# Reactions of Cyclohexanone with Metal Vapors

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Metal atom vapors of several d and f transition elements were cocondensed with cyclohexanone at –196 °C. Radical reduction of cyclohexanone to [1,1'-bicyclohexyl]-1,1'-diol, a pinacol, was observed for elements which are both highly electropositive and form strong metal–oxygen bonds, for example, the early transition, lanthanide, and actinide elements. High yields of aldol condensation products were produced along with a small amount of bicyclohexylidene. Metal atoms of the latter transition elements were much less reactive with cyclohexanone and did not yield a pinacol product. Titanium clusters were prepared by codepositing titanium atoms with a large excess of solvent. Titanium clusters were less reactive than titanium atoms toward cyclohexanone radical reduction reactions. High surface area titanium powders produced by solution techniques yield pinacols when cyclohexanone reacts in excess and further deoxygenate pinacolic dianions to olefins under conditions of limited stoichiometry.
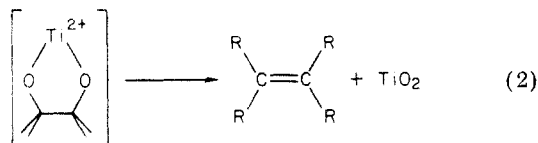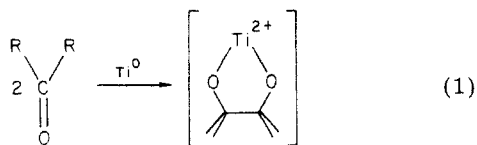
Within the past few years, there have been a number of investigations which have used transition-metal compounds to effect the reduction of aldehydes and ketones. These reduction reactions lead, depending upon the exact reducing agent, to either dimeric pinacol products or dimeric olefin products. Yields are often excellent, and the method is quite general toward carbonyl reduction.

A number of titanium-based compounds have been used to effect the reduction of carbonyl compounds to pinacols (Table I). Ti(II) is a strong reducing agent and is believed to transfer an electron to the carbonyl group to form a radical–anion intermediate.[1,4]

Although aryl ketones are easily coupled to give pinacols by many reducing agents, only the most reactive reagents are capable of coupling aliphatic ketones to pinacols. Reactivity and selectivity are sensitive functions of the exact method of Ti(III) reduction.

In addition to the reduction of carbonyl compounds to pinacols, carbonyl compounds have been deoxygenatively coupled to olefins. A number of compounds capable of olefin production are listed in Table II. Deoxygenative coupling of ketones to olefins is a more difficult reaction than the corresponding pinacol coupling reaction, requiring stronger reducing agents.

For reductions which use low-valent titanium compounds, olefin production is believed to proceed by a two-step mechanism,[5,6] eq 1 and 2.



$$(1)$$



$$(2)$$

The first step of olefin production is identical with the process for pinacol production described above. Active titanium metal produces radical–ion intermediates which couple to pinacol dianions. The pinacolic dianion is further

**Table I. Materials for Reductive Coupling of Cyclohexanone to [1,1'-Bicyclohexyl]-1,1'-diol**

| material | % yield | ref |
|---|---|---|
| $Mg(Hg)/TiCl_3$ | 93 | 1 |
| $6(C_5H_5)TiCl_2/4.5LiAlH_4$ | 89 | 1 |
| $(C_6H_6)TiCl_2 \cdot 2AlCl_3$ | 90 | 1 |
| $Mg/TiCl_3$ | 45 | 2 |
| $Zn/TiCl_3$ | 24 | 1 |
| $Al(Hg)$ | 55 | 3 |
| $TiCl_3/n$-BuLi | NA (poor)$^a$ | 1 |
| $TiCl_3/DIBAL$ | NA (poor)$^a$ | 1 |

$^a$ NA indicates not available.

