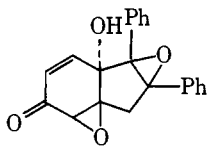
Table II. Reduction Potentials of Reactants

compd	$E_{1/2}$ (V vs. SCE)	compd	$E_{1/2}$ (V vs. SCE)
1/**1**$^{-}$·	−0.97[a]	ZnTPP^{+}·/ZnTPP[f]	+0.73[e]
TMPD^{+}·/TMPD[b]	+0.22[c]	TPP^{+}·/TPP[g]	+0.95[e]
CoTPP^{+}·/CoTPP[d]	+0.66[e]		

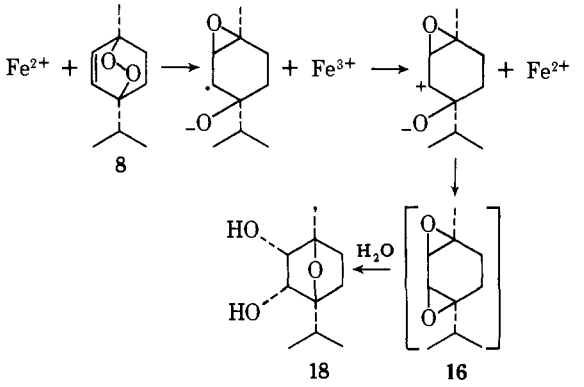
[a] Reference 19. [b] *N,N,N',N'*-tetramethylphenylenediamine. [c] $E°$: S. N. Frank and A. J. Bard, *J. Am. Chem. Soc.*, **97**, 7427 (1975). [d] Cobalt *meso*-tetraphenylporphine. [e] A. Wolberg, *Isr. J. Chem.*, **12**, 1031 (1974). [f] Zinc *meso*-tetraphenylporphine. [g] *meso*-tetraphenylporphine.

amine in acetone at −10 °C. Furthermore, the major product of the reaction with triethylamine was not **9** but the hydroxy ketone **17**.[6]



17

An electron-exchange mechanism for the rearrangement can be written, and such a mechanism has been suggested for the ferrous ion catalyzed rearrangement of ascaridole (**8**) to compound **18**.[17] However, it seems unlikely that such a mechanism would give diepoxide **16** in even moderate yield, as rearrangements might be expected.



8 18 16

If the catalyzed rearrangement of endoperoxides proceeded by pure outer sphere electron exchange in our case, the more easily oxidized TMPD should have promoted more rapid rearrangement than CoTPP; however, as was noted above, the reaction was actually much slower. Furthermore, since the reduction potential of peroxide **1** was found to be −0.97 V vs. SCE,[19] complete electron transfer with either CoTPP or TMPD is endothermic by >1 V. Instead, a mechanism involving complex formation between the oxidizing peroxide and the reducing catalyst without separation of ion pairs is proposed.

The facile, low temperature, and high yield rearrangement by CoTPP strongly suggests that a similar catalytic reaction (possibly with excited dye as the donor) can account for the rearrangements which occur readily under some conditions during the photooxidation of indenes.[2]

When coupled with singlet oxygen oxidation of the diene to give the endoperoxide, this procedure provides a mild, high yield, "one-pot" method of converting conjugated dienes to *syn*-diepoxides. Similar oxidations of dienes with *m*-chloroperbenzoic acid give *anti*-diepoxides and require forcing conditions for complete reaction. However, epoxidation with *tert*-butyl peroxide catalyzed by $VO(acac)_2$ gave a *syn*-diepoxide,[20] but the scope of this reaction has not been investigated.

Studies on the mechanism and scope of this rearrangement are being conducted.

Acknowledgment. We thank Dr. Pauline M. Allen for her suggestions on the electrochemical sections.

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(21) Summer Research Fellow, Associated Western Universities.

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Carbon–Carbon Bond Formation Catalyzed by Vitamin B_{12} and a Vitamin B_{12} Model Compound. Electrosynthesis of Bicyclic Ketones by 1,4 Addition[1]

Sir:

Vitamin B_{12} derivatives and vitamin B_{12} model compounds have recently been found to catalyze the electrochemical reduction of alkyl halides[2] as well as the zinc–acetic acid promoted reduction of nitriles,[3a] α,β-unsaturated nitriles,[3b] α,β-unsaturated carbonyl derivatives,[3c] olefins,[3d] alkyl halides,[3d] and alcohols.[3d] Evidence was presented[2,3d] that the above-mentioned reactions proceed through intermediates containing a Co–C bond, which is reductively cleaved and transformed into a C–H bond. It seemed of interest to investigate the potential of such intermediates for the formation of C–C bonds.

