

Deoxygenation and Desulfurization of Organic Compounds via Transition Metal Atom Cocondensation

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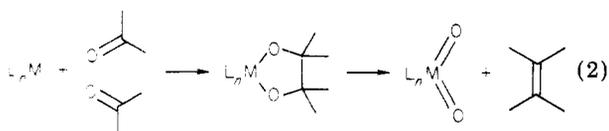
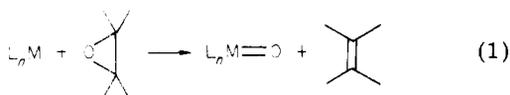
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Reactions resulting from the cocondensation of transition metal atoms with a variety of oxygen- and sulfur-containing organic compounds are surveyed. Alkenes are the major or exclusive volatile products when epoxides are reacted with Ti, V, Cr, Co, and Ni atoms. 2,6-Dimethylpyridine *N*-oxide and dimethyl sulfoxide undergo deoxygenation upon cocondensation with chromium, but diisopropyl ether and decyl methyl ether do not. Dibenzyl ether yields bis(η^6 -dibenzyl ether)chromium(0) with Cr atoms, but dibenzyl sulfide undergoes desulfurization. Cyclohexanone and cycloheptanone afford low yields of reductive coupling and aldol products when cocondensed with Cr, Co, and Ni atoms. Nitro- and nitrosoarenes are deoxygenated to coupled azo and azoxy products with Cr atoms. Carbazole (3) is obtained from 2-nitrosobiphenyl, implicating nitrene or nitrenoid intermediates. Whereas isocyanides are not formed from isocyanates and metal atoms, they are produced when isothiocyanates are cocondensed with Cr and V atoms.

Introduction

The transfer of oxygen atoms between organic and inorganic compounds has fascinated organic and inorganic chemists alike. Among their many interesting aspects, these reactions can be of substantial preparative importance. A number of high-valent metal oxides (KMnO₄, OsO₄, CrO₃, CrO₂Cl₂, SeO₂)¹ serve as useful oxidants for a variety of organic substrates. Of more recent vintage, however, are low-valent reagents which effect the *reductive deoxygenation* of organic molecules.

Deoxygenation reactions can be classified into two principal types: (1) those in which oxygen is simply abstracted from a molecule, and (2) those in which oxygen removal occurs in tandem with intermolecular coupling. The former is best exemplified by the deoxygenation of epoxides to alkenes (eq 1). This reaction can be executed



with a number of reagents such as TiCl₃/LiAlH₄,² WCl₆/2(*n*-C₄H₉Li),³ (η -C₅H₅)₂TiCl₂/Na,⁴ (η -C₅H₅)₂WO/NaHg,⁵ Fe(CO)₅/tetramethylurea,⁶ and (η -C₆H₆)₂Ti.⁷ The most common example of the second mode of deoxygenation is the reductive coupling of ketones and aldehydes to olefins (eq 2). This reaction is most effectively accomplished with the TiCl₃/LiAlH₄² and TiCl₃/K⁸ reagents

developed in McMurry's laboratory. However, other low-valent systems such as WCl₆/2(*n*-C₄H₉Li),³ WCl₆/LiAlH₄,⁹ and (η -C₆H₆)₂Ti⁷ can also be employed.

The exact nature of the deoxygenating agent produced in many of the forementioned "recipes" is unknown. However, transition metal atoms¹⁰ constitute well-defined and easily generated¹¹ zerovalent entities and are substantially more reactive than bulk metal by virtue of the 70–200 kcal/mol required for their formation.¹² A variety of reactions—such as π -complexation¹³ and oxidative addition¹⁴—have been demonstrated to proceed rapidly at 77 K in matrices of metal atoms and organic compounds. The only experimental restriction is that the organic compound must be employed in at least a tenfold excess, since metal atom reaggregation is a low activation energy process which can compete with desired reactions. Hence we embarked upon a study directed at identifying the *organic* deoxygenation (or desulfurization) products formed when transition metal atoms are cocondensed with organic molecules.¹⁵

Results

Metal atoms were cocondensed with organic compounds at 77 K in resistive heating reactors^{10–12,16} as described in the Experimental Section. For some experiments with epoxides, a "micro" reactor (see Experimental Section) was employed. For each cocondensation, the quantity of metal in the matrix was determined by applying a titrimetrically determined correction factor to the total amount of metal evaporated. Reactions of epoxides were investigated first.

The cocondensation of titanium, vanadium, chromium, cobalt, and nickel with cyclohexene oxide (1) resulted

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Table I. Products from the Cocondensation of Metal Atoms with Cyclohexene Oxide (1) in the "Micro" Reactor

metal (mmol)	1, mmol	cyclohexene formed, mmol	benzene formed, mmol	1,3-cyclohexadiene formed, mmol	total products, mmol	total products + recovered 1, mmol	oxygen abstracted per metal atom
Ti (0.85)	8.40	0.73	0.08	trace	0.81	6.23	0.95
V (0.31)	13.9	0.77	0.05	0.05	0.87	10.6	2.80
Cr (0.50)	14.9	1.15	0.04	0.15	1.34	14.7	2.68
Co (0.97)	12.4	0.84	0.09	0.24	1.17	12.4	1.21
Ni (0.81)	15.1	0.36	0.13	trace	0.49	15.1	0.60
Ni (0.80)	16.6	0.36	0.07	0.00	0.43	16.6	0.54

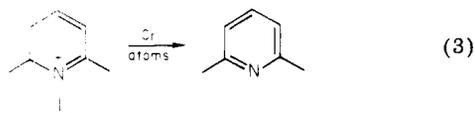
primarily in the formation of cyclohexene. Data obtained by utilizing the "micro" reactor are summarized in Table I. Smaller amounts of benzene (3–25% of products) and 1,3-cyclohexadiene (0–20% of products) were also produced. Cyclohexane could not be detected in any of these experiments. With each metal except nickel, at least one oxygen atom was abstracted per metal atom. Although the absolute yields of cyclohexene were low (Ti, 8.7%; V, 5.6%; Cr, 7.8%; Co, 6.8%; Ni, 2.4%), conversion yields (i.e., based upon 1 consumed) were in the 70–85% range for Cr, Co, and Ni. The last two entries in Table I illustrate that reasonable reproducibility can be achieved.

When chromium alone was evaporated onto the walls of the "micro" reactor, followed by deposition of 1, less than 0.6% of 1 was deoxygenated, as opposed to 9.1% during a normal cocondensation (Table I). When chromium was cocondensed with 1 as usual, but the volatiles were pumped directly into a U-tube as the matrix warmed (1-h warmup period under static vacuum eliminated; see Experimental Section), yields were unaffected. When 1 was passed over hot, nonevaporating tungsten filaments in the "micro" reactor, up to 4% conversion to deoxygenated products was observed.

Results similar to those in Table I were obtained in conventional reactors, except that the average numbers of oxygen atoms abstracted per metal atom were somewhat lower. For instance, when 24.6 mmol of 1 was cocondensed with 0.53 mmol of titanium, 0.44 mmol of cyclohexene and 0.05 mmol of benzene were produced. Only 14.2 mmol of products and reactants was recovered; a considerable fraction of the cyclohexene oxide was converted in the reactor. Polymer formation was also noted with vanadium.

Other epoxides were cocondensed with chromium atoms, as summarized in Table II. In each case, alkenes were formed in 2–10% absolute yields. While no double bond migrations were observed, mixtures of *cis* and *trans* olefins were formed from *cis* epoxides. In a separate experiment, chromium (0.26 mmol, corrected) was cocondensed with *cis*-4-decene (10.6 mmol). Isomerization to *trans*-4-decene occurred in 13% yield based upon olefin.

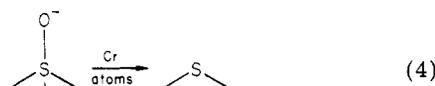
By use of a conventional design reactor, reactions of metal atoms with heteroatom oxides were investigated next. When 2,6-dimethylpyridine *N*-oxide (11.1 mmol) was cocondensed with chromium atoms (0.28 mmol), 0.25 mmol of 2,6-dimethylpyridine was produced (eq 3). When 2,6-



dimethylpyridine *N*-oxide (15.0 mmol) was condensed onto a preformed chromium surface (1.02 mmol), only 0.003 mmol of 2,6-dimethylpyridine was formed.