**Table II. Materials for Carbonyl Reduction to Olefins**

| material | % yield | | ref |
|---|---|---|---|
| | alkyl | aryl | |
| $2TiCl_3/LiAlH_4$ | 95 | 95 | 5 |
| $TiCl_3/3K$ | 85 | NA | 6 |
| $WCl_6/Li$ | 43 | 55 | 7 |
| $W(CO)_6$ | | 21 | 7 |
| $W(CO)_5PPh_3$ | | 9 | 7 |
| $W(CO)_5=C(Ph)OCH_3$ | | 13 | 7 |
| $WCl_6/1.6n$-BuLi | 10 | 76 | 8 |
| $WCl_6/2Li$ | NA | NA | 8 |
| $K_2WCl_6$ | NA | NA | 8 |
| $UCl_4/4K$ | | 55 | 9 |

$^a$ NA indicates not available.

reduced by the $Ti^{2+}$ ion to olefin and $TiO_2$. It is not known whether eq 2 proceeds in a sequential or in a concerted manner, but it is believed that the carbon–oxygen bond cleavage proceeds through a radical intermediate.

Tungsten and molybdenum compounds have also been used to deoxygenatively couple ketones. For all systems which have been studied, tungsten-induced couplings give fair to poor yields and are restricted to aryl ketones and aldehydes. Tungsten compounds are believed to produce a tungsten–carbene complex which leads to product formation.[7] Although tungsten–carbene complexes do couple carbonyl compounds, no products are derived from the carbene attached to the metal.

In a separate study of tungsten(IV) compounds, it was found that many of the same compounds which reduce ketones and aldehydes to olefins reduce 1,2-diols to olefins.[10] Tungsten reduction of pinacols to olefins was found

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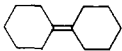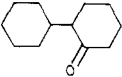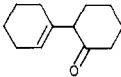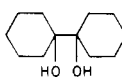(5) J. E. McMurry and M. P. Fleming, *J. Am. Chem. Soc.*, **96**, 4708 (1974).
(6) J. E. McMurry and M. P. Fleming, *J. Org. Chem.*, **41**, 896 (1976).

(7) Y. Fujiwara, R. Ishikawa, F. Akiyama, and S. Teranishi, *J. Org. Chem.*, **43**, 2477 (1978).
(8) K. B. Sharpless, M. A. Umbreit, M. T. Nieh, and T. C. Flood, *J. Am. Chem. Soc.*, **94**, 6538 (1972).
(9) R. R. Reike and L. D. Rhyne, *J. Org. Chem.*, **44**, 3445 (1979).

### Table III. Reaction Products of Cyclohexanone and Metal Atom Vapors

| metal (amt, g) | yield, % (mg) | | | | mole ratio | |
|---|---|---|---|---|---|---|
| | | | | | aldol/ pinacol | pinacol/ metal |
| Ti (0.120) | 8.0 (10) | | 21 (27) | 71 (100) | 0.29 | 0.21 |
| Cr (0.366) | 2.0 (23) | | 70 (620) | 27 (270) | 2.5 | 0.19 |
| Nd (0.184) | | | 76 (380) | 24 (130) | 2.1 | 0.50 |
| U (0.378) | 3.0 (6.5) | | 71 (150) | 26 (60) | 2.8 | 0.19 |
| Co (0.825) | | 8.6 (8.4) | 91 (89) | | | |
| Ni (0.657) | | 69 (52) | 31 (23) | | | |

to be very active, reducing alkyl diols in high yield. Active intermediates are believed to be radical species. Finally, one brief report exists on the reduction of cycloheptanone by magnesium metal atoms.[11] In that study, magnesium atoms deoxygenated cycloheptanone to produce cycloheptene (46%), norcarane (2%), cycloheptane (2%), [1,1'-bicycloheptyl]-1,1'-diol (19%), and aldol condensation products (31%). Carbene intermediates were proposed to account for the presence of seven-membered deoxygenetated hydrocarbon products. High surface area, clean magnesium powders, however, were found to be unreactive toward ketones.

From the previous studies, several questions come to mind. What is the general scope of transition-metal reduction of ketones and aldehydes to pinacols or olefins? Which metals would be expected to produce pinacol products, and which would be expected to produce olefin products? Finally, what molecular properties are most responsible for the preparation of effective carbonyl reducing agents?

Transition-metal-atom vapors are extremely reactive and can be prepared under conditions suitable for study with organic molecules.[12,13] In addition, very reactive metal slurries can be prepared by codepositing metal atoms in a solvent matrix. The reactivity of these metal species is highly dependent on the choice of solvent.[14] It was hoped that a study of many different metals would allow the previously posed questions to be answered.

