that aldehydes rapidly reduce ruthenate ion at room temperature, thus confirming that k_5 and k_6 must also be large at 85°. Using these initial assumptions the program then generated the values of k_2 and k_4 summarized in Table I.

The values for k_2 could be obtained with good precision ($\pm 3\%$ or better) and may be accepted with considerable confidence because they can be verified independently from initial reaction rate studies. Unfortunately, the inherent uncertainties in the k_4 values obtained this way are much greater (about $\pm 30\%$). Consequently, it is not possible to draw conclusions regarding isotope effects or the effect of substituents on this step of the reaction except to note that a comparison of the rate constants for acrylate, crotonate, and β-methylcrotonate ions seems to indicate that methyl substitution at the double bond decreases the rate of reaction significantly.

The observation that the magnitude of k_2 increases when the vinyl hydrogens are replaced by deuterium indicates that the initial step of the reaction involves a change in hybridization of the α and β carbons from sp^2 to sp^3,[7] and is in agreement with the proposed formation of a cyclic ruthenium(IV) diester.[8] The small effect of ring substituents on the magnitude of k_2 is also similar to that observed in other reactions which involve 1,3-dipolar additions.[9]

The magnitude of k_2 was found to decrease as the basicity of the medium increased during the oxidation of cinnamate ion, presumably because of an equilibrium between $RuO_4{}^{2-}$ and $HRuO_4{}^-$ as in step 1 of Scheme I. By comparison with other oxy anions it is not unreasonable to expect that protonation would increase the vigor of the oxidant.[10] At high base concentrations ($[NaOH] \leq 2$ M) the rate of oxidation of crotonate ion increases, indicating that additional reactions may be occurring. However, under all other conditions Scheme I was found to accommodate the experimental results adequately, and, since a large number of other reaction sequences were found to be inadequate, it appears quite probable that the reaction proceeds by this rather logical sequence of reactions. The scheme is also consistent with the observed products of the reaction; the oxidation of cinnamate ion, for example, gave benzoate ion in a 99% yield.

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Deoxygenation of Epoxides by Metal Atom Cocondensation

Summary. Epoxides are converted to alkenes upon cocondensation with first-row transition metal atoms.

Sir: Transition metal atoms are substantially more reactive than the corresponding bulk metals by virtue of the 70–200 kcal/mol required for their formation.[1] This reactivity has been previously used to effect oxidative insertion reactions[2] and π-complex formation.[3] We now report a third reaction type, herein exemplified by the facile deoxygenation of epoxides (1) to alkenes (2). We believe this will be the first in a
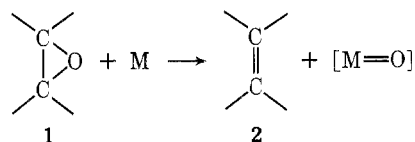
series of synthetically useful reductive deoxygenations which can be effected by transition metals in their atomic form.[4]

The relative reactivities of several first row transition metal atoms were determined by high vacuum cocondensation with at least a tenfold excess of cyclohexene oxide at 77 K. Atoms were produced by resistive heating of coated tungsten rods in either a conventional[2] or a new "micro" reactor,[5] the latter suitable for experiments with less than a gram of organic compound. After 1 h, during which time the reactor was allowed to warm to room temperature, the products were pumped into a cold trap and subjected to NMR and GC analysis. The results are presented in Table I. Chromium and vanadium emerged as the most effective (based upon metal), abstracting over 2 equiv of oxygen. Titanium afforded slightly lower yields (epoxide polymer was formed in some runs) and nickel was distinctly less reactive. Cyclohexene production was accompanied by small amounts of benzene (3–10% of product) and varying amounts (0–20%) of 1,3-cyclohexadiene, but cyclohexane could not be detected. With less volatile titanium and vanadium, control experiments indicate a small portion of the observed deoxygenation may be effected by the presence of the hot metal filament per se.

Studies with chromium atoms (Table II) indicate the reaction is general for epoxides. With *cis*-stilbene oxide and allylbenzene oxide, no stable volatile organometallic complexes were noted, although π-complex formation might precede deoxygenation in the matrix. No double-bond migrations were observed, but cis–trans isomerization did take place. In separate experiments, *cis*-4-decene was isomerized

Table I. Cocondensation of Metal Atoms with Cyclohexene Oxide [a]

Metal	Equiv of oxygen removed/ metal[b]	Cyclohexene yield,[c] %
Ti	0.9	8.7
V	2.8	5.6
Cr	2.7	7.8
Co	1.2	6.8
Ni	0.6	2.3

[a] 0.4–1.4 mmol of metal with 10–15 mmol of epoxide. All numbers are corrected for metal reaching the reaction zone. This was determined by depositing a Cr film in the reactor, digestion of the film with 70% $HClO_4$, and titration via standard $Fe^{2+}/Cr_2O_7{}^-$ methods: G. H. Ayres, "Quantitative Chemical Analysis", 2nd ed, Harper and Row, New York, N.Y., 1968, pp 625–627. [b] These data were obtained in the "micro" reactor and were somewhat lower in the conventional reactor. [c] Absolute yields; those with Cr, Co, and Ni are 70–90% if corrected for recovered starting material.