When dimethyl sulfoxide (21.1 mmol) was cocondensed with chromium atoms (0.45 mmol), a beautiful red matrix

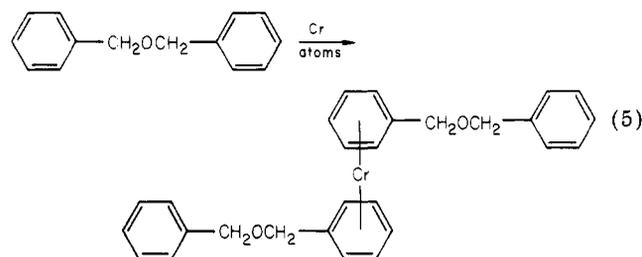
was produced. Workup yielded 0.72 mmol of dimethyl sulfide (eq 4). When dimethyl sulfoxide (28.1 mmol) was



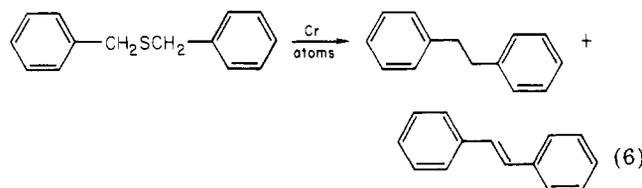
condensed onto a preformed chromium surface (2.73 mmol), 0.23 mmol of dimethyl sulfide was formed.

When triethylphosphine oxide (17.3 mmol) was cocondensed with chromium atoms (2.98 mmol), triethylphosphine (0.37 mmol) was produced. When triethylphosphine oxide (17.3 mmol) was condensed onto a preformed chromium surface (3.06 mmol), 0.09 mmol of triethylphosphine was formed. In other runs, up to 1% of the triethylphosphine oxide condensed onto a chromium surface was converted to triethylphosphine.

Simple ethers did not afford volatile deoxygenation products when cocondensed with chromium. When diisopropyl ether (49.8 mmol) was cocondensed with chromium (0.65 mmol), only starting material (49.1 mmol) was recovered. The cocondensation of dibenzyl ether (28.4 mmol) and chromium (1.39 mmol, corrected) afforded bis(η^6 -dibenzyl ether)chromium(0) (0.45 mmol; 32% based upon chromium, eq 5). Less than 0.002 mmol of bibenzyl



was formed. However, the cocondensation of dibenzyl sulfide (45 mmol) with chromium atoms (2.8 mmol) yielded bibenzyl (0.09 mmol) and *trans*-stilbene (0.17 mmol) (eq 6). Trace quantities of a volatile yellow product were also



noted.

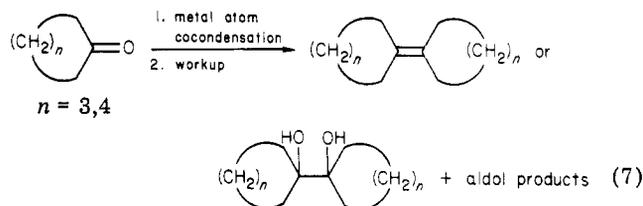
An additional type of experiment was conducted to look for ether-metal atom reactions. Decyl methyl ether (n -C₁₀H₂₁OCH₃; 21.4 mmol) was cocondensed with chromium (0.75 mmol, corrected). The matrix was warmed to room temperature, and after 0.5 h, remaining decyl methyl ether was pumped off. While still under vacuum, water (166.7 mmol) was distilled onto the reactor residue. After 12 h at room temperature, the reactor was extracted with ether; no hydrocarbons in the C₈–C₁₁ range were detectable by GC.

Table II. Data on the Cocondensation of Chromium Atoms with Epoxides

epoxide (mmol)	reactor ^a	Cr, mmol	alkenes formed (mmol)	alkenes + recovered epoxide, mmol	absolute yield of alkenes, %	oxygen abstracted per metal atom
<i>cis</i> -stilbene oxide (5.00)	conventional	0.46	<i>cis</i> -stilbene (0.06) <i>trans</i> -stilbene (0.09)	4.01	3.0	0.32
<i>cis</i> -4-decene oxide (8.15)	conventional	1.0	<i>cis</i> -4-decene (0.28)	7.46	9.7	0.79
allylbenzene oxide (15.8)	conventional	1.63	<i>trans</i> -4-decene (0.51)	14.20	2.9	0.28
allylbenzene oxide (15.8)	"micro"	0.18	allylbenzene (0.46)	14.36	2.3	3.00
1-methylcyclopentene oxide (8.64)	"micro"	0.44	1-methylcyclopentene (0.39)	5.83	4.5	0.89
cyclohexene oxide (14.9)	"micro"	0.50	cyclohexene (1.15) benzene (0.04) 1,3-cyclohexadiene (0.15)	14.70	9.1	2.68

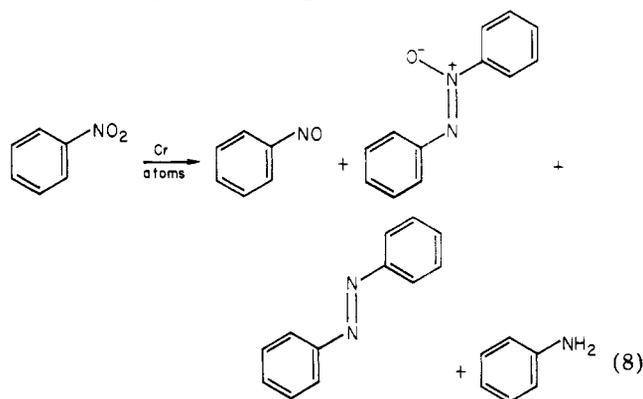
^a See Experimental Section.

Cocondensations of metal atoms with ketones were examined in a conventional design reactor. The results obtained with cycloheptanone and cyclohexanone are summarized in Table III. Volatile C₇ or C₆ products (cycloheptene, norcarane, cycloheptane, etc.) were not formed, but dimeric products such as coupled olefins and diols could be extracted from the reactor residue (eq 7). Aldol



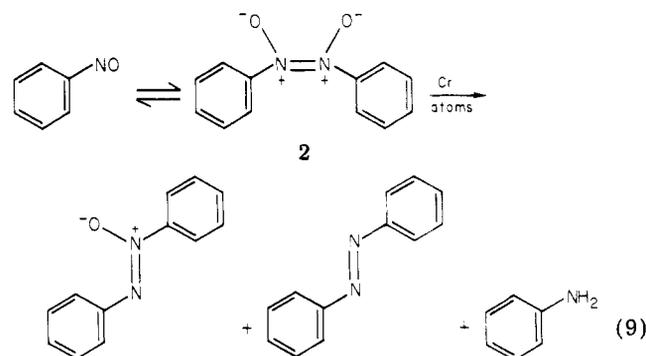
products were also obtained. Since oxygen abstraction from ketones was much less efficient than from epoxides (0.00–0.05 equiv of oxygen abstracted per metal atom), surface control experiments were not conducted.

Reactions of chromium atoms with nitro- and nitrosoarenes were subsequently investigated. When nitrobenzene (24 mmol) was cocondensed with chromium (1.67 mmol, corrected), a green matrix was produced. Workup afforded nitrosobenzene (0.015 mmol), azoxybenzene (0.060 mmol), azobenzene (0.087 mmol), and aniline (0.05 mmol), as depicted in eq 8. In this experiment, each chromium atom



abstracted an average of 0.33 oxygen atom. When higher ratios of nitrobenzene to chromium were employed, nitrosobenzene constituted as much as 77% of the product mixture, and the yield based upon chromium increased. When nitrobenzene (19.5 mmol) was condensed onto a preformed chromium surface (1.07 mmol), less than 0.002 mmol of nitrosobenzene was detected; no other products were present.