## Results and Discussion

**Metal Atom Cocondensation with Cyclohexanone.** Metal atom vapors of the d and f transition elements were reactive toward cyclohexanone, and the organic products are given in Table III. By use of Table III, the metal atoms may be divided into two types on the basis of this reaction with cyclohexanone. Type I metals reductively couple cyclohexanone to [1,1'-bicyclohexyl]-1,1'-diol, a pinacol, with little formation of bicyclohexylidene. In addition, for most type I metals, aldol condensation derived compounds were the major product. Metals of type II show much less reactivity toward cyclohexanone reduction than do type I metals, and type II metals show no tendency to reductively couple alkyl ketones to pinacols or olefins.

Despite the wide range of metallic properties of the metals of type I (Ti, Cr, Nd, and U), the product selectivity and general reactivity of each metal is remarkably similar. With the exception of Nd, the yields of pinacol were nearly

constant, approximately 20% based on the amount of metal deposited. Nd atoms, however, show far greater reactivity than all other metals toward pinacolic coupling of cyclohexanone. One equivalent of Nd yields 0.50 equiv of [1,1'-bicyclohexyl]-1,1'-diol. The higher yield of pinacol coupling for Nd relative to the other type I metals may be explained, in part, by higher oxidation potential of Nd metal as compared with the oxidation potentials of the other metals. Unlike magnesium metal atom reactions, d and f transition-metal vapors produce no volatile deoxygenated carbene-derived products.

Unlike any of the previously reported reduction materials (Tables I and II), metal atoms produce high yields of aldol condensation products. With the exception of titanium, aldol condensation products were the major product. Even for titanium, aldol condensation products account for 20% of the total product. Aldol condensation reactions can and most often do result from the addition of a strong base to an alkyl ketone.[15] The pinacolic dianion, which is the actual reduction product prior to hydrolysis, is a sufficiently strong base to attack cyclohexanone, leading to 2-(1-cyclohexen-1-yl)cyclohexanone, an aldol-derived product.[11]

It is somewhat surprising that titanium atoms cocondensed with cyclohexanone lead to low yields of bicyclohexylidene. From predictions based on cyclohexanone reductions by known titanium reducing agents,[5,6] one would have expected that titanium atoms would not only produce bicyclohexylidene in high yield but that bicyclohexylidene would have been the only product. Since carbonyl reduction has been shown to be highly dependent on the nature of the reducing agent, several additional attempts were made to produce titanium compounds by the metal atom vaporization technique which would reduce cyclohexanone to bicyclohexylidene.

**Cyclohexanone Reduction with Titanium Atom/ Solvent Clusters.** Titanium clusters prepared from the deposition of titanium atoms with a large excess of solvent were found to be reactive toward cyclohexanone reduction. These clusters were maintained at −196 °C while a layer of cyclohexanone was added to the surface of the matrix. Cyclohexanone reduction occurred on matrix warm-up. Although Klabunde has characterized several distinct phases for nickel atom solvent clusters,[13] no other titanium atom phases were tested for reactivity in this study. Cyclohexanone reduction products for titanium atom/solvent clusters are presented in Table IV.

From Table IV it can be seen that titanium atoms condensed with saturated solvents, hexane, and tetrahydrofuran are less reactive toward cyclohexanone radical reduction processes than are titanium atoms in a matrix of cyclohexanone. In addition, titanium–hexane and titanium–THF reactions produce high yields of aldol con-

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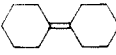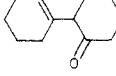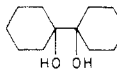
(12) P. L. Timms, *Adv. Inorg. Chem. Radiochem.*, **14**, 121 (1972).

(13) K. J. Klabunde, *Acc. Chem. Res.*, **8**, 393 (1975).

(14) K. J. Klabunde, H. F. Efner, T. O. Murdock, and R. Ropple, *J. Am. Chem. Soc.*, **98**, 1021 (1976).

(15) A. T. Nielsen and W. J. Houlihan, *Org. React.*, **16**, 1 (1968).

