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(3) (a) Reported at the meeting of the Japanese Society of Agricultural Chemistry, Kyoto, Japan, April 1976. (b) **Note Added in Proof.** A synthesis of **2** (diastereoisomeric mixture, mp 40–41 °C) has now also been reported by Professor Ishii's group along with data showing biological activity equivalent to that of the natural pheromone but greater than that of **1**: R. Nishida, T. Sato, Y. Kuwahara, H. Fukami, and S. Ishii, *Agric. Biol. Chem.*, **40**, 1407 (1976).

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(6) In our experience, bioassays conducted with either American cockroach antennae[1] or male German cockroach antennae[2] give comparable results.

(7) Although our test results on synthetic **1** are in accord with those in ref 2a, which noted "distinct activity [for both natural **1** and synthetic **1**] at a concentration of 50 μg/ml" in CCl_4 toward "sexually mature males which had been segregated from females for 1 to 2 weeks after their adult emergence", apparently higher activities are recorded in ref 2b. In the latter report, 50% response to synthetic **1** at 1.7 μg/ml ("3.7×10^{-9} mol/ml") and to 3-methyl-2-heneicosanone at 22.4 μg/ml ("6.9×10^{-8} mol/ml") was indicated for males "segregated from females for 12–13 days after their adult emergence".

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(11) Prepared in 68% overall yield by alkylation of 1,6-dibromohexane (3 equiv) with the NaH-generated enolate (1 equiv) of ethyl acetoacetate in benzene–dimethylformamide (5:1) at 55–60 °C, followed by hydrolysis–decarboxylation at 25–30 °C in 48% HBr–acetic acid (1:1) for 40 h; bp 83–85 °C (0.01 mm).

Selective Reduction of Sulfoxides[1]

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Sulfoxides are important intermediates in a variety of synthetic transformations. The successful application of these procedures generally requires the removal of the residual sulfoxide moiety and a number of processes have been devised for achieving such transformations. Ostensibly, one of the simplest of these involves the reduction of the sulfoxide to a sulfide which is then further reduced by treatment with Raney nickel or a reducing metal system such as lithium in liquid ammonia or amine.

The mildest and therefore the most desirable procedures for effecting the reduction of sulfoxides to sulfides involve either their prolonged treatment with triphenylphosphine in refluxing carbon tetrachloride,[2] reaction with titanium(III),[3] or their conversion to an alkoxysulfonium salt, which in turn is reduced by reaction with borohydride[4a] or (more selectively) cyanohydride borate.[4b] Each of these procedures possess disadvantages: the former two have limited selectivity, the latter are inconvenient at best.

We wish to report that the reaction of sulfoxides with various complex ions of molybdenum(II), -(III), and tungsten(III) provides a procedure for the reduction of a sulfoxide to the corresponding sulfide that is facile, efficient, and highly selective. This procedure seems applicable to the reduction of a broad spectrum of sulfoxides under mild conditions. Although water is generally a good solvent, the use of methanol as a solvent or cosolvent resulted in improved yields in those instances where (1) the sulfoxide has only a very limited solubility in water or (2) the complex ion is relatively unstable in neutral water as, for example, are salts of octachlorodimolybdenum(II) ion, $Mo_2Cl_8^{4-}$.

Numerous reagents are capable of effecting deoxygenations of various organic substrates. Most of these are not specific. Thus, for example, phosphites and phosphines, two of the most commonly employed deoxygenating agents, will reduce a variety of functional groups including nitrile oxides to nitriles,[6] epoxides to olefins,[7] and certain alkyl halides to the corresponding hydrocarbon. In addition, these reagents also react in less well-defined ways with *N*-oxides, nitro, nitroso, and related functional groups.[8] In contrast, the reduction of sulfoxides to sulfides by the reagents reported here appears to be highly specific. Thus, organic halides (*n*-octyl iodide and benzotrichloride), sulfones, phosphine oxides, epoxides (cyclohexene oxide), ketones, (including *α*,*β*-unsaturated ketones), esters, nitriles, and nitro compounds (nitrobenzene) can all be recovered unchanged under the reduction conditions outlined in Table I. It is clear from the results presented that these reagents afford a mild, efficient, and highly selective procedure for the reduction of sulfoxides.