When nitrosobenzene (28.0 mmol) was cocondensed with chromium atoms (2.41 mmol, corrected), workup afforded azoxybenzene (1.70 mmol), azobenzene (0.33 mmol), and aniline (0.17 mmol), as depicted in eq 9. In this experi-



ment, each chromium atom abstracted an average of 1.05

Table III. Data on the Cocondensation of Metal Atoms with Cyclic Ketones

metal (mmol)	ketone (mmol)	products formed (mmol)	recovered ketone, mmol
Cr (2.44)	cycloheptanone (42.4)	cycloheptylidencycloheptane (0.06) 2-cycloheptylidencycloheptanone (0.13)	38.9
Co (3.20)	cycloheptanone (42.4)	cycloheptylidencycloheptane (0.01) 2-cycloheptylidencycloheptanone (0.01)	39.6
Ni (0.34)	cycloheptanone (42.4)	cycloheptylidencycloheptane (trace) ^a 2-cycloheptylidencycloheptanone (trace)	40.8
Cr (1.49)	cyclohexanone (48.3)	bicyclohexyl-1,1'-diol (0.77) 2-(1-hydroxycyclohexyl)cyclohexanone (0.13) 2,6-bis(1-cyclohexenyl)cyclohexanone (0.38)	37.0
Co (0.72)	cyclohexanone (48.3)	bicyclohexyl-1,1'-diol (0.05) 2-(1-hydroxycyclohexyl)cyclohexanone (0.02)	46.2
Ni (0.18)	cyclohexanone (48.3)	bicyclohexyl-1,1'-diol (trace) ^a 2-(1-hydroxycyclohexyl)cyclohexanone (trace)	47.7

^a Detectable by TLC.

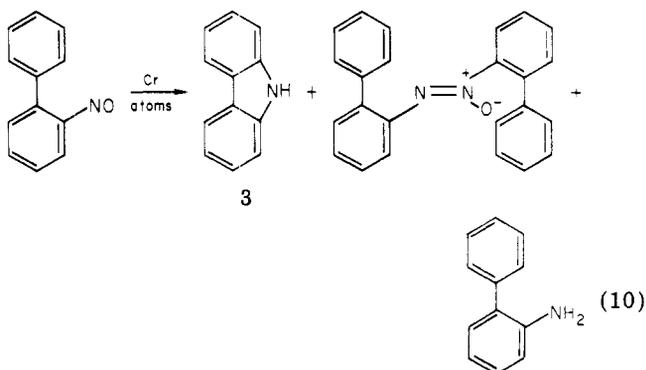
Table IV. Data on the Cocondensation of Metal Atoms with Isothiocyanates

reactant (mmol)	metal (mmol)	products (mmol)	recovered starting material, mmol	absolute yield of products, %	sulfur abstracted per metal atom
cyclohexyl isothiocyanate (22.4)	Cr (2.10)	cyclohexyl isocyanide (1.57)	19.3	7.0	0.75
cyclohexyl isothiocyanate (22.4)	V (1.26)	cyclohexyl isocyanide (0.60)	20.0	2.7	0.48
cyclohexyl isothiocyanate (15.0)	Cu (1.40)	none ^a	13.4	0.0	0
phenyl isothiocyanate (25.6)	Cr (2.45)	phenyl isocyanide (1.12) phenyl cyanide (0.12)	23.2	4.8	0.51

^a Trace odor of cyclohexyl isocyanide.

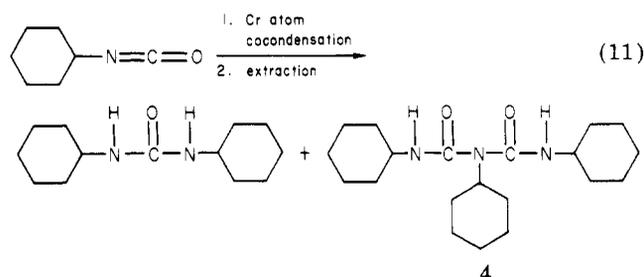
oxygen atoms. When nitrosobenzene (18.7 mmol) was deposited onto a preformed chromium surface (0.51 mmol), less than 0.02 mmol of deoxygenated products formed. When nitrosobenzene (colorless) was evaporated alone onto a 77 K glass surface, a light blue matrix was produced.

The cocondensation of 2-nitrosobiphenyl (14.7 mmol) with chromium atoms (0.18 mmol, corrected) yielded 0.125 mmol of carbazole (3), as well as some azoxybiphenyl (0.089 mmol) and 2-aminobiphenyl (eq 10). No 2-nitrosobiphenyl was present.



When isocyanates were cocondensed with metal atoms, clear-cut deoxygenation was not observed. No cyclohexyl isocyanide was obtained from the cocondensation of chromium (1.86 mmol) with cyclohexyl isocyanate (39.2 mmol, corrected). However, some products could be extracted from the polymer-like reactor residue. Thus iso-

lated were *N,N*-dicyclohexylurea (0.42 mmol) and the imide 4 (0.13 mmol; eq 11). With cyclohexyl isocyanate



and cobalt and nickel atoms, some *N,N*-dicyclohexylurea was formed. No reaction occurred when cyclohexyl isocyanate was introduced into the reactor with a hot, nonevaporating filament in place of the usual metal atom source.

When isothiocyanates were cocondensed with metal atoms, isonitriles were obtained as the major or exclusive products (eq 12). Results are summarized in Table IV.



Discussion

The virtual absence of any deoxygenation when cyclohexene oxide is condensed onto a preformed chromium surface, coupled with the deoxygenation observed when chromium is cocondensed with several epoxides (Table II), strongly suggests that atomic chromium can efficiently

abstract oxygen from epoxides. It should be kept in mind that highly reactive small metal aggregates are formed when some metal atom-organic compound matrices are warmed.^{16,17} However, the yields of deoxygenated products were not dependent upon the contact time between the solid and liquid phases of a melted chromium-cyclohexene oxide matrix.

Little can be said regarding the mechanism of epoxide deoxygenation. The reaction might be concerted, or require prior coordination of the epoxide oxygen to chromium, or involve insertion of chromium into a carbon-oxygen bond to yield a four-membered metallocyclic intermediate. These details are amenable to study by matrix spectroscopy techniques.¹¹ In terms of stereospecificity, *cis* epoxides afford appreciable amounts of *trans* olefins (Table II). However, since *cis*-4-decene is partially isomerized to *trans*-4-decene upon cocondensation with chromium, isomerization might occur subsequent to deoxygenation.

The formation of benzene and 1,3-cyclohexadiene from cyclohexene oxide can be ascribed to dehydrogenation of initially formed cyclohexene. Cyclohexene undergoes dehydrogenation over a variety of heterogeneous catalysts.¹⁸

While the data in Table I provide some feeling for the relative deoxygenating abilities of Ti, V, Cr, Co, and Ni, some caution must be exercised since the close contact of the organic vapor with the metal filament in the "micro" reactor (see Experimental Section) may lead to some deoxygenation in itself. For example, a hot tungsten filament (heated to a temperature slightly greater than that needed to evaporate Ti and V—the least volatile of the five metals studied) deoxygenated ca. 4% of the cyclohexene oxide passed over it. We believe that this type of reaction negligibly contributes to the results obtained with Cr, Co, and Ni. Nonetheless, the remainder of our studies were conducted in a conventional design reactor.

The abstraction of significantly more than one oxygen per metal atom by vanadium and chromium (Table I) clearly requires that an initially formed low-valent metal oxide can also deoxygenate cyclohexene oxide. The formation of H₂ via cyclohexene dehydrogenation provides additional reducing equivalents which may contribute to the yield.

In related work, Skell and Shevlin have observed epoxide deoxygenations with arc¹⁹ and chemically²⁰ generated carbon atoms. The stereochemical outcome of these reactions has been shown to depend upon the spin state of carbon. Interestingly, molecular-orbital calculations suggest that the deoxygenation of ethylene oxide by singlet carbon atoms is a direct, concerted reaction with no local energy minima on the way to carbon monoxide and ethylene.²¹

2,6-Dimethylpyridine *N*-oxide, dimethyl sulfoxide, and triethylphosphine oxide all underwent deoxygenation when cocondensed with chromium atoms (eq 3 and 4). However, the latter deoxygenation occurred in relatively low yield, and comparable results could be realized with preformed chromium surfaces. Since phosphorus-oxygen bonds are considerably stronger than sulfur-oxygen or nitrogen-

oxygen bonds, less efficient deoxygenation is to be expected. Lagowski has obtained bis(η^6 -2,6-dimethylpyridine)chromium(0) from the reaction of 2,6-dimethylpyridine with chromium atoms.²² However, we did not observe any evidence for the formation of this species from 2,6-dimethylpyridine *N*-oxide. Similarly, volatile bis(arene)chromium complexes were not formed subsequent to the deoxygenation of *cis*-stilbene oxide and allylbenzene oxide (Table II).

