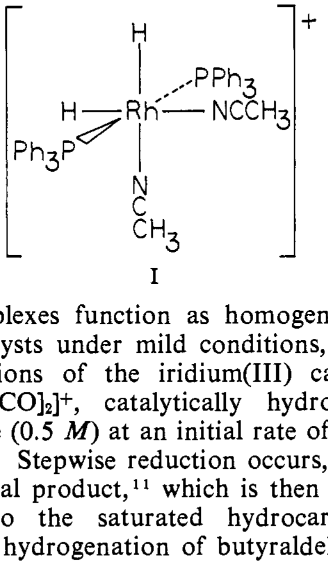
$[IrH_2(PPh_3)_4]^+$,[8] can be isolated. The nmr spectrum of the diacetone complex (0.1 *M* in $CDCl_3$) shows only one methyl resonance (relative intensity = 12) at τ 8.23 (at 28°). On addition of dry acetone, only one broad methyl resonance is observed, which is now shifted toward the free acetone resonance (at τ 7.91). Thus rapid exchange of free and coordinated acetone is occurring on the complex. Similar results are found for the analogous rhodium species.

Complexes with coordinated solvents such as acetonitrile, 2-butanone, dimethylacetamide, and ethyl alcohol are also readily isolated. Interestingly, however, the nmr spectrum of the bisacetonitrile–rhodium complex, $[RhH_2(PPh_3)_2(CH_3CN)_2]^+$, in dichloromethane at 28° shows a single sharp methyl resonance at τ 8.4, and, on addition of acetonitrile, two somewhat broad lines are observed at τ 8.1 and 8.4. In this case, the ligand exchange is considerably slower than in the diacetone complex.[9] The high-field overlapping triplets are at τ 27.4 (J_{Rh-H} = 17.0 Hz; J_{P-H} = 13.0 Hz). Taken with infrared evidence which indicates *cis*-hydrides and *cis*-acetonitriles, structure I is proposed for this complex.



I

These complexes function as homogeneous hydrogenation catalysts under mild conditions, *e.g.*, 5 m*M* acetone solutions of the iridium(III) cation, $[IrH_2(PPh_3)_2[(CH_3)_2CO]_2]^+$, catalytically hydrogenate 1,5-cyclooctadiene (0.5 *M*) at an initial rate of *ca.* 0.1 M^{-1} hr^{-1} at 25°.[10] Stepwise reduction occurs, cyclooctene being the initial product,[11] which is then more slowly converted into the saturated hydrocarbon. Interestingly, slow hydrogenation of butyraldehyde to give 1-butanol at 50° has been observed when this catalyst is used in dioxane solution.[12]

The analogous rhodium(III) cations, $[RhH_2(PPh_3)_2S_2]^+$ (S = solvent), can be prepared by treating a solution of the rhodium(I) species, $[Rh(NBD)(PPh_3)_2]^+$, with hydrogen in the requisite solvent. The complexes (S = $(CH_3)_2CO$, C_2H_5OH) dissolved in solvents such as tetrahydrofuran[13] very effectively catalyze the hydrogenation of olefinic and acetylenic bonds. Details of the catalytic process are still under study, but the following general observations may be noted at present.

(a) The rate of hydrogenation of monoolefins decreases in the sequence: hex-1-ene > cyclohexene ~ *cis*-hex-2-ene > *trans*-hex-2-ene ≫ 1-methylcyclohexene.

(b) Norbornadiene is reduced very rapidly, whereas 1,5- and 1,3-cyclooctadiene are reduced more slowly. Again, as in the iridium catalysis, intermediate formation of monoolefin is observed.

(c) Acetylenes are hydrogenated faster than the corresponding olefins: hex-1-yne > hex-2-yne > hex-1-ene.

(d) Unsaturated ketones and esters are readily hydrogenated without reduction of the carbonyl group.[14] The behavior with unsaturated aldehydes will be discussed elsewhere.

(e) The hydrogenation process is inhibited by the presence of excess triphenylphosphine or use of good donor solvents such as acetonitrile.

These general observations must be treated, however, with caution. We find that not only the absolute value but also the relative order of the rate of substrate reduction is strongly solvent dependent. We are currently investigating the possibility of using this solvent behavior to facilitate selective reductions, *e.g.*, inhibiting the reduction of dienes and acetylenes at the monoolefin stage.

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[8] M. Angoletta, *Gazz. Chim. Ital.*, **92**, 811 (1962).

[9] Temperature-dependent nmr studies are now in progress in order to investigate the relationship, if any, between the rate of solvent exchange and the catalytic efficiency of a given complex. In addition, the low-temperature studies will aid the structural elucidation of these dihydrido complexes which because of exchange processes show only ill-defined broad lines at high field at room temperature.