**Table IV.  Reaction Products of Titanium Atom Vapor/Solvent Plus Cyclohexanone**

| | | yield, % (mg) | | | mole ratio | |
| --- | --- | --- | --- | --- | --- | --- |
| amt of Ti, g | solvent | ⬡=⬡ | ⬡-⬡(O) | ⬡-⬡(HO OH) | aldol/ pinacol | pinacol/ metal |
| 0.100 | hexane | 1.5 (2.4) | 81 (150) | 18 (37) | 4.4 | 0.09 |
| 0.110 | THF | 4.7 (11) | 81 (200) | 14 (39) | 5.6 | 0.09 |
| 0.151[a] | toluene | | 24 (68) | 76 (240) | 0.31 | 0.39 |
| 0.120 | cyclohexanone | 8.3 (10) | 21 (27) | 71 (100) | 0.29 | 0.21 |

[a] Some solvent products were observed.

densation product, 2-(1-cyclohexenyl-1-yl)cyclohexanone.

In a recent study of reaction of metal atoms with neopentane, titanium atoms were found to be highly reactive toward oxidative addition of carbon–hydrogen and carbon–carbon bonds.[16]  Oxidative addition reactions are believed to occur immediately upon titanium atom impact with the alkane at -196 °C.  Although the final metal oxidation states were not determined, the presence of reactive metal alkyl fragments and metal hydrides was established.  Other metals have been shown to behave similarly although are less reactive than titanium.[16,17]

Titanium atom solvent reactions can be seen to effect carbonyl reductive coupling reactions in two ways.  First, zero-valent species are partially oxidized through carbon–hydrogen and carbon–carbon oxidative addition reactions with the solvent prior to reaction with cyclohexanone.  Yields of the corresponding pinacol are lower.  Second, reactive metal alkyl and hydride fragments attack carbonyl compounds, leading to nonradical routes of carbonyl reduction/aldol condensation reactions.
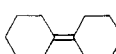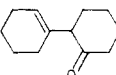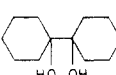
The reaction of titanium atoms with arene solvents produces high yields of bis(arene)titanium(0) compounds.[18]  These sandwich compounds are reactive toward cyclohexanone, reacting immediately on matrix warm-up.  Bis(toluene)titanium(0) is the most effective reducing agent produced by the metal atom technique for reductively coupling alkyl ketones to pinacols.  Yields are twice as high as even metal atom reactions with cyclohexanone.

A number of titanium species listed in Table IV have been produced and have been used as reducing agents with cyclohexanone.  Despite the vastly differing properties of the various titanium metal–cyclohexanone systems, none of these titanium species have been effective reducing agents for the transformation of cyclohexanone to bicyclohexylidene.

**Titanium Tetrachloride–Potassium Reduction of Cyclohexanone.**  From the above studies it seemed evident that reduction of cyclohexanone to bicyclohexylidene requires more than the presence of high surface area, zero-valent titanium metal.  Titanium species produced by the use of the metal atom technique have consistently failed to produce olefins from carbonyl compounds.  On the other hand, titanium powders prepared by the reduction of titanium tetrachloride have consistently coupled alkyl ketones to olefins.[5]  Because of these differences in reduction properties, reduction of cyclohexanone with titanium tetrachloride–potassium metal, which has been the most effective reductant reported, was reinvestigated.
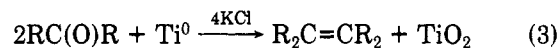
Reduction of titanium tetrachloride with 4 equiv of potassium metal in refluxing THF produces a highly re-

**Table V.  Reaction Products of Cyclohexanone by TiCl₄/4K Powders**

| | | yield, % (mg) | | |
| --- | --- | --- | --- | --- |
| amt of TiCl₄,[a] g | equiv of C₆H₁₀O | ⬡=⬡ | ⬡-⬡(O) | ⬡-⬡(HO OH) |
| 2.42 | 2.00 | 0.8 (12) | 81 (1300) | 18 (330) |
| 2.35[b] | 0.25 | 100 (69) | | |

[a] The solvent was THF in both cases.  [b] Extensive solvent decomposition was observed.

active black solid.  From the proposed mechanism, 2 equiv of ketone should be reduced to 1 equiv of olefin and 1 equiv of titanium dioxide[5,6] (eq 3).  Surprisingly, cyclohexanone

$$2RC(O)R + Ti^0 \xrightarrow{4KCl} R_2C{=}CR_2 + TiO_2 \qquad (3)$$

fails to be reduced to bicyclohexylidene under these conditions, even after THF reflux overnight.  The observed products are given in Table V.  It can be seen from Table V that the product yield and distribution are similar to those of products produced by the metal atom technique (Table IV).  In the literature preparation of bicyclohexylidene from cyclohexanone, McMurry and Fleming used 1 equiv of ketone/equiv of titanium metal.[5,19]  When as little as $^1/_4$ equiv of cyclohexanone/equiv of metal is used, bicyclohexylidene is, indeed, the only observed cyclohexanone-reduced product.