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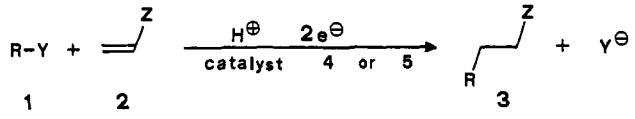
Scheme I



Y = leaving group
Z = π-acceptor group

Here we report a novel 1,4 addition[4] of alkyl derivatives **1** to Michael Olefins **2** by chemically catalyzed controlled potential electrolysis (cf. Scheme I).

Catalysts for this reaction are aquocobalamine (vitamin B_{12a}, **4**)[5] or dibromo[1-hydroxy-8*H*-HDP]cobalt(III) (**5**).[6] Either of these allows reductive coupling[7] to take place at a cathode potential, at which neither compound **1** nor **2** nor a mixture of both undergoes a reaction.[8]

For preparation of **3**, a mixture of **1** and **2** in a solvent (e.g., DMF, CH_3OH, THF-H_2O) containing a proton source (e.g., NH_4Br), a supporting electrolyte (e.g., $LiClO_4$), and catalytic amounts of **4** or **5** (1-20 mol % based on **1**, **2**) is reduced at a constant potential which depends on the reaction conditions, but is generally in the range of −1.4 to −1.9 V (Ag/Ag^+).[9]

Results of the electrolysis of bromocyclohexenones **8** and **11** bearing the functional groups of **1** and **2** within the same molecule[10] are summarized in Table I.

The electrolysis of **8** or **11** leads to two types of products which are formed by competing reactions: bicyclic ketones **9** or **12** by 1,4 addition and open-chain products **10** or **13** by reductive protolysis. Cyclization predominates if the reactive center at the end of the side chain can easily adopt a spatial position favorable for 1,4 attack leading to six- and seven-membered rings by endocyclic closure (entry 2 and 3) or to five- and six-membered rings by exocyclic closure (entry 5 and 6). Thus our experimental findings are in agreement with the general rules for ring closure.[14] Tertiary alcohols formed by attack at the carbonyl group[15] or polymeric products by intermolecular 1,4 addition[10] have not been observed.

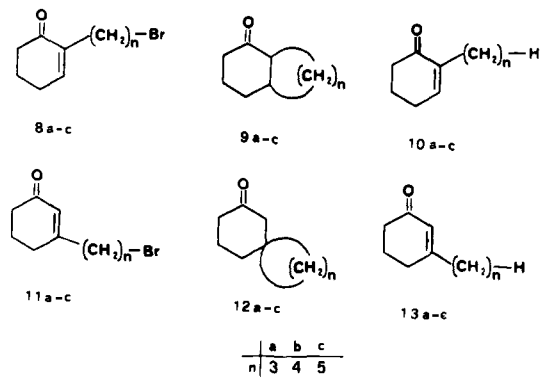
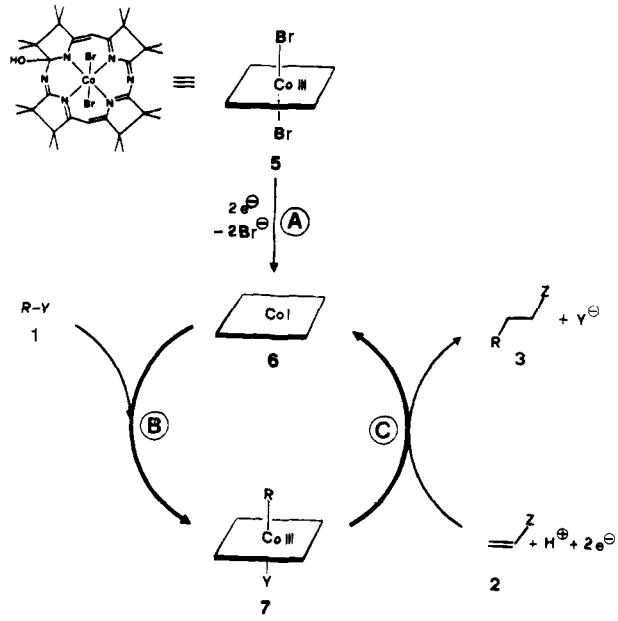


Table I. Electroreduction of Bromocyclohexenones **8** and **11** in the Presence of Catalytic Amounts of **4** or **5**[a]

entry	starting material[b,c]	products[d] (% yield[e])
1	**8a**	**9a** (<2), **10a** (90)
2	**8b**	**9b** (95),[f,g] **10b** (<2)
3	**8c**	**9c** (70),[h] **10c** (10)
4	**11a**	**12a** (<2), **13a** (90)
5	**11b**	**12b** (95), **13b** (<2)
6	**11c**	**12c** (45), **13c** (40)