Sharpless and co-workers[9] have studied the deoxygenation of epoxides, aldehydes, and ketones using lower valent tungsten complexes of an undefined nature. The mechanism(s) of these conversions as well as the reduction of sulfoxides by $Mo_2Cl_8^{4-}$, $Mo_2Cl_8H^{3-}$, $MoCl_6^{3-}$, and $W_2Cl_9^{3-}$ is still unclear. However, it is reasonable to assume that the successful utilization of the lower valent complexes of titanium, molybdenum, and tungsten in effecting the deoxygenation of certain organic molecules is in substantial part a consequence of the unusually high thermodynamic stability of titanium–, molybdenum–, and tungsten–oxo bonds.[10,11]

Experimental Section[14]

Tripotassium ennachloroditungstate(III),[5] $K_3W_2Cl_9$, pentaammonium nonachlorodimolybdenum(II) monohydrate,[12] $(NH_4)_4Mo_2Cl_8 \cdot NH_4Cl \cdot H_2O$, and tricesium 1,1,1,2,2,2-hexachloro-*μ*-(hydrido)bis-*μ*-(chloro)dimolybdenum(III),[13] $Cs_3Mo_2Cl_8H$, were prepared according to literature procedures. Tripotassium hexachloromolybdenum(III), K_3MoCl_6, was obtained from Climax Molybdenum.

Procedures for Reduction. Similar procedures were used to carry out the reductions for all the sulfoxides examined. Representative procedures for each sulfoxide follow.

Reduction of Diphenyl Sulfoxide Using $K_3W_2Cl_9$. Tripotassium ennachloroditungstate(III) (1.40 g, 1.74 mmol) was placed in a 50-ml flask equipped with a condenser and containing a Teflon-coated stirrer bar, 10 ml of water, and 1 ml of methanol. Diphenyl sulfoxide (0.250 g, 1.26 mmol) and a known amount of hexadecane (GLC internal standard) were added and the flask heated at 60 °C with stirring for 3 h under a static head of nitrogen. Additional water (15 ml) was added and the resulting mixture extracted with three 10-ml portions of chloroform. The combined organic extracts were dried ($MgSO_4$), gravity filtered, and analyzed by GLC.

Reduction of Di-*n*-butyl Sulfoxide with $(NH_4)_4Mo_2Cl_8 \cdot NH_4Cl \cdot H_2O$. In a typical experiment, 1.12 g (1.80 mmol) of pentaammonium ennachlorodimolybdenum(II) monohydrate was placed in a 50-ml flask containing a Teflon-coated stirrer bar. Methanol (10 ml) was added along with 0.260 g (1.61 mmol) of di-*n*-butyl sulfoxide. The flask was equipped with a condenser stoppered with a rubber septum and flushed with nitrogen. The resulting mixture was stirred under a static head of nitrogen for 2 h at 50 °C. Upon cooling to room temperature, 0.180 g of tridecane (GLC internal standard) was added. Water (25 ml) was added and the resulting mixture extracted with three 5-ml portions of chloroform. The combined extracts were dried ($MgSO_4$) and analyzed by GLC.

Reduction of Benzyl Methyl Sulfoxide Using $Cs_3Mo_2Cl_8H$. Into a 50-ml flask equipped with condenser capped with a rubber septum and containing a Teflon-coated stirrer bar was placed benzyl methyl sulfoxide (0.250 g, 1.61 mmol) and $Cs_3Mo_2Cl_8H$ (1.58 g, 1.80 mmol). The contents of the flask were flushed with nitrogen before adding

Table I. Reaction of Sulfoxides and Related Substrates with $W_2Cl_9{}^{3-}$, $Mo_2Cl_8{}^{4-}$, $Mo_2Cl_8H^{3-}$, and $MoCl_6{}^{3-}$

		Sulfide, %^{a}			
Registry no.	Substrate	$K_3W_2Cl_9{}^b$	$(NH_4)_4Mo_2Cl_8\cdot NH_4Cl\cdot H_2O^c$	$Cs_3Mo_2Cl_8H^d$	$K_3MoCl_6{}^e$
68-68-5	Dimethyl sulfoxide	$100_3{}^f$	$75_2{}^f$	$74_2{}^f$	$47_2{}^f$
2168-93-6	Di-*n*-butyl sulfoxide	95_3	90_{18}	91_{18}	76_{18}
1193-82-4	Phenyl methyl sulfoxide	92_3	94_2	95_2	90_{72}
824-86-2	Benzyl methyl sulfoxide	92_3	72_2	92_{18}	70_{72}
19093-37-9	Allyl phenyl sulfoxide	88_3	59_{18} (63_{72})	54_{18} (60_{72})	54_{18}
4170-69-8	Isopropyl phenyl sulfoxide	97_3	94_{18}	91_{18}	72_{18}
945-51-7	Diphenyl sulfoxide	99_3	97_{22}	99_{72}	79_{72}
33840-74-3	α-Phenylsulfoxyl acetone	95_3	62_{48}	65_{48} (65_{72})	66_{72}
4381-25-3	Phenyl methyl sulfoximine	14_3	56_2	7_2	2_{72}
67-71-0	Dimethyl sulfone	$<1_6$	$<1_{72}$	$<1_{72}$	$<1_{72}$