Reduction of ketones to pinacols by potassium-reduced titanium tetrachloride has not been previously reported; however, pinacolic dianions have been proposed as intermediates in the reductive coupling of ketones to olefins[5,6] (eq 1 and 2).  Reductive coupling of two carbonyl groups to the pinacolic dianion (eq 1) is a two-electron reduction.  Further reduction of the dianion to olefin (eq 2) is a two-electron reduction as well.  In the presence of excess ketone, there is a competition for available metal electrons to further reduce pinacolic dianions to olefin product or to react with excess ketone to form additional pinacolic dianion.  From these results, it may be concluded that the rate of formation of the pinacolic dianion is, at least, several times faster than reduction of the coordinated dianion to olefin.  In addition, it is clear that stoichiometric control of the reactants is critical to the product distribution for reduction of carbonyl compounds by titanium metal.  It is likely that stoichiometric control of the carbonyl compound is important in reduction reactions induced by other transition-metal compounds as well.  For each of the reactions using the metal atom technique, cyclohexanone was always present in great excess, relative to the amount of metal deposited.  The observed products were [1,1'-bicyclohexyl]-1,1'-diol, a pinacol, and 2-(cyclohexene-1-yl)cyclohexanone, an aldol.  Under the conditions

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of the metal atom technique, neodymium, uranium, and chromium metal atoms displayed the same general reduction characteristics as titanium metal atoms. In addition, titanium atoms display reduction properties identical with conventional solution techniques when subjected to the same stoichiometric conditions.

## Conclusions

The results of this work demonstrate several important features about the reductive coupling of carbonyl compounds to pinacolic dianions and the further reduction of pinacols to olefins. First, the reduction of alkyl ketones to pinacols is a general reaction brought about by many metals in addition to the titanium compounds which are presently known. Materials capable of pinacol formation possess two important properties. All compounds or metals which are effective coupling reagents are highly electropositive while nonpinacol-producing metals, on the other hand, are only slightly electropositive. Although oxidation–reduction potentials are an important consideration, in carbonyl coupling reactions, high oxidation potentials are, however, not a sufficient condition to ensure pinacol product formation. For example, potassium metal has a higher oxidation potential than any transition metal, yet cyclohexanone reduction by potassium produces only traces of [1,1'-bicyclohexyl]-1,1'-diol.

In addition to favorable oxidation potentials, uranium, neodymium, titanium, and chromium form strong metal–oxygen bonds. Nickel, cobalt, and potassium, on the other hand, form relatively weak metal–oxygen bonds. Successful coupling of carbonyl compounds requires a strong metal–oxygen interaction. As the metal atom transfers an electron to the carbonyl function, a very reactive radical–anion intermediate is formed. Because of the strong metal ion–oxygen interaction, the metal ion stabilizes the highly reactive radical intermediate. Metal-stabilized radicals then proceed in high yields to pinacolic dianions.

Deoxygenative coupling of ketones to olefins was not a high-yield reaction under the conditions of the metal atom reaction. Low olefinic yields have been shown to be due to the large excess of ketone required in such reactions. The presence of bicyclohexylidene in cyclohexanone/metal atom reductions is significant, even though the yields are low. Under the conditions of limited stoichiometry, uranium, chromium, and neodymium metal powders would be expected to deoxygenate pinacolic dianions to alkenes similar to the previously reported compounds of titanium, molybdenum, and tungsten. Recently, uranium metal prepared by potassium reduction of uranium tetrachloride reduced benzophenone to tetraphenylethylene in 50% yield.[9] This result demonstrates that the deoxygenative reduction of carbonyl compounds is a general reaction and may occur for many low-valent, transition-metal compounds and metals not yet reported.

