbonyl absorptions in CH_2Cl_2 (2049 (m), 2004 (s), 1956 (m, broad) cm^{-1}), not identifiable with any previously isolated polynuclear carbonyl hydrides[3,5] nor with the polymeric species claimed to be $[Re(CO)_4]_n$.[11] We may assume the formation of either $(n\text{-}C_4H_9)_4N^+\text{-}HRe_4(CO)_{16}{}^-$ or the neutral $H_2Re_4(CO)_{16}$, on which studies are in progress.

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Thus the anion $Re_4(CO)_{16}^{2-}$ is not a precursor of previously isolated polynuclear carbonyl hydrides but a higher homolog of a series most likely derived from a common building unit. We would like to propose an intermediate substituted anion such as $LRe(CO)_4^-$ (L = loosely bound ligand such as tetrahydrofuran, the solvent) which would give rise by displacement of L, without or with loss of electrons, to such anions as $Re_3(CO)_{12}^{3-}$ or $Re_4(CO)_{16}^{2-}$, respectively. Furthermore, attack of $LRe(CO)_4^-$ by 2 moles of $Re(CO)_5^-$ would produce, after loss of L and oxidation, the anion $Re_3(CO)_{14}^-$. This mechanism would account for the polynuclear carbonyls thus far isolated after acidification or the anion reported in this work. The search for higher homologs of the $[Re(CO)_4]$ series or for anions in a series corresponding to lower carbonyls in the metallate solutions of rhenium and related metals is now in progress.

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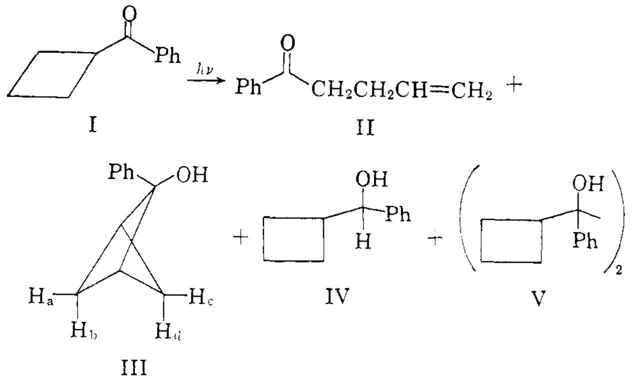
Photochemical Formation of a Substituted Bicyclo[1.1.1]pentane[1]

Sir:

The distorted geometry of bicyclo[1.1.1]pentane suggests that it (and its substituted derivatives) may show the effects of bond angle deformation in the form of unusual chemical behavior.[2] Unfortunately the previously reported syntheses are tedious and not amenable to the preparation of sufficient quantities of functionalized material for extensive studies.[3-6] We now report a simple photosynthesis of 2-hydroxy-2-phenylbicyclo[1.1.1]pentane (III) which also has the feature of great generality for the preparation of other substituted bicyclo[1.1.1]pentanes and related hetero systems.

Irradiation of cyclobutyl phenyl ketone (I) in benzene at 25° with ultraviolet light for 8 hr afforded 1-phenyl-4-penten-1-one (II, 24%), 2-hydroxy-2-phenylbicyclo[1.1.1]pentane (III, 38%), cyclobutylphenylcarbinol (IV, 8%), and the pinacol of I (V, 10%).[7] The structure of II follows from inspection of its spectra: ultraviolet λ_{max} (95% ethanol) 243 mμ (ϵ 10,000), infrared λ_{max} (carbon tetrachloride) 5.98, 6.11, 10.92 μ, 60-Mc nmr (deuteriochloroform) multiplet at τ 2.80, three overlapping triplets (J = 16.0, 9.0, 6.0 cps) centered at τ 4.20, two overlapping doublets centered at τ 5.07 and 5.16, a triplet (J = 7.0 cps) at τ 7.11, and a quartet (J = 7.0, 6.0 cps) at τ 7.69. The peak areas are in the ratio of 5:1:2:2:2; mass spectrum (m/e): 160 (M^+), 105 (base peak), 91, 77, 51, 41, and 39. Structure II was further confirmed by comparison of its semicarbazone derivative with an authentic sample synthesized by the method of Vavon and Conia.[8]



The structure of III was elucidated on the basis of physical and chemical data cited. Pure bicyclo[1.1.1]pentane (III) was a solid, mp 64-65°. The elemental analysis of this component (*Anal.* Calcd for $C_{11}H_{12}O$: C, 82.46, H, 7.55. Found: C, 82.29, H, 7.46) indicates that it is an isomer of I. The infrared spectrum shows hydroxyl bands at 2.87 and 3.02 μ and a carbon-oxygen stretching band at 8.25 μ. The ultraviolet spectrum (95% ethanol) with maxima at 264, 258, 252, 247 mμ (ϵ 160, 220, 195, 155) is characteristic of an isolated benzene ring. The 100-MHz nmr spectrum[9] is in excellent agreement with the proposed structure. The bicyclo[1.1.1]pentane III shows the aromatic hydrogens as a singlet at τ 2.73, the two bridgehead hydrogens as a singlet at τ 7.08, the hydroxyl proton as a singlet at τ 7.70, H_c as a doublet of doublets (J = 10.0, 3.0 cps) at τ 7.24, H_d as a doublet (J = 3.0 cps) at τ 8.31, H_b as a doublet (J = 3.0 cps) at τ 8.58, and H_a as a doublet of doublets (J = 10.0, 3.0 cps) at τ 8.73. The peak areas are in the ratio of 5:2:1:1:1:1:1. These assignments for the spin-spin coupling interactions were tested through double-resonance experiments. When H_c was saturated with an external field, the H_d doublet collapsed to a singlet, H_b was unaffected, and H_a collapsed to a doublet (J = 3.0 cps). It is interesting to note that the methylene-methylene long-range coupling constant (J = 10.0 cps) is the same as that for the *exo* hydrogens of bicyclobutane[10] and for the parent bicyclo[1.1.1]pentane,[4] indicating that the geometrical arrangement of the hydrogens is essentially the same for all three compounds. The two bridgehead carbon-hydrogen bonds lie at right angles to the plane of the other hydrogens, and a negligible spin-spin coupling constant would be anticipated.[11] The strong upfield shift of the *exo*-oriented hydrogen (H_a) is readily attributable to long-range shielding by the π electrons of the phenyl ring.[12] The mass spectrum of III included peaks with m/e 160 (M^+), 159, 105 (base peak), 91, 77, 55, 51, and 39 and is very similar to that of I and II. In view of the parallel

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(1) Photochemical Transformations of Small Ring Carbonyl Compounds. XVI. For part XV, see A. Padwa, R. Gruber, and L. Hamilton, *J. Am. Chem. Soc.*, **89**, 3077 (1967).

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