Although we failed to observe volatile deoxygenation products from diisopropyl ether, decyl methyl ether, or dibenzyl ether, carbon atoms have been observed to deoxygenate cyclic ethers.¹⁹ The desulfurization of benzyl sulfide upon chromium atom cocondensation (eq 9) is probably a consequence of the weaker carbon-sulfur bond strength. Skell has reported that cyclic thioethers are desulfurized and dehydrosulfurized when reacted with singlet carbon atoms,¹⁹ and the desulfurization of thiophenes upon cocondensation with chromium and iron has been noted.²³

Recently, Billups and Margrave²⁴ have found that the cocondensation of dimethyl ether with calcium, barium, strontium, or iron, followed by removal of excess dimethyl ether and hydrolysis of the reactor residue, results in the formation of appreciable quantities of C₁-C₈ hydrocarbons. Together with D₂O quench results, it is obvious that the cleavage of C-O and numerous C-H bonds is occurring. We did not observe analogous hydrocarbon products when the reactor residue from a decyl methyl ether/chromium cocondensation was quenched with water. Therefore it may be that chromium is not an effective metal for this hydrolytic deoxygenation mode.

Although reductive coupling of cycloheptanone and cyclohexanone does take place upon metal atom cocondensation (eq 7), the yields were extremely low (Table III). Therefore we hesitate to ascribe any of the observed reactions to atomic metal. Cycloheptanone is a good probe for the formation of the carbene deoxygenation product cycloheptylidene, since subsequent formation of cycloheptene and norcarane is known to occur.²⁵ However, neither of these compounds were detected. Interestingly, the cocondensation of magnesium atoms with cycloheptanone does yield cycloheptene and norcarane.²⁶ A critical difference may be that magnesium atoms are singlets in the ground state, whereas first-row transition-metal atoms are not. Singlet-state carbon atoms also deoxygenate ketones to carbenes.²⁷ Finally, as was noted with magnesium atoms and ketones,²⁶ we also observed the formation of aldol products (Table III). It seems reasonable that an initially formed 1,2-diol alkoxide (cf. eq 2) could serve as the requisite base. Since enones are produced in most instances, liberating H₂O, the formation of 1,2-diols does not necessarily require the adventitious introduction of H₂O during workup.

Most heteroatom-oxygen double bonds are weaker than carbon-oxygen double bonds. Therefore it is understandable that nitrosoarenes undergo facile deoxygenation upon chromium atom cocondensation (eq 9 and 10). Since preformed chromium surfaces afford little or no deoxy-

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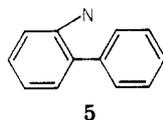
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genation, chromium atoms are implicated as active species. However, the origin of coupled products in these reactions is not unambiguous. In solution, nitrosobenzene monomer (blue green) exists in equilibrium with the colorless dimer 2 (eq 9).²⁸ Therefore the formation of azoxybenzene could occur via nitrene or nitrenoid intermediates, or by simple deoxygenation of the nitrosobenzene dimer. Azobenzene could form by either of these paths, or along the lines of eq 2. The nitrene 5 has been previously generated from



numerous precursors²⁹ and invariably yields carbazole (3, eq 10) as the major product. Therefore the formation of 3 from 2-nitrosobiphenyl and chromium atoms (eq 10) rigorously establishes that nitrene or nitrenoid intermediates can be formed under the reaction conditions. Hence we believe that nitrene or nitrenoid species are precursors—but not necessarily exclusive precursors—to the coupled products in eq 8 and 9.

Arylamines (eq 8–10) are commonly observed decomposition products of aryl nitrenes; phenyl nitrene has been shown to abstract hydrogen from a variety of sources.³⁰ Since nitrosoarenes thermally disproportionate to nitroarenes and azoxyarenes,³¹ the absence of 2-nitrobiphenyl in eq 10 is significant. Streitwieser has noted that nitroarenes undergo similar reductive deoxygenation reactions when treated with uranocenes.³² However, 2-nitrobiphenyl yielded only 2,2'-azobiphenyl and 2-aminobiphenyl; carbazole was not detected.

Although cyclohexyl isocyanide is not formed when cyclohexyl isocyanate is cocondensed with metal atoms, some type of decarbonylation or deoxygenation appears to occur (eq 11). Although H₂O was not added during the extraction of products from the reactor residue, the primary nonpolymeric products seem to have undergone hydrolysis. The mechanism of product formation was not probed, except to note that isocyanate decomposition did not occur when introduced into the reactor in the presence of a hot tungsten filament.

The desulfurization of isothiocyanates to isocyanides (Table IV) proceeds in roughly the same yield (based upon metal) as epoxide deoxygenation. Previously, scattered reports have appeared on the conversion of isothiocyanates to isocyanides: photolysis³³ and reactions with triethylphosphine,³⁴ triphenyltin hydride,³⁵ and copper³⁶ have all been reported to effect desulfurization. Notably, copper atoms did not desulfurize cyclohexyl isothiocyanate. Based upon our success with transition metal atoms, we attempted to develop a low-valent transition metal reductant

for preparative isothiocyanate desulfurization. None of the reagents surveyed (TiCl₄/Mg, TiCl₃/LiAlH₄, WCl₆/*n*-BuLi, NiCl₂/K, etc.) afforded appreciable yields of isocyanide product.³⁷

Conclusion

Deoxygenation and desulfurization constitute two important fundamental reactivity modes of organic molecules with metal atoms. Of the five metals studied most intensively (Ti, V, Cr, Co, Ni), nickel consistently affords the lowest yields of volatile products. When the direct abstraction of oxygen from a molecule produces another stable molecule and the bonds being broken are not too strong (epoxides, amine oxides, sulfoxides), deoxygenation occurs readily. Since most cyclopropanes are not cleaved by metal atoms (cyclopropylbenzene and chromium afford a bis(arene)chromium complex),¹⁶ strain cannot be the sole driving force for the reactions of epoxides. While nitrogen-oxygen multiple bonds can be cleaved by chromium atoms, affording nitrene or nitrenoid intermediates, carbenes are not generated from cyclic ketones. Oxygen is not directly abstracted from simple ethers by chromium; however, the recent Billups-Margrave studies²⁴ have demonstrated other possible reaction modes involving C-H and C-O bond insertion. When direct comparisons are made, metal atoms effect desulfurization more readily than deoxygenation. Thus thioethers undergo desulfurization, and isothiocyanates (but not isocyanates) can be converted to isocyanides.

This study has shown that metal atoms are chemoselective reducing agents. While some similarities with solution-phase low-valent transition-metal reductants are evident (e.g., eq 1), there are some important contrasts (e.g., eq 2). Consequently, useful synthetic applications can be envisioned for reagents which are capable of releasing metal atoms into solution.

Experimental Section

General Procedures. NMR spectra were obtained on Varian T-60 and CFT-20 spectrometers. All chemical shifts are relative to a (CH₃)₄Si internal standard. IR spectra were obtained on a Perkin-Elmer 521 spectrometer. Mass spectra were obtained on an AEI MS9 instrument. Gas chromatographic analyses were performed on either DC-710 or Carbowax 20M columns; in all cases, yields were corrected for detector response factors. Melting points reported herein are not corrected.

Organic Substrates. Cyclohexene oxide and an authentic sample of 1,3-cyclohexadiene were purchased from Aldrich Chemical Co. *cis*-Stilbene and *cis*-4-decene were obtained from Chemical Samples Corp. Allylbenzene and 1-methylcyclopentene were purchased from Aldrich. Epoxides were prepared from these olefins with *m*-chloroperbenzoic acid via standard procedures.³⁸

2,6-Dimethylpyridine and 2,6-dimethylpyridine *N*-oxide were obtained from Aldrich Chemical Co. Triethylphosphine was obtained from Orgmet, Inc. Triethylphosphine oxide was prepared by air oxidation of triethylphosphine.