[a] Subscript denotes reaction time (h). Unless otherwise indicated yields were determined by quantitative vapor phase chromatography and are based on sulfoxide. [b] See ref 5; reaction solvent H_2O-CH_3OH (11:1). [c] See ref 11; reaction solvent CH_3OH. [d] See ref 12; reaction solvent H_2O-CH_3OH (5:1). [e] Obtained from Climax Molybdenum; reaction solvent H_2O-CH_3OH (5:1). [f] Dimethyl sulfide was determined gravimetrically as its mercuric chloride complex: W. F. Faragher, J. C. Morell, and S. Comay, *J. Am. Chem. Soc.*, **51**, 2728 (1929).

10 ml of methanol. The resulting mixture was heated at 50 °C for 18 h, then allowed to cool before adding a known amount of tridecane (GLC internal standard). Water (25 ml) was added, the resulting mixture extracted with three 5-ml portions of chloroform, and the combined extracts dried ($MgSO_4$) and analyzed by GLC.

Reduction of Dimethyl Sulfoxide with K_3MoCl_6. Into a three-necked, 100-ml flask was placed a Teflon-coated magnetic stirrer bar, 1.29 g (3.22 mmol) of tripotassium hexamolybdate, and 30 ml of a 5:1 water–methanol mixture. A condenser was attached. The condenser and the remaining side arms were stoppered with rubber septums and the system purged briefly with nitrogen before injecting dimethyl sulfoxide (0.155 g, 2.00 mmol) by syringe. With vigorous stirring the resulting mixture was heated at 60 °C. Throughout the course of the reaction a slow stream of nitrogen was passed over the reaction mixture and allowed to ebullate through a 0.125-in. Teflon tube that terminated in 75 ml of saturated aqueous solution of mercuric chloride. When no further precipitation was observed (~2 h), the resulting solid was collected by suction filtration and dried in vacuo over P_2O_5 to a constant weight. The yield of dimethyl sulfide was determined gravimetrically as $[(CH_3)_2S]_2(HgCl_2)_3$ (see Table I, footnote *f*).

Registry No.—$W_2Cl_9{}^{3-}$, 23403-17-0; $(NH_4)_4Mo_2Cl_8\cdot NH_4Cl$, 40902-25-8; $Cs_3Mo_2Cl_8H$, 24436-25-7; K_3MoCl_6, 13600-82-3.

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Atomic Oxygen. 7. Reactions of Alkynes with Oxygen (^3P) Atoms[1]

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The reactions of oxygen atoms with alkynes can produce a wide variety of intermediates, including oxirenes, 1,3-biradicals, ketocarbenes, and excited ketenes. The existence of these intermediates is not experimentally reflected in previous studies[2] of the reactions of acetylene and propyne, which are dominated by the fragmentation of initially formed excited reaction products. On the other hand, the reaction of 2-butyne with $O(^3P)$ produces significant amounts of an unfragmented product, 3-buten-2-one, in a pressure dependent process.[3] This pattern has its parallel in the reactions of olefins, in which ethylene and propene show large amounts of fragmentation, while the butenes yield mainly C_4H_8O products.[1,4]

To shed further light on the reactions of $O(^3P)$ with alkynes, we have studied the gas-phase reactions of some C_4, C_5, and C_6 acetylenes. The products of these reactions are summarized in Table I. The relatively low material balance of these reactions and the quenched reactions described below is partially due to the competing reaction of atomic oxygen with mercury.

A major portion of the isolated reaction product consisted of unfragmented carbonyl compounds. The composition of these products is reminiscent of the products obtained from the reactions of peracids with alkynes[5] and also from the decomposition of diazo ketones.[3,6,7] The fragmented products, carbon monoxide and olefins and cyclopropanes, are probably formed by the decomposition of excited ketenes to carbenes. A scheme which summarizes these transformations is shown for the 2-pentyne reaction.