[10] Other dienes such as norbornadiene and 1,5-hexadiene are hydrogenated at about the same rate.

[11] Small amounts of 1,3- and 1,4-cyclooctadiene are formed during hydrogenation, possibly indicating that hydride transfer to the olefin in this system is stepwise and not synchronous.[14] If the structure of the active dihydrido species is as in I, stepwise transfer is also the most probable mechanism.

[12] *Cf.* R. S. Coffey, *Chem. Commun.*, 923 (1967).

[13] Other solvents we have used are dioxane, 2-methoxyethanol, dimethylacetamide, and acetone.

[14] *Cf.* J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, 1711 (1966).

[15] National Science Foundation Fellow.

[16] National Institutes of Health Fellow.

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Electrochemical Preparation of Cyclopropanediol Derivatives

Sir:

We wish to report what we believe to be the first examples of an intramolecular pinacol reduction leading to isolable cyclopropanediol derivatives. Cyclopropanediols themselves have been postulated as intermediates in the abnormal Clemmensen reduction of 1,3-diketones,[1] and a considerable body of inferential evidence has accumulated supporting this viewpoint.[2,3] This led us to search for conditions under which reduction of 1,3-diketones might be stopped at the cyclopropanediol state. The marked lability of cyclopropanols toward acids and bases[4] placed rather stringent limitations on the types of reducing agents which could be employed for this purpose, and we therefore undertook a study of the electrochemical reduction of diketones in nominally aprotic media.

The compound chosen for initial study was 2-methyl-2-acetylcyclohexanone, **1**, whose Clemmensen reduction was reported to lead to the rearranged products **2** and **3** *via* the diol **4a**.[2] As a probe into the electro-

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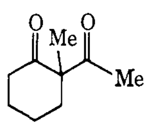
[1] D. Staschewski, *Angew. Chem.*, **71**, 726 (1959).

[2] E. Wenkert and E. Kariv, *Chem. Commun.*, 570 (1965).

[3] (a) N. J. Cusack and B. R. Davis, *Chem. Ind.* (London), 1426 (1964); (b) K. M. Baker and B. R. Davis, *ibid.*, 768 (1966); (c) N. J. Cusack and B. R. Davis, *J. Org. Chem.*, **30**, 2062 (1965).

[4] C. H. De Puy, *Accounts Chem. Res.*, **1**, 33 (1968).

chemistry of **1** we employed triangular wave cyclic voltammetry, a simple and powerful technique for the investigation of organic electrode processes.[5] At the hanging drop mercury electrode in acetonitrile with tetraethylammonium bromide as supporting electrolyte, **1** showed a redox couple having a well-defined cathodic wave at −2.8 V (*vs.* saturated calomel electrode) and a small but definite anodic wave at −2.6 V. The relative height of the anodic wave increased with increasing scan rate, indicating that the reduced species, although apparently unstable, had a lifetime of the order of seconds under these conditions.



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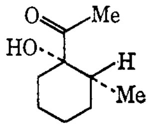

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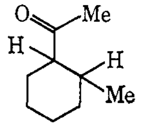

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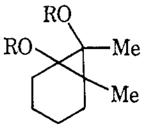
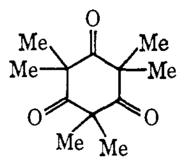


4a, R = H
b, R = Ac

Attempts to isolate cyclopropanediols from controlled potential electrolyses of **1** at a stirred mercury pool cathode were without useful issue until the solvent was changed from acetonitrile to tetrahydrofuran. Using tributylethylammonium tetrafluoroborate as supporting electrolyte[6] and employing acetic anhydride as a trapping agent for reactive anions, we obtained a mixture of products containing *inter alia* up to 33% of the two stereoisomers of **4b**. The isomers were separated from the mixture by glpc in approximately equal amounts. Analytical figures were in agreement with the formula $C_{13}H_{20}O_4$. Both isomers showed strong acetate absorption at 1749 and 1230 cm^{-1} in the ir. Isomer A (a liquid) showed singlets in the nmr at δ 2.00, 1.00, and 1.37 (intensity ratio 2:1:1). Isomer B (a crystalline solid, mp 36–38°) showed similar absorption at δ 1.96, 1.94, 1.45, and 0.95. Mass spectra of the two isomers were superimposable except for a small molecular ion at 240 in isomer A which was absent in B. Prominent peaks occurred at *m/e* 180 (loss of acetic acid), 43 (CH_3CO^+), and 138 (loss of acetic anhydride or equivalent). Treatment of each isomer with methanolic acid led to **2** (24% yield from isomer A, 66% from isomer B). The weight of evidence clearly supported structure **4b**.[7]