Diisopropyl ether, dibenzyl ether, benzyl sulfide, and *trans*-stilbene were obtained from Aldrich. Decyl methyl ether was prepared from decanol and excess methyl iodide via (*n*-C₄H₉)₄N⁺HSO₄⁻ phase-transfer catalysis at 40–45 °C.³⁹ Bibenzyl was purchased from Eastman. Cyclohexanone, cycloheptanone, norcarane, and cycloheptene were obtained from Aldrich. Authentic samples of bicyclohexyl-1,1'-diol and cyclohexylidene-

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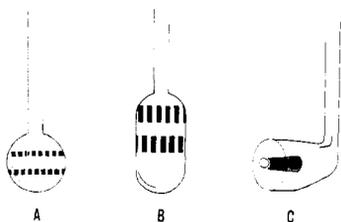


Figure 1. Inlet tips for reactor.

cyclohexane (obtained as a byproduct) were prepared by Corey's method.⁴⁰

Nitrosobenzene, 2-nitrobiphenyl, 2-aminobiphenyl, and carbazole were purchased from Aldrich. Azobenzene and azoxybenzene were obtained from Eastman. 2-Nitrosobiphenyl was prepared by a published route,⁴¹ which in our hands also afforded substantial amounts of 2-azoxybiphenyl (mp 159–160 °C after ethanol recrystallization)⁴² as byproduct. Isocyanates, isocyanides, and *N,N'*-dicyclohexylurea were purchased from Aldrich; isothiocyanates were obtained from either Aldrich or Trans World Chemicals.

Metal Atom Reactor. The general features of the metal atom reactor employed in this study have been recently described.¹⁶ It is based upon designs previously published by Skell, Timms, and Klabunde.^{10–14}

Depending upon the compound and the quantity employed, three different inlet tips were used to direct organic substrates onto the walls of the reactor (refer to Figures 1 and 2, ref 16). For most experiments, the standard design inlet tip A (Figure 1) was utilized. For experiments with 2-nitrosobiphenyl, inlet tip B was used. The substrate was loaded directly into the cavity at the bottom of inlet tip B, which was wrapped with Nichrome wire. Resistive heating with an externally controlled Variac was then used to evaporate 2-nitrosobiphenyl onto the walls of the reactor. Numerous organic compounds of low volatility (triphenylene, hexaphenylbenzene, etc.) can be conveniently cocondensed with metal atoms by using this inlet tip.

Several cocondensations of epoxides were conducted in a "micro" reactor fitted with inlet tip C. Organic vapors were concentrated onto a small portion of the reactor wall by shaping the inlet in the form of a "horn". Metals were evaporated onto the same area from a filament (pure wire or coated tungsten rod) running through the horn. The filament was supported by two stainless-steel electrodes which buttressed each side of the horn. A semicircular glass shield around the rear of the filament prevented direct contact with the incoming organic vapors.

While this "micro" inlet tip worked well for some compounds, certain problems are associated with it. For substrates with bp <100 °C (760 mm), the matrix tended to diffuse during the cocondensation because of the high heat flux directed onto a small portion of the reactor walls.

Chromium-coated tungsten rods (2 in. × 0.05 in. diameter, coated to a diameter of 0.080 in.) were obtained from GTE Sylvania. Tungsten rods coated with Ti, V, Ni, Fe, and Co were obtained from Materials Research Corporation. Alumina-coated tungsten spiral crucibles (ca. 0.5-mL capacity) were obtained from GTE Sylvania.

Previously described titrimetric experiments¹⁶ indicated that 76% of the metal evaporated from a filament in the conventional reactor reaches the matrix zone. Similar experiments in the "micro" reactor show that 40% of the evaporated metal reaches the matrix zone. These correction factors were applied to all experimental data.

Epoxide Cocondensations. For the experiments summarized in Table I, cyclohexene oxide was introduced into the "micro" reactor (tip C, Figure 1) from a –10 to –20 °C ligand reservoir.¹⁶ Metal atoms were simultaneously evaporated from coated tungsten rods which had been weighed prior to the reaction. After co-

condensation (0.5–1.0-h duration), the matrix was allowed to warm to room temperature under a static vacuum over a 1-h period. Volatiles (bp ≤200 °C (760 mm)) were then pumped into a U-tube and weighed. The metal filament was reweighed, and the appropriate correction factor (vide supra) was applied to determine the amount of metal reaching the reactor zone.

The volatiles from the U-tube were analyzed neat by ¹H NMR. The ratios of cyclohexene oxide, cyclohexene, 1,3-cyclohexadiene, and benzene were determined by integration of characteristic resonances at δ 2.92, 5.58, 5.76, and 7.25. Product identities were confirmed by GC analysis. Data are summarized in Table I.

cis-Stilbene oxide was introduced into the reactor (conventional; tip A, Figure 1) by heating the ligand reservoir with a heat gun. Chromium was evaporated from a coated rod. After cocondensation and matrix warm-up, a 50 °C oil bath was placed around the reactor and starting material and products were distilled into a U-tube. This mixture was analyzed by GC; results are summarized in Table II. Product identities were confirmed by co-injection with authentic samples.

cis-4-Decene oxide was introduced into the reactor from a 35–40 °C ligand reservoir while chromium was evaporated from a coated rod (quantities: Table II). After matrix warm-up, volatile material (0.9653 g) was pumped into a U-tube. Silica gel column chromatography (pentane solvent) afforded 0.091 g of a mixture of *trans*- and *cis*-4-decene; a 64:36 ratio was established by GC.

Allylbenzene oxide was introduced into the reactor from a 35 °C ligand reservoir while chromium was evaporated from a coated rod (quantities: Table II). After matrix warm-up, volatile material was pumped into a U-tube, weighed, and ¹H NMR and GC analyzed (Table II). No β-methylstyrene was present.

1-Methylcyclopentene oxide was evaporated from a –25 °C ligand reservoir while chromium was evaporated from a coated rod. After matrix warm-up, volatile material was pumped into a U-tube, weighed, and analyzed by ¹H NMR. The yield of 1-methylcyclopentene was determined by integration of the olefinic hydrogen resonance at δ 5.4.

Control Experiments. Using the "micro" inlet, 1.16 mmol (corrected) of chromium was evaporated onto the walls of the reactor. Subsequently, 15.3 mmol (1.50 g) of cyclohexene oxide was evaporated onto the metal film over a 1-h period. The "matrix" was allowed to warm to room temperature under static vacuum over a 1-h period. Volatiles were then pumped into a U-tube, weighed (1.50 g), and shown to contain ≤0.6% cyclohexene by ¹H NMR. No benzene was detected.

Using the "micro" inlet, 1.61 mmol of chromium (corrected) was cocondensed with 14.9 mmol of cyclohexene oxide. Volatiles were pumped directly into a U-tube as the matrix warmed (no 1-h period under static vacuum as above). Analysis by ¹H NMR indicated cyclohexene (1.51 mmol), benzene (0.14 mmol), 1,3-cyclohexadiene (0.05 mmol), and starting cyclohexene oxide (11.55 mmol) to be present.

By use of the "micro" inlet, 14.85 mmol (1.455 g) of cyclohexene oxide was distilled into the reactor over a white-hot but non-evaporating tungsten filament (2.6 V, 92 A—as compared to the 1.9 V, 76 A, used to evaporate chromium from a coated tungsten rod, or 2.9 V, 90 A, used to evaporate titanium from a coated tungsten rod). The "matrix" was allowed to warm as usual and the volatiles (1.369 g) were collected in a U-tube. ¹H NMR analysis indicated this material to be 95.9% cyclohexene oxide, 3.4% cyclohexene, 0.6% 1,3-cyclohexadiene, and 0.1% benzene.

In the conventional reactor, chromium (0.26 mmol, corrected) was evaporated from a coated rod while *cis*-4-decene (1.49 g, 10.6 mmol) was distilled into the reactor from a room-temperature reservoir. After the standard matrix warm-up, volatiles (1.54 g) were collected in a U-tube; GC analysis indicated a 87:13 mixture of *cis*:*trans* 4-decene. No other olefins were present.

2,6-Dimethylpyridine *N*-Oxide Experiments. 2,6-Dimethylpyridine *N*-oxide (11.1 mmol, 1.37 g) was distilled into the reactor (conventional) from a 65–70 °C reservoir while chromium (0.28 mmol, corrected) was evaporated from a coated tungsten rod. After the matrix was warmed to room temperature under a static vacuum over a 1.5-h period, volatiles (1.16 g) were pumped into a U-tube and analyzed by GC; 0.28 mmol of 2,6-dimethylpyridine was present. A green residue remained in the reactor, but no material sublimed when heated to 80 °C (10^{–5} mm).