Two mechanisms have been reported for the reduction of carbonyl compounds to olefins.[5,7] The results of this study are in agreement with the mechanism proposed by McMurry and Fleming[5] (eq 1 and 2). Ketone reduction is a two-step radical reduction, proceeding, first, to a pinacolic dianion which may further be reduced to dimeric alkene products in a radical-deoxygenation step under conditions of limited stoichiometry. In addition, reaction rates for pinacolic reduction are faster than reaction rates for alkene formation. The generalized mechanism for ketone reduction does not specifically require titanium as the reducing agent. Any low-valent compound or metal of an electropositive d or f transition metal which forms strong metal–oxygen bonds should participate, in principle,

in radical-type ketone reduction reactions.

Although metal species served as the primary reducing agents throughout this study, zero-valent compounds may be excellent reducing agents as well. For titanium, bis-(arene)titanium(0) compounds proved to be the most effective reducing agent prepared. The increased reactivity for zero-valent titanium compounds may be attributed primarily to the increase in surface area afforded by the solubility of the compound. Although soluble compounds increase reactive metal surface areas, metal–ligand bonding reduces metal reactivity relative to metal atom vapors. As a result, increased molecular stability limits unwanted side reactions, for example, solvent attack. However, if ligand–metal bonding forces become too strong, molecular reducing agents may become partially or totally unreactive. In the future, by careful control of the metal coordination sphere as well as control of the metal and metal oxidation state, one may be able to design highly reactive and highly selective carbonyl reducing agents which will effect reductions in the presence of other reactive functional groups.

## Experimental Section

Several excellent reviews are available which discuss equipment and general experimental requirements for the metal atom vaporization technique.[12,20] The most important equipment requirements are a need for a reaction chamber capable of sustaining a high vacuum, a high-vacuum diffusion pump (<$10^{-5}$ mmHg), and a suitable metal-vaporization source. The experimental apparatus used in this study is similar to other metal atom reactors, with metal atoms being generated by resistive heating methods. A complete description of this equipment has been reported.[21]

**Spectral Data.** $^1H$ NMR data were recorded on either a Varian HA-100 or a Varian CFT-80A spectrophotometer with Me$_4$Si as an internal standard. $^{13}C$ NMR spectra were recorded on the Varian CFT-80A spectrometer with Me$_4$Si as an internal standard. IR spectra were obtained on a Perkin-Elmer 727 B spectrometer, and peaks were calibrated by using the 1601-cm$^{-1}$ absorption of polystyrene as a standard. Gas chromatographic-mass spectral data were obtained by using a Varian MAT Gmb H CH7 Massenspectrometer at an ionization potential of 70 eV interfaced with a Varian 1200 gas chromatograph.

Bicyclohexylidene, C$_{12}$H$_{20}$: $^1H$ NMR (CCl$_4$) (see ref 22): δ 1.51 (s, 3 H), 2.13 (s, 2 H); IR (CCl$_4$) 855 (m), 895 (w), 1015 (m), 1105 (s), 1239 (m), 1268 (m), 1370 (w), 1452 (s), 2855 (vs), 2944 (vs); mass spectrum (70 eV), m/e 164 (M$^+$), 135 (M − C$_2$H$_5$), 122 (M − C$_3$H$_6$), 107 (M − C$_4$H$_9$), 93 (M − C$_5$H$_{11}$), 91 (C$_7$H$_7$), 82 (C$_6$H$_{10}$), 81 (C$_6$H$_9$), 79 (C$_6$H$_7$), 67 (C$_5$H$_7$), 55 (C$_4$H$_7$), 53 (C$_4$H$_5$), 41 (C$_3$H$_5$). 2-(1-cyclohexene-1-yl)cyclohexanone, C$_{12}$H$_{18}$O: $^1H$ NMR$^{23a}$ δ 1.60 (m), 1.90 (m), 2.31 (m), 2.74 (m), 5.32 (s); IR (neat)$^{24a}$ 816 (w), 840 (w), 934 (m), 1038 (w), 1079 (m), 1138 (s), 1212 (m), 1198 (w), 1532 (m), 1260 (m), 1460 (s), 1720 (vs), 2872 (vs), 2948 (vs); mass spectrum (70 eV), m/e 178 (M$^+$), 149 (M − C$_2$H$_5$), 135 (M − C$_3$H$_7$), 121 (M − C$_4$H$_9$), 107 (C$_8$H$_{11}$), 93 (C$_7$H$_9$), 91 (C$_7$H$_7$), 79 (C$_6$H$_7$). 2-Cyclohexylcyclohexanone, C$_{12}$H$_{20}$O: $^1H$ NMR$^{23b}$ (CCl$_4$) 1.19 (d), 1.64 (m), 1.96 (t), 2.22 (d); $^{13}C$ NMR δ 55.4, 40.76, 35.6, 30.4, 28.2, 26.8, 25.4, 25.3, 22.9 (carbonyl carbon absent); IR (neat)$^{24b}$ 837 (w), 882 (w), 1020 (w), 1063 (m), 1131 (m), 1237 (w), 1298 (w), 1318 (w), 1454 (s), 1716 (vs), 2857 (vs), 2935 (vs); mass spectrum (70 eV), m/e 180 (M$^+$), 98 (C$_6$H$_{10}$O), 83 (C$_6$H$_{11}$), 70 (C$_5$H$_{10}$), 67 (C$_5$H$_7$), 55 (C$_4$H$_7$, C$_3$H$_3$O). [1,1'-Bicyclohexyl]-1,1'-diol, C$_{12}$H$_{22}$O$_2$:

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(21) C. W. DeKock, S. R. Ely, T. E. Hopkins, and M. A. Brault, *Inorg. Chem.*, **17**, 625 (1978).

(22) C. J. Rouchert and J. R. Campbell, "The Aldrich Library of NMR Spectra", Aldrich Chem. Co., Milwaukee, WI, 1974, Vol. 1, p 41B.

(23) (a) "Sadtler Standard Spectra—NMR Standard Spectra", Sadtler Research Laboratories, Philadelphia, PA, 1976, p 9759; (b) *ibid.*, p 6166; (c) *ibid.*, 16911.

(24) (a) "Sadtler Standard Spectra—Infrared Prism Standard Spectra", Sadtler Research Laboratories, Philadelphia, PA, 1976, p 25040; (b) *ibid.*, p 21528; (c) *ibid.*, p 25042.

$^1$H NMR$^{23c}$ (CCl$_3$D) $\delta$ 1.5, 1.55, 1.60, 1.78 (10 H), 2.15 (1 H); IR$^{24c}$ (CCl$_4$) 925 (m), 1263 (m), 1480 (s), 1560 (s), 2875 (s), 2955 (vs) 3450 (vs, br); mass spectrum (70 eV), $m/e$ 180 (M – H$_2$O), 178 (M – H$_2$O – H$_2$), 99 (C$_6$H$_{11}$O), 98 (C$_6$H$_{10}$O), 81 (C$_6$H$_9$), 55 (C$_4$H$_7$, C$_3$H$_3$O).

**Materials.** Ti, Cr, Co, Ni, Nd, and U were obtained from Research Chemicals or MC/B and were better than 99.5% pure. TiCl$_4$ was purchased from the Alfa division of Ventron Corp. and was used without purification. Cyclohexanone (analytical reagent grade), hexane (Spectrograde), and toluene (Spectrograde) were obtained from Mallinckrodt Chemical Works, were dried over molecular sieves, and were degassed by successive freeze–thaw cycles under reduced pressure (<10$^{-3}$ mmHg).

Tetrahydrofuran (THF, Mallinckrodt, analytical reagent grade) was dried over Na/benzophenone or LiAlH$_4$ and distilled under N$_2$ prior to use.

**General Procedure for Metal Atom Vapor Plus Cyclohexanone Cocondensation.** At 40 °C approximately 15 mL of cyclohexanone (145 mmol) was condensed with from 0.1 to 0.7 g (2–15 mmol) of metal at –196 °C over 45–60 min. The pressure inside the reaction vessel was kept below 2 × 10$^{-4}$ mmHg. For most metals used, a reaction could be seen to take place at –196 °C, with matrices turning orange to gold. After deposition was complete, the liquid N$_2$ bath was removed, and the matrix was allowed to warm to room temperature. Volatile products were pumped off and collected in a liquid N$_2$ trap. VPC analysis showed that only cyclohexanone was present. The reaction vessel was filled with N$_2$, and dry Et$_2$O was added. The reaction mixture was hydrolyzed slowly, dropwise, with H$_2$O. **Caution:** Highly divided metal powders are often pyrophoric and may react vigorously on hydrolysis with gas evolution. Hydrogen evolution was not observed for any of the metals studied. After 15 mL of H$_2$O had been added, the mixture was acidified with 1 M HCl. Organic products were extracted with Et$_2$O or pentane (3 × 50 mL). The combined extracts were dried over Na$_2$SO$_4$ and reduced to a 2–3-mL volume. Solutions were diluted to exactly 5 mL, and yields were determined by VPC ($^1/_4$ in. × 20 in. column, 10% UCW 982) using benzophenone as an external standard. The products were collected by preparative VPC ($^3/_8$ in. × 8 ft column, 20% OV 101)