Table II. Chromium Atom Deoxygenation of Epoxides

Starting material	Product ratios
Cyclohexene oxide	Cyclohexene (86)
	Benzene (3)
	1,3-Cyclohexadiene (11)
	Cyclohexane (0)
cis-Stilbene oxide	cis-Stilbene (40)
	trans-Stilbene (60)
Allylbenzene oxide	Allylbenzene (100)
cis-4-Decene oxide	cis-4-Decene (36)
	trans-4-Decene (64)
1-Methylcyclopentene oxide	1-Methylcyclopentene (100)

by cocondensation with chromium (no olefin dismutation); hence the deoxygenation itself may well be stereospecific. Total conversion to products ranged from 3 to 10%.

Cyclohexene yields were decreased by over an order of magnitude when cyclohexene oxide was condensed onto a preformed chromium surface. When products were pumped off a chromium–cyclohexene oxide matrix without the customary 1-h warmup, yields were unaffected. These results are consistent with initial reaction at the atomic chromium stage. Consequently, the data in Table I likely reflect both the rate of metal reaction with epoxide *and* the rate of metal aggregation.[2]

Skell and Shevlin have observed epoxide reductions with arc[6] and chemically[7] generated carbon atoms. Deoxygenation can in principle occur by either concerted or stepwise mechanisms; intermediates formed via oxygen complexation and/or carbon–oxygen bond insertion are possible. Interestingly, molecular orbital calculations suggest that the deoxygenation of ethylene oxide by carbon atoms is a direct, concerted reaction with no local energy minima on the way to carbon monoxide and ethylene.[8]

Chromium also effects oxygen abstraction from heteroatom oxides. 2,6-Dimethylpyridine was obtained from 2,6-dimethylpyridine *N*-oxide, without formation of any stable π complexes.[9] Dimethyl sulfoxide afforded dimethyl sulfide via a red matrix, and triethylphosphine oxide was converted (green matrix) to triethylphosphine. Yields (1–5%) were significantly lower when a preformed chromium surface was employed. Reactions of other oxygenated organic compounds are currently under study.[4]

Large-scale deoxygenations of organic compounds, including epoxides, are often executed with ill-defined low valent transition metal reagents.[10] We believe metal atoms offer an obvious advantage. While the metal atom reactor is a rapid and definitive means for assaying the relative reactivities of atomic metals, it requires the utilization of excess organic reactant,[2] limiting product yields. Hence, results such as ours should be used as guidelines for the development of reagents which release a slow steady state of metal atoms into solution. Work toward this end is underway in this laboratory[5] and others.[11]

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Control of Ring Size Resulting from γ-Epoxy Sulfone and γ-Epoxynitrile Cyclization. Formation of Either Cyclopropyl or Cyclobutyl Derivatives

Summary: γ-Epoxy sulfones and γ-epoxynitriles of the type 1 (R_3 = H) may be cyclized either to the cyclopropylcarbinols 2 or cyclobutanols 3 using lithium diisopropylamide and CH_3MgI, respectively.

Sir: The work of Stork and coworkers[1] on the cyclization of epoxynitriles as a new method of ring formation has stimulated considerable interest.[2–5] Stork initially suggested[1b] that "epoxynitrile cyclization always yields the smaller ring when both ends of the epoxide are equally substituted". Cyclopropanes were always formed at the expense of cyclobutanes regardless of the relative degree of substitution of the epoxide ring. Lallemand and Onaga[2] have, however, shown that the preference of cyclobutyl vs. cyclopentyl ring formation in 1 may be related to the stereochemistry of the epoxide ring. Exclusive cyclobutyl formation was observed with the cis epoxide **1a**, but reaction of the trans epoxide **1b** (R = CH_3,
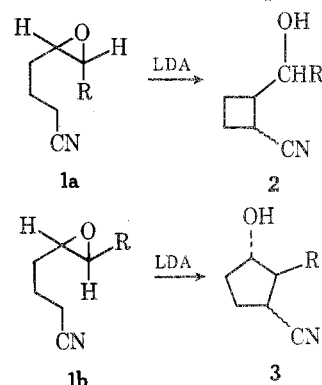
C_4H_9, C_5H_{11}) led to mixtures of the cyclobutyl and cyclopentyl derivatives in about a 35:65 ratio.

This type of cyclization has also been used to prepare 3-cyano-4-hydroxymethylpyrrolidines[3] and chrysanthemic acid.[4] Quite recently, Gaoni[5] has shown that γ-epoxy sulfones such as **4b** could be cyclized with *n*-BuLi in THF at −15 °C to the cyclopropyl derivative **5b**.

We have also been studying the reaction reported by Gaoni and found, in agreement with him, that epoxy sulfones of the type 4 react with CH_3Li or lithium diisopropylamide (LDA) to give 1-phenylsulfonyl-2-hydroxymethylcyclopropanes (**5**).[6] With the exception of **4b**, in which a nucleophilic displacement at a tertiary center is required, the isolated yields of the cyclopropanes were in the 85–95% range (Table I).

In contrast to these results, we have found that treatment of the same epoxy sulfones 4 (R_3 = H) with ~2 equiv of a