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An experiment was conducted similar to the one above except that 2,6-dimethylpyridine *N*-oxide (15.0 mmol) was evaporated onto a chromium surface (1.02 mmol). Only 0.003 mmol of 2,6-dimethylpyridine was present in the volatiles by GC.

Dimethyl Sulfoxide Experiments. Dimethyl sulfoxide (21.1 mmol, 1.64 g) was distilled into the reactor (conventional) from a 30–40 °C reservoir while chromium (0.45 mmol, corrected) was evaporated from a coated rod. A red matrix formed, which turned white while warming to room temperature under static vacuum. After 1 h, volatiles (1.68 g) were collected; GC analysis indicated 0.72 mmol of dimethyl sulfide to be present.

An experiment was conducted similar to the one above except that dimethyl sulfoxide (28.1 mmol) was evaporated onto a preformed chromium surface (2.73 mmol). Analysis of the volatiles by GC indicated 0.23 mmol of dimethyl sulfide to be present.

Triethylphosphine Oxide Experiments. Triethylphosphine oxide (17.3 mmol, 2.32 g) was distilled into the reactor (conventional) from a 90–110 °C reservoir while chromium (2.98 mmol, corrected) was evaporated from a coated tungsten rod. After the matrix was allowed to warm for 1 h under static vacuum, a hot-water bath was placed around the reactor and products were distilled into a U-tube (1.25 g). Analysis by GC (Carbowax 20 M, 100–200 °C) indicated 0.37 mmol of triethylphosphine to be present.

An experiment was conducted similar to the one above except that triethylphosphine oxide (17.3 mmol) was condensed onto a preformed chromium surface (3.06 mmol). Product analysis by GC indicated 0.09 mmol of triethylphosphine to be present.

Cocondensation of Diisopropyl Ether with Chromium Atoms. Diisopropyl ether (49.8 mmol, 5.075 g) was distilled into the reactor (conventional) from a –50 to –45 °C reservoir while chromium (0.65 mmol, corrected) was evaporated from a coated tungsten rod. After the matrix was warmed over a 1-h period under static vacuum, volatiles (5.002 g) were pumped into a U-tube. By ¹H NMR, only starting material was present; no 2,3-dimethylbutane had formed.

Cocondensation of Decyl Methyl Ether with Chromium Atoms. Decyl methyl ether (3.68 g, 21.4 mmol) was distilled into the reactor (conventional) from a 55–65 °C reservoir while chromium (0.75 mmol, corrected) was evaporated from a coated tungsten rod. The green brown matrix turned brown upon warming. After 0.5 h under static vacuum, the reactor was immersed in a 50 °C water bath and volatiles were pumped into a U-tube. Water (3 mL, 166.7 mmol) was then distilled onto the reactor residue and allowed to stand for 12 h.

The reactor residue was then extracted with ether and 1,2,4,5-tetramethylbenzene standard added. Analysis by GC failed to indicate the presence of any C₈–C₁₂ aliphatic or olefinic hydrocarbons; less than 0.01% (based upon chromium) of any product would have been easily detected. Similar GC analysis of the U-tube volatiles showed only the presence of decyl methyl ether.

Cocondensation of Dibenzyl Ether with Chromium Atoms. Dibenzyl ether (5.63 g, 28.4 mmol) was distilled into the reactor (conventional) from a ligand reservoir wrapped with heating tape while chromium atoms (1.39 mmol, corrected) were evaporated from a coated tungsten rod. An orange brown matrix formed, which became yellow as it was allowed to warm to room temperature over 1 h under static vacuum. The reactor was removed to a glovebox¹⁶ and extracted with ether. After filtration, ethyl ether was removed from the yellow solution (3.775 g of residue). Dibenzyl ether was then carefully distilled off and found to contain a trace (<0.002 mmol) of bibenzyl by GC. A yellow green powder (0.200 g), mp 64–65 °C (sealed tube), remained. Spectral properties indicated the powder to be bis(η⁶-dibenzyl ether)chromium(0): ¹³C NMR (C₆D₆) 139.4, 128.6, 127.8, 127.6 (uncomplexed arene ring), 88.8, 77.6, 75.2 (complexed arene ring), 73.4, 71.9 (CH₂) ppm; ¹H NMR (C₆D₆) δ 7.10 (m, 5 H), 4.32 (s, 4 H), 4.15 (br s, 5 H); mass spectrum, *m/e* (%) 448 (17), 250 (91), 158 (100).

Cocondensation of Dibenzyl Sulfide with Chromium. Dibenzyl sulfide (45 mmol, 9.69 g) was distilled into the reactor from a ligand reservoir wrapped with heating tape while chromium (2.8 mmol, corrected) was evaporated from a coated rod. A red brown matrix formed, which was allowed to warm to room temperature over 1.3 h under static vacuum. From the reactor residue, 8.36 g of material was sublimed to a cold finger; inside a glovebox,

0.52 g of additional material was obtained by ether and CHCl₃ extraction of the reactor residue. These extracts were principally dibenzyl sulfide and devoid of any bis(arene)chromium(0) complexes by ¹H NMR. The above materials were combined (8.88 g) and shown to contain 0.09 mmol of bibenzyl and 0.17 mmol of *trans*-stilbene by GC. No diphenylacetylene was detected.

Cycloheptanone Experiments. Cycloheptanone (5.0 mL, 4.755 g) was distilled into the reactor (conventional) from a 34–35 °C ligand reservoir while metals (Table III; Cr: coated rod; Co, Ni: W/Al₂O₃ crucible) were being evaporated. After cocondensation (70–75 min), the matrix was allowed to warm to room temperature under static vacuum (1–2 h). Volatiles were pumped into a U-tube and analyzed by GC. Only starting ketone was present; no C₇H₁₄ or C₇H₁₂ products were formed.

The reactor residues were exposed to air and extracted with ether, affording 279 mg (Cr), 135 mg (Co), and 16 mg (Ni) of material. TLC analysis (10% ethyl acetate/hexane) indicated two major products in each case. These were separated by preparative TLC and shown to be cycloheptylidencycloheptane (mass spectrum, *m/e* (16 eV) 192 (M⁺, 93%), 97 (32), 96 (100), 95 (45); ¹H NMR (CDCl₃) δ 2.23 (m, 8 H), 1.52 (m, 16 H)) and 2-cycloheptylidencycloheptanone (mass spectrum, *m/e* (16 eV) 206 (M⁺, 92%), 163 (100); IR (CHCl₃) 1675 (s), 1595 (w) cm⁻¹; 2,4-dinitrophenylhydrazone, mp 145–146 °C (lit.⁴³ mp 144–145 °C)). For isolated product yields see Table III.

Cyclohexanone Experiments. Cyclohexanone (5.0 mL, 4.577 g) was distilled into the reactor (conventional) from a room-temperature ligand reservoir while metals (Table III) were being evaporated. Workup and product analysis were conducted as described above for cycloheptanone. No C₆ hydrocarbon products were formed. TLC (5% CH₃OH in CH₂Cl₂) indicated three principal products in the reaction with chromium. These were separated and shown to be bicyclohexyl-1,1'-diol (by chromatographic and spectroscopic comparison to an authentic sample),⁴⁰ 2,6-bis(1-cyclohexenyl)cyclohexanone (mass spectrum, *m/e* (16 eV) 258 (M⁺, 6%), 192 (19), 178 (82), 176 (100), 174 (77), 149 (68), 148 (70); ¹H NMR (CDCl₃) δ 5.49 (m, 2 H), 2.95 (m, 2 H), 2.5–1.5 (m, 22 H); IR (CD₂Cl₂) 1700 (s), 1566 (sh, m) cm⁻¹; 2,4-dinitrophenylhydrazone, mp 155–157 °C), and 2-(1-hydroxycyclohexyl)cyclohexanone (mass spectrum, *m/e* (16 eV) 196 (M⁺, 1%), 178 (M⁺ – 18, 10%), 98 (100%); IR (CHCl₃) 3465 (m), 1690 (s), 1125 (m) cm⁻¹; positive ferric nitrate test for OH⁴⁴). For isolated product yields see Table III.