[a] Solutions of 1 mmol of **8** or **11** and 0.05 mmol of **4** (or 0.2 mmol of **5**) in 25 mL of electrolyte (0.1 N $LiClO_4$, 0.05 N NH_4Br in DMF) were electrolyzed at −1.9 V[9] in a divided (H-type) cell at a stirred Hg-pool cathode under Ar at 20 °C in the dark. Products were isolated by extraction with pentane. [b] **8a-c** were prepared by reductive alkylation of 2-methoxybenzoic acid according to Taber[11] using appropriate dibromides. **11a-c** were synthesized following the method of Dolby[12] starting from 2-cyclohexenone and corresponding dibromides. [c] $E_{1/2}$'s of **8** or **9** in electrolyte (see *a*) are −2.3 V.[9] [d] Products were isolated and characterized by spectral data. [e] GC yield based on **8** or **11**. [f] ≈1:1 cis:trans (trans isomer predominates when CH_3OH was used as solvent). [g] Isolated *trans*-1-decalone showed $[\alpha]^{20}_D$ + 0.14° (*c* 6.8, CH_3OH) and corresponds to an optical yield of 0.5% of the 9*R*,10*S* enantiomer.[13]

Scheme II



The action of the catalyst has been studied in more detail in case of the B_{12} model compound **5**[6] (cf. Scheme II).

The reaction is initiated (path A) by the formation of the catalytically active Co(I) species **6** obtained from **5** in two reductive steps at $E_{1/2}(1) = -0.36$ and $E_{1/2}(2) = -1.08$ V[9] coupled to extrusion of the axial ligands.[16,17]

Compound **6** behaves as a supernucleophile[18] very much like B_{12s} and reacts rapidly with alkylating agents **1** to yield octahedral alkyl-Co(III) complexes **7** (path B). The addition of **6** to α,β-unsaturated ketones **2**[19,3b,c] was not observed if an alkylating agent (**1**) was present in the reaction mixture.[20] If the potential is not lower than −1.3 V,[9] the complexes **7** are not further converted. Exhaustive electrolysis of **5** in presence of **1** at −1.2 to −1.3 V[9] is therefore a convenient route for the preparation of alkyl-Co(III) complexes **7** in high yield.[21]

Alkyl-Co(III) complexes **7** are reduced by transfer of one electron at −1.4 to −1.7 V[9] to yield Co(II) intermediates,[22] They decay by uptake of one more electron with cleavage of the Co-C and the Co-Y bond.[23] In the presence of a Michael olefin (**2**) and a proton source, the 1,4-addition product **3** and the hydrocarbon R-H are formed in varying yields depending on the reaction conditions; concomitantly the Co(I) complex **6** is regenerated (path C).

Since the two Co complexes **4** and **5** give the same results in the conversion of **8** and **9** and since they show close relation in their structure and electrochemical behavior, we conclude that their action as catalysts is most likely the same.

Because of the extremely mild, nonbasic reaction conditions, this chemically catalyzed reductive coupling of alkyl halides to Michael olefins provides a versatile tool for the formation of C-C bonds.

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(7) For uncatalyzed reductive coupling, cf. (a) L. Eberson and H. Schäfer, *Top. Curr. Chem.*, **21**, 113–124 (1971); (b) M. M. Baizer, Ed., "Organic Electrochemistry", Marcel Dekker, New York, 1973, pp 399–411, 679–704; (c) O. R. Brown, *Spec. Period. Rep.: Electrochem.*, **5**, 222–228 (1975).

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(9) All potentials were measured vs. the Ag/0.01 N $AgNO_3$ reference system in DMF or CH_3OH. The potential difference between the Ag/Ag^+ electrode in acetonitrile vs. SCE is −0.29 V. Cf. R. C. Larson, R. T. Iwamoto, and R. N. Adams, *Anal. Chim. Acta*, **25**, 371 (1961). In DMF we measured a difference of −0.36 V.

(10) Examples of intermolecular reductive coupling, catalyzed by **4** or **5**, will be published elsewhere.

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(16) Measured by cyclic voltametry (CV) at the glassy carbon electrode in DMF–tetraethylammonium perchlorate (TAAP). The coupled stepwise extrusion of Br^- has been confirmed by measuring the dependency of $E_{1/2}(1)$ and $E_{1/2}(2)$ on the free bromide concentration. Exhaustive electrolysis of **5** in aprotic solvent at −1.7 V[6] under Ar consumes 2 equiv of electrons and leads to a stable green solution of **6**.