and identified spectroscopically by standard IR, $^1$H NMR, and gas chromatographic–mass spectrometric techniques. Spectra were compared with the literature data.

**General Procedure for Titanium Atom Vapor/Solvent Plus Cyclohexanone Cocondensation.** Approximately 50 mL of dry, degassed hexane (380 mmol) as the solvent was condensed with approximately 0.10 g of titanium metal (2.1 mmol) at –196 °C, and approximately 5 mL of cyclohexanone (48 mmol) was condensed on top of the reaction matrix. The liquid N$_2$ bath was removed, and the temperature was raised to room temperature. The reaction vessel was filled with N$_2$, and a magnetic stir bar was added. The vessel was partially evacuated (approximately 350 mmHg), and the mixture was heated to reflux with stirring. The water-cooled electrodes served as the condenser. Refluxing continued for 2 h. After cooling to room temperature, the mixture was hydrolyzed, and the products were isolated and identified as before.

**Cyclohexanone Reduction by Potassium-Reduced Titanium Tetrachloride Metal Powders.**$^6$ A 1.99-g (50.9 mmol) sample of freshly cut K metal was added to approximately 60 mL of dry THF in a Schlenk flask under a N$_2$ atmosphere. The Schlenk flask was fitted with a reflux condenser, and the THF was heated with rapid stirring. Under THF reflux, the K melted, producing many small spherical globules. To this K sand was added 1.40 mL (12.7 mmol) of TiCl$_4$ dropwise by syringe. Addition of TiCl$_4$ to K–THF was followed by a vigorous reaction producing a great deal of heat and an insoluble violet solid. The mixture was refluxed for an additional 3 h, resulting in an insoluble black solid. A 2.65-mL sample of cyclohexanone (25.4 mmol) in 10 mL of THF was added dropwise over 5 min to the Ti metal powder. The reaction mixture was refluxed overnight (18 h). Unlike metal atom reactions, hydrolysis was vigorous. The products were obtained and identified as described.

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# Studies of Sulfinyl Radicals. 1. Thermal Decompositions of Benzhydryl p-Tolyl Sulfoxide and Benzhydryl Methyl Sulfoxide
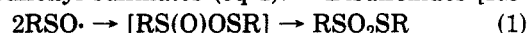
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The kinetics and mechanism of the thermal decompositions of benzhydryl p-tolyl sulfoxide (BTSO) and benzhydryl methyl sulfoxide (BMSO) were studied. Product analysis, ESR, and CIDNP results showed that both sulfoxides gave p-toluenesulfinyl and methanesulfinyl radicals, respectively, by the scission of carbon–sulfur bonds at 100–130 °C. The presence of a small amount of a base such as pyridine has been found to suppress the formation of other products than the coupling products (the corresponding thiosulfonates and tetraphenylethane), which may be formed by ionic reactions of BTSO and BMSO. The mechanism of BTSO decomposition is complex, since it is in equilibrium with benzhydryl p-toluenesulfenate (BTSN) at 100–130 °C. On the other hand, BMSO, showing simple decomposition behavior, indicated that the decomposition rates decreased on the addition of hydroxylic solvents.

Sulfinyl radicals,$^1$ unlike thiyl and sulfonyl radicals, are unreactive toward olefins such as 1,1-diphenylethylene,$^2$ styrene,$^3$ cyclohexene,$^4$ and 2-butene,$^5$ and benzoquinone,$^4$ which usually react with organic free radicals. So far, the only reaction which sulfinyl radicals are known to undergo is the coupling reaction which gives thiosulfonates probably through sulfenyl sulfinates (eq 1).$^6$ Disulfoxides [RS-

$$2RSO\cdot \rightarrow [RS(O)OSR] \rightarrow RSO_2SR \qquad (1)$$

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