Nitrobenzene Experiments. Nitrobenzene (24 mmol, 3.0 g) was distilled into the reactor (conventional) from a 40 °C reservoir while chromium (1.67 mmol, corrected) was evaporated from a coated tungsten rod. After the matrix was allowed to warm for 1 h under static vacuum, the reactor was immersed in a 150 °C oil bath and most of the material, including an orange product, volatilized into a U-tube (1.989 g). The reactor residue was extracted with ether, providing another 0.025 g of products. By GC, the U-tube material was shown to contain nitrobenzene (16.03 mmol), nitrosobenzene (0.015 mmol), azoxybenzene (0.043 mmol), and aniline (0.030 mmol). The reactor extract consisted of aniline (0.020 mmol), nitrobenzene (0.004 mmol), azobenzene (0.040 mmol), and azoxybenzene (0.060 mmol). These product identities were verified by GC and TLC comparisons with authentic samples.

An experiment was conducted similar to the one above except that nitrobenzene (19.5 mmol) was condensed onto a preformed chromium surface (1.07 mmol); only 0.002 mmol of nitrosobenzene (and no other products) could be detected in the recovered volatile material.

Nitrosobenzene Experiments. Nitrosobenzene (28.0 mmol, 3.0 g) was distilled into the reactor (conventional) from a 75–80 °C reservoir, while chromium (2.41 mmol, corrected) was evaporated from a coated tungsten rod. After the matrix was allowed to warm for 1 h under static vacuum, the reactor was immersed in a 60–70 °C water bath, and volatile products were collected in a U-tube over a 3.7-h period (2.2830 g). The reactor residue was extracted with ether and toluene to obtain 0.1304 g of additional material, which was mainly azoxybenzene by GC and

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TLC. Quantitative GC analysis of the U-tube and reactor extract indicated 14.95 mmol of nitrosobenzene, 1.70 mmol of azoxybenzene, 0.33 mmol of azobenzene, and 0.17 mmol of aniline to have been formed.

An experiment was conducted similar to the one above except that nitrosobenzene (18.7 mmol, 2.09 g) was deposited onto a preformed chromium surface (0.51 mmol). The 1.8492 g of recovered volatile material consisted only of nitrosobenzene. From the reactor residue, 0.0027 g of material could be extracted. This was shown by GC to be nitrosobenzene containing a trace of azoxybenzene.

Cocondensation of 2-Nitrosobiphenyl with Chromium Atoms.

The cocondensation of 2-nitrosobiphenyl (14.7 mmol, 2.93 g) with chromium atoms (0.18 mmol, corrected) was conducted by using inlet tip B (Figure 1); the rate of deposition was controlled as described above. After a 1-h matrix warm-up under static vacuum, the reactor was opened and extracted with CH_2Cl_2 , yielding 2.874 g of material. Column chromatography on acidic alumina followed by preparative TLC (10% v/v ethyl acetate/hexane) afforded 2-nitrosobiphenyl (2.665 g, 13.4 mmol, mp 108–109 °C), 2-azoxybiphenyl (0.0316 g, 0.089 mmol, mp 154–157 °C), 2-aminobiphenyl (0.0647 g, 0.383 mmol, mp 42–44 °C), and carbazole (0.0209 g, 0.125 mmol, mp 245–246 °C) in order of elution. Product identities were established by TLC and mixture melting point comparisons with authentic samples. No 2-nitrobiphenyl or 2-azobiphenyl⁴⁵ was present.

An experiment was carried out as described above except that 5.42 mmol of 2-nitrosobiphenyl was cocondensed with 0.69 mmol (corrected) of chromium atoms. Matrix extraction with CH_2Cl_2 as described above, followed by silica gel preparative TLC, afforded 2-nitrosobiphenyl (0.7400 g, 4.04 mmol), 2-azoxybiphenyl (0.0477 g, 0.14 mmol), 2-aminobiphenyl (0.0081 g, 0.05 mmol), and carbazole (0.0316 g, 0.19 mmol) as the only products.

Cyclohexyl Isocyanate Experiments. Cyclohexyl isocyanate (5.0 mL, 4.90 g, 39.2 mmol) was introduced into the reactor (conventional) from a 20 °C ligand reservoir while chromium (1.86 mmol, corrected) was evaporated from a coated rod. After matrix warm-up under static vacuum (1.5 h), volatiles (3.852 g, 30.8 mmol) were pumped into a U-tube and shown by GC and NMR to be exclusively starting material. The reactor residue was extracted with ether, acetone, methanol, and methanol- CH_2Cl_2 , affording 0.659 g of material. Insoluble residue (0.497 g) remained. After phthalate plasticizer removal, components of the ether extract were separated by preparative TLC. All other extracts were combined and the components similarly separated. The two most abundant products were found to be *N,N'*-dicyclohexylurea (0.095 g, 0.42 mmol; mass spectrum, *m/e* 224 (M^+); identified by TLC, melting point, and IR comparisons with a commercial sample) and the imide **4** (0.0445 g, 0.13 mmol). **4**: mp 202–203 °C after hexane recrystallization; ¹H NMR (CDCl_3) δ 1.27–1.88 (m, 30 H), 3.67 (br m, 3 H), 6.62–6.75 (br m, 2 H); IR (Nujol) 3270 (NH), 1682 and 1623 (C=O) cm^{-1} ; mass spectrum (16 eV), *m/e* 349 (M^+ , 4%), 268 (12), 252 (3), 224 (44), 186 (31), 143 (28), 126 (12), 98 (100).

Cyclohexyl isocyanate (3.0 mL, 2.94 g, 23.5 mmol) was introduced into the reactor from a 20 °C ligand reservoir while cobalt (0.93 mmol, corrected) was evaporated from a W/ Al_2O_3 crucible. Workup as described above yielded 2.406 g (19.2 mmol) of starting material and 0.238 g of ether- and ethanol-soluble material from the reactor residue. One major product was present by TLC; several acetone recrystallizations yielded 0.086 g (0.33 mmol) of *N,N'*-dicyclohexylurea, which was spectroscopically identical (¹H NMR ($\text{CF}_3\text{CO}_2\text{H}$) δ 1.2–2.2 (m, 20 H), 3.82 (br s, 2 H), 8.23 (br s, 2 H)) with an authentic sample prepared from oxalyl chloride and cyclohexylamine. The melting point after benzene/cyclohexane/ethanol recrystallization was 273–274 °C (lit.⁴⁶ mp 273 °C); mmp 272–274 °C.

Cyclohexyl isocyanate (3.0 mL, 2.94 g, 23.5 mmol) was cocondensed with nickel (0.25 mmol, corrected) as described above for cobalt. When volatiles were distilled into the U-tube, starting material (2.633 g, 21.0 mmol) was accompanied by some *N,N'*-dicyclohexylurea. The reactor was extracted with ether and

acetone. After purification by preparative TLC and recrystallization, combined yields of *N,N'*-dicyclohexylurea (0.110 g, 0.492 mmol) and *N,N'*-dicyclohexylureamide (0.060 g, 0.238 mmol) were obtained.

In a control experiment, cyclohexyl isocyanate (4.90 g) was condensed into a reactor containing a hot tungsten rod (1.6 V, 30 A) in place of the normal metal atom source. No reaction occurred; starting material was recovered (4.848 g) unchanged (GC, TLC, and NMR).

Cocondensation of Cyclohexyl Isothiocyanate and Chromium. Cyclohexyl isothiocyanate (22.4 mmol, 3.17 g) was introduced into the reactor from a 45 °C ligand reservoir while chromium (2.1 mmol, corrected) was evaporated from a coated rod. After the usual matrix warm-up, some volatiles were pumped into a U-tube (2.360 g); the reactor residue was extracted with CH_2Cl_2 , filtered, and passed through silica gel to provide 0.404 g of additional material. Quantitative GC analysis indicated the U-tube material to contain 2.281 g (16.15 mmol) of starting material and 0.071 g (0.65 mmol) of cyclohexyl isocyanide. The extract contained 0.302 g (2.14 mmol) of starting material and 0.101 g (0.92 mmol) of cyclohexyl isocyanide. Combined yield data are given in Table IV.

Cocondensation of Cyclohexyl Isothiocyanate and Vanadium. Cyclohexyl isothiocyanate (22.4 mmol, 3.17 g) was introduced into the reactor from a 40–43 °C ligand reservoir while vanadium (1.26 mmol, corrected) was evaporated from a coated rod. After the usual matrix warm-up, volatiles were pumped into a U-tube (2.92 g). Analysis by GC indicated 2.830 g (20.0 mmol) of starting material and 0.065 g (0.6 mmol) of cyclohexyl isocyanide to be present.