(17) For the corresponding reduction of aquocobalamine **4**, cf. (a) H. P. C. Hogenkamp and S. Holmes, *Biochemistry*, **9**, 1886 (1970); (b) D. Lexa and J. M. Savéant, *J. Am. Chem. Soc.*, **98**, 2652 (1976); (c) D. Lexa, J. M. Savéant, and J. Zickler, *ibid.*, **99**, 2786 (1977); (d) N. R. de Tacconi, D. Lexa, and J. M. Savéant, *ibid.*, **101**, 467 (1979).

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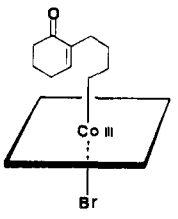
(20) Electrolysis of equimolar amounts of **5** and **8b** at −1.3 V[9] in DMF (0.1 N $LiClO_4$, 0.05 N NH_4Br) leads to the corresponding alkyl-Co(III) complex **7b** which was isolated and crystallized in >80% yield. Its constitution was determined by analysis ($C_{42}H_{66}BrCoN_6O_2$) and spectral data; polarography at DME in the same electrolyte shows two waves at $E_{1/2}$ = −1.62 and −1.84 V.[9] Further electrolysis at −1.9 V[9] in the same electrolyte afforded >90% decalone **10b**. Thus the intermediacy of alkyl-Co(III) complexes **7** during the catalyzed reductive cyclization is clearly demonstrated. Electrolysis of **8b** at −1.9 V[8] under the same conditions but in the absence of **4** or **5** shows no conversion; at a more negative potential (−2.4 V[9]) a mixture of several organic compounds as well as organomercurials was formed, but decalone **10b** could not be detected.

(21) (a) G. Rytz, thesis, University of Berne, 1979; (b) L. Walder, thesis, University of Berne, 1979.

(22) **7** easily exchanges the axial ligand Y. $E_{1/2}(1)$ of **7** (determined by CV in DMF, TAAP): −1.38 (R = CH_3; Y = ClO_4); −1.44 (R = CH_3; Y = Br); −1.72 V[9] (R = CH_3; Y = CN).

(23) For the corresponding reduction of methylcobalamine, see D. Lexa and J. M. Savéant, *J. Am. Chem. Soc.*, **100**, 3220 (1978), and literature cited therein.



7b

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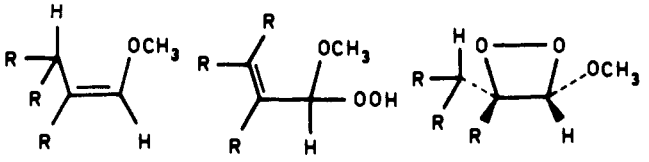
Formation of 1,2-Dioxetanes and Probable Trapping of an Intermediate in the Reactions of Some Enol Ethers with Singlet Oxygen

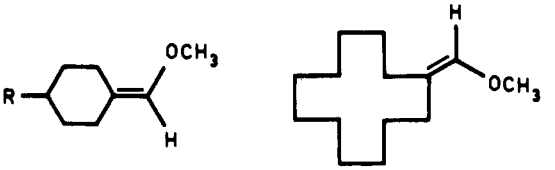
Sir:

Practical as well as theoretical interest accrues to methods for diverting the "ene reaction" of alkenes with singlet oxygen to a cycloaddition pathway. This goal is usually reached either by using alkenes devoid of allylic hydrogens or by circumventing by steric strain[1] the allylic shift ubiquitous to the ene reaction.[2] Enol ethers (**1**) bearing an allylic hydrogen atom also undergo dye sensitized photooxygenation to give hydroperoxides (**2**).[3] However, for enol ethers it is known that product distributions also respond to solvent polarity,[3d,e] which fact might open a general route to 1,2-dioxetanes (**3**). With this



1 **2** **3**

knowledge in mind, coupled with the general and qualitative observation that 1,2-dioxetanes incorporating carbocyclic rings, especially six-membered, often have good stability, the effect of changing some experimental parameters on the reactions of **1a–c** was examined.



1a: R = H **1c**

1b: R = $(CH_3)_3C$

The effect of changing solvent *and temperature* on the photooxygenations of **1a–c** is shown in Table I. As reported,[3a] photooxygenation of **1a** in C_6H_6 at room temperature affords virtually exclusively **2a.** However, on changing the solvent to CH_2Cl_2 27% **3a** is formed and this becomes the major product on lowering the temperature or using CH_3OH as solvent (but

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