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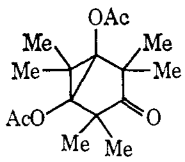

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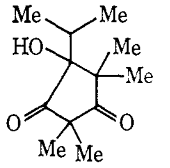

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A similar electrolysis of trione **5** in acetonitrile led in 71% yield to diacetate **6**, mp 125–126°. Again analytical data supported this structure, as did ir (1750, 1240, 1210, 1060 cm^{-1}) and mass spectra (peaks at *m/e* 43 for CH_3CO^+ and 194 for loss of acetic anhydride or equivalent). The nmr spectrum of **6** in 1:1 carbon tetrachloride–benzene solution showed five clearly visible groups of methyls occurring as singlets at δ 1.87 (two methyls), 1.35 (two methyls), 1.19 (one methyl), 1.15 (two methyls), and 1.02 (one methyl). Acid hydrolysis of **6** gave in 48% yield the hydroxydione **7**, identical with material prepared[8] by Clemmensen reduction of **5**.

Examination of the cyclic voltammetry curves of **5** in the presence and absence of acetic anhydride suggested that the reduction of this molecule was proceeding by sequential electron and acetic anhydride additions. Electrolysis of **5** in the cavity of an esr spectrometer produced a radical showing a single broad line.[9] Although this may be the anion radical of **5**, the absence of any fine structure made identification uncertain, and consequently no light was shed on the intriguing possibility of a delocalized structure for such a radical.

Besides adding further support for the intermediacy of cyclopropanediols in the abnormal Clemmensen reductions of 1,3-diketones, our work opens a convenient synthetic route to derivatives of a novel class of compounds. Work in progress indicates that the chemistry of these substances holds some interesting surprises. We plan to report these results in the near future.[10]

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[5] R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964), and references therein.

[6] T. J. Curphey and J. H. Williams, unpublished results. Tributylethylammonium tetrafluoroborate is easily prepared from tributylamine and triethyloxonium tetrafluoroborate, has none of the explosive hazard of the more commonly used quaternary ammonium perchlorates, and has exceptionally good solubility in media of low polarity. It appears to be a useful and convenient electrolyte for electrochemical investigations in nonaqueous solvents.

[7] Based on the slight difference in nmr spectra, isomer A has been assigned the structure with *cis* acetoxy groups and isomer B that with *trans* groups. This assignment rests on rather tenuous arguments which will not be presented here and is to be regarded as provisional.

[8] T. J. Curphey and R. L. McCartney, *J. Org. Chem.*, in press.

[9] We thank Sr. Mary Hertrich for help in performing this experiment.

[10] By using zinc powder in acetic anhydride saturated with hydrogen chloride as the reducing agent [see S. Yamamura and Y. Hirata, *J. Chem. Soc., C*, 2887 (1968)], we have succeeded in synthesizing **4b** (isomer A) and **6** from **1** and **5**, respectively. Yields were high in both cases. This reduction and the related abnormal Clemmensen reduction of unsaturated ketones [for examples and references see B. R. Davis and P. D. Woodgate, *ibid.*, 2006 (1966)] are being investigated as general routes to cyclopropanediol and cyclopropanol derivatives.

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The Photolysis of Azine Monoxides. A Novel Electrocyclic Reaction[1]

Sir:

A vast amount of work has been reported within the past couple of years dealing with the photochemical transformations of various aromatic amine N-oxides.[3] In all cases, the only reactions which were reported, other than simple deoxygenation processes, were those in which the oxygen initially migrated to an adjacent carbon atom, ostensibly *via* an oxaziridine intermediate.

Most recently Kumler and Buchardt showed[4] that

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[1] Thermal and Photochemical Rearrangements of Azine Oxides. II. For paper I, see ref 2.

[2] W. M. Williams and W. R. Dolbier, Jr., *J. Org. Chem.*, **34**, 155 (1969).

[3] (a) B. Singh, *J. Am. Chem. Soc.*, **90**, 3893 (1968); (b) O. Buchardt and B. Jensen, *Acta Chem. Scand.*, **22**, 877 (1968); (c) O. Buchardt, B. Jensen, and I. K. Larsen, *ibid.*, **21**, 1841 (1967); (d) O. Buchardt, C. Lohse, A. M. Duffield, and C. Djerassi, *Tetrahedron Letters*, 2741 (1967).

[4] P. L. Kumler and O. Buchardt, *J. Am. Chem. Soc.*, **90**, 5640 (1968).