Cocondensation of Cyclohexyl Isothiocyanate and Copper. Cyclohexyl isothiocyanate (15.0 mmol, 2.11 g) was distilled into the reactor while copper (1.40 mmol, corrected) was evaporated from a W/ Al_2O_3 crucible. The red brown matrix was allowed to warm to room temperature over a 1-h period under static vacuum. Volatiles (1.88 g) were then pumped into a U-tube and found to contain only starting material by GC. The reactor residue was extracted with ether, affording an additional 0.133 g of material; no cyclohexyl isocyanide was present by GC, but the characteristic isocyanide odor was noted.

Cocondensation of Phenyl Isothiocyanate and Chromium. Phenyl isothiocyanate (3.47 g, 25.6 mmol) was distilled into the reactor from a 36–40 °C reservoir while chromium (2.45 mmol) was evaporated from a coated tungsten rod. After the matrix was warmed to room temperature under static vacuum over a 1.3-h period, some volatiles (2.90 g) were pumped into a U-tube. Ether and acetone extraction of the reactor residue afforded another 0.379 g of material. No phenyl isocyanide was present in the volatiles by GC. The residue extract contained 0.116 g (1.12 mmol) of phenyl isocyanide, 0.013 g (0.12 mmol) of phenyl cyanide, and 0.237 g (1.75 mmol) of starting material by GC.

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Registry No. 1, 286-20-4; 2, 35506-28-6; 3, 86-74-8; 4, 73728-34-4; Ti, 7440-32-6; V, 7440-62-2; Cr, 7440-47-3; Co, 7440-48-4; Ni, 7440-02-0; *cis*-stilbene oxide, 1689-71-0; *cis*-4-decene oxide, 60788-60-5; allylbenzene oxide, 4436-24-2; 1-methylcyclopentene oxide, 16240-42-9; cycloheptanone, 502-42-1; cyclohexanone, 108-94-1; cyclohexyl isothiocyanate, 1122-82-3; phenyl isothiocyanate, 103-72-0; 2,6-dimethylpyridine *N*-oxide, 1073-23-0; dimethyl sulfoxide, 67-68-5; triethylphosphine oxide, 597-50-2; dibenzyl ether, 103-50-4; nitrobenzene, 98-95-3; 2-nitrosobiphenyl, 21711-71-7; cyclohexyl isocyanate, 3173-53-3; cyclohexene, 110-83-8; benzene, 71-43-2; 1,3-cyclohexadiene, 592-57-4; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0; *cis*-4-decene, 19398-88-0; *trans*-4-decene, 19398-89-1; allylbenzene, 300-57-2; 1-methylcyclopentene, 693-89-0; cycloheptylidene-cycloheptane, 51175-34-9; 2-cycloheptylidene-cycloheptanone, 7027-33-0; bicyclohexyl-1,1'-diol, 2888-11-1; 2-(1-hydroxycyclohexyl)cyclohexanone, 28746-99-8; 2,6-bis(1-cyclohexenyl)cyclohexanone, 24344-21-6; cyclohexyl isocyanide, 931-53-3;

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phenyl isocyanide, 931-54-4; phenyl cyanide, 100-47-0; 2,6-dimethylpyridine, 108-48-5; dimethyl sulfide, 75-18-3; triethylphosphine, 554-70-1; bis(η^6 -dibenzyl ether)chromium (0), 67775-55-7; 2-cycloheptylidencycloheptanone-2,4-DNP, 73728-35-5; 2,6-bis(1-

cyclohexenyl)cyclohexanone-2,4-DNP, 73728-36-6; nitrosobenzene, 586-96-9; aniline, 62-53-3; azobenzene, 103-33-3; azoxybenzene, 495-48-7; 2-azoxybiphenyl, 7334-10-3; 2-aminobiphenyl, 90-41-5; *N,N'*-dicyclohexylurea, 2387-23-7; *N,N'*-dicyclohexyloxamide, 3299-64-7.

Nickel-Catalyzed Conjugate Addition of Alkynyl Groups to α,β -Unsaturated Ketones

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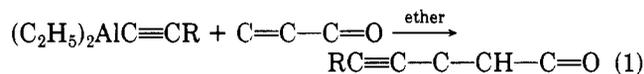
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The complex formed by reaction of $\text{Ni}(\text{acac})_2$ and DiBAH (1:1) catalyzes conjugate addition of dialkylaluminum acetylides to α,β enones; on hydrolysis, 3-alkynyl ketones are produced in high yield. Through this procedure conjugate addition of alkynyl groups to either *S*-cis or *S*-trans enones can be effected. This procedure is the first one which permits conjugate addition of terminal alkynyl units to ordinary *S*-trans enones. In cases where more than one stereochemical outcome is possible, conjugate addition of alkynyl units gives only one of these. Only 1,4-addition is observed and this only of the alkynyl unit. Complications arising from oxygen substitution in the alkynyl side chain are described.

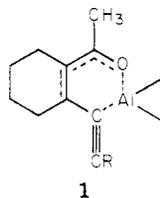
The conjugate addition of an alkynyl group to an α,β -unsaturated ketone has been a formidable synthetic challenge. Organocuprates, the most commonly used reagents for 1,4-addition of alkyl and alkenyl groups to α,β enones, cannot be employed in alkylation reactions owing to the tenacity with which copper binds alkynyl ligands.¹ In fact, this inability of cuprates to transfer alkynyl groups has been used to advantage by Corey and Beames.² By the use of a mixed cuprate complex, $(\text{RC}\equiv\text{C})\text{R}_t\text{CuLi}$, in which R_t represents the group to be transferred, they were able to circumvent the necessity of wasting one unit of the group R_t ; in each case studied, where R_t = alkyl or alkenyl, the alkynyl group was never transferred.

Acetylenic alanes conjugately add their alkynyl units to α,β enones but only under certain circumstances. If the α,β -unsaturated ketone is able to achieve an *S*-cis conformation, it has been found that reaction 1 will then



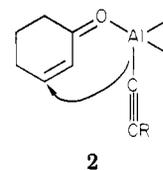
R = alkyl or phenyl

proceed in fair to excellent yield.³ Cyclic ketones in which the enone system is rigidly constrained to a transoid geometry, such as 2-cyclohexenone, react with the alane reagent to give the tertiary carbinol (80–85%) derived from 1,2- rather than 1,4-addition of the acetylenic unit. A reasonable explanation for this reactivity mode involves the necessity for a six-membered transition state for conjugate addition (1). In cases involving transoid enones



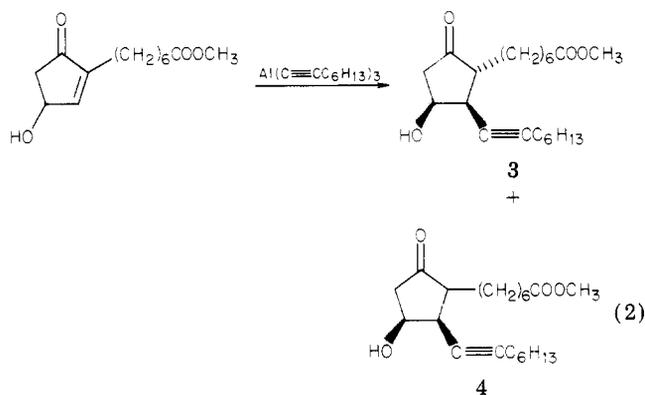
1

(e.g., cyclohexenone) geometrical restraints prohibit 1,4-addition, so that 1,2-addition occurs instead (2).



2

In their investigations into the application of 1,4-addition reactions to the synthesis of prostaglandins, Pappo et al.⁴ were able to perform reaction 2 on a fixed *S*-trans



enone. Compounds 3 and 4 were obtained in approximately a 1:2 ratio. The fact that the entering octynyl group added *cis* to the hydroxy function indicates participation of that group in the 1,4-addition process by way of a five-membered cyclic intermediate analogous to structure 1. Blockage of the hydroxy function by a tetrahydropyranyl group prevented reaction with the aluminum reagent. Pappo and co-workers⁵ used this method of conjugate addition to obtain 11-epiprostaglandin derivatives in 40% yield (reaction 3).

The Pappo group⁶ also demonstrated that a trialkynyl boron derivative would conjugatively add one of its alkynyl groups to an enone able to achieve an *S*-cis conformation. The following reaction proceeded to give adduct 5 in 48%

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