ppm from Me_4Si) 40.028, 29.087, 28.850, 28.613, 28.052; osmometric molecular weight, found 823 (calcd 890). Anal. Calcd: C, 48.60; H, 8.15; S, 42.25. Found: C, 48.61; H, 7.52; S, 41.93.

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Registry No. 7a, 71370-11-1; **7b**, 71370-12-2; **7c**, 71370-13-3; **7d**, 71370-14-4; **7e**, 61775-37-9; **7f**, 71370-15-5; **7g**, 71370-16-6; **7h**, 71370-17-7; **7i**, 71370-18-8; **12**, 71370-19-9; **13**, 71370-20-2; **14**, 71370-21-3; **16**, 71370-22-4; 1,2-ethanedithiol, 540-63-6; 1,3-propanedithiol, 109-80-8; 1,4-butanedithiol, 1191-08-8; 1,5-pentanedithiol, 928-98-3; 1,6-hexanedithiol, 1191-43-1; 1,7-heptanedithiol, 62224-02-6; 1,8-octanedithiol, 1191-62-4; 1,9-nonanedithiol, 3489-28-9; 1,10-decanedithiol, 1191-67-9; carbomethoxysulfenyl chloride, 26555-40-8.

Structure of the Dimethyl Sulfoxide–Oxalyl Chloride Reaction Product. Oxidations of Heteroaromatic and Diverse Alcohols to Carbonyl Compounds[1a]

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"Activation" of dimethyl sulfoxide (Me_2SO) by oxalyl chloride (OC) at low temperatures in methylene chloride yields an unstable intermediate that instantaneously loses CO_2 and CO. Low-temperature ^{13}C NMR and IR coupled with chemical evidence show that the product after loss of gas is identical with that obtained from the low-temperature reaction of dimethyl sulfide with chlorine. Reaction of this product with about 30 diverse alcohols (heteroaromatic, heterocyclic, small ring and allylic alcohols, carbohydrate ketals, diols, and ketols) followed by basification gives high to quantitative yields of carbonyl compounds in most cases without overoxidation or interference by other functional groups. Methyl chloroglyoxylate is also a useful "activator" for Me_2SO but offers no advantage over OC. The oxidation of allenic alcohols and most acetylenic alcohols fails with the Me_2SO–OC reagent.

Oxalyl Chloride–Me_2SO Reaction Product. Oxalyl chloride (OC) reacts explosively with dimethyl sulfoxide (Me_2SO) at room temperature; therefore, successful "activation" of Me_2SO by OC and survival and use of the requisite intermediate **1** in synthetic applications require low temperatures (eq 1). Intermediate **1** reacts rapidly with primary and secondary alcohols to form the alkoxysulfonium salts **2** that are convertible to carbonyl compounds in high to quantitative yields upon addition of triethylamine (TEA) (eq 2).[2,3]

$$Me_2SO + (COCl)_2 \xrightarrow[-60\ ^\circ C]{CH_2Cl_2} [\underset{\mathbf{1a}}{Me_2\overset{+}{S}OC(O)C(O)Cl}\ Cl^-] \xrightarrow[-CO]{-CO_2} [\underset{\mathbf{1b}}{Me_2\overset{+}{S}Cl}\ Cl^-] \quad (1)$$

$$\mathbf{1} + R^1R^2CHOH \rightarrow [\underset{\mathbf{2}}{Me_2\overset{+}{S}OCHR^1R^2}\ Cl^-] \xrightarrow{TEA} R^1R^2C{=}O + Me_2S \quad (2)$$

Of the numerous Me_2SO "activators" we and others have studied,[2-5] OC is the most efficient and generally useful one. With only a few exceptions, use of Me_2SO–OC permits the high-yield, selective oxidation of primary and secondary alcohols to the corresponding carbonyl compounds without overoxidation in the presence of other potentially oxidizable functional groups.

In the first part of this paper we discuss the structure of **1** and provide evidence that, of the two possibilities (**1a** or **1b**), it is best written as **1b** derived from **1a** by virtually instantaneous loss of CO_2 and CO at −60 or −140 °C. Intermediate **1b** is the same as that obtained by Corey and Kim from chlorine and dimethyl sulfide at low temperature.[6,7] In the second part we report expansion of the range of oxidations possible with Me_2SO–OC to include heteroaromatic and other diverse alcohols.

The initial clue that the "activated" intermediate is not **1a** was the observation that only one of the acyl halide functions of OC is displaceable by Me_2SO at −60 °C, whereas both (if present) would be expected to react. Also, with a molar ratio of OC–Me_2SO–2-octanol of 1:2:2, the yield of 2-octanone is only 50%, and 50% of the starting alcohol is recovered. With a molar ratio of reactants of 1:2:1 or 1:1:1, the yield of 2-octanone is >95%. The conclusion that only one chlorine is displaced is consistent with the observation that the exothermic reaction between OC and Me_2SO ceases after 1 mol of Me_2SO has been added to OC.

Low-temperature IR (−140°C) and ^{13}C NMR (−60 °C) examination of the intermediate show no carbonyl group absorptions or ^{13}C-carbonyl carbon signals, respectively, thus excluding **1a**. (In the absence of Me_2SO, the ^{13}C NMR signal of OC in CD_2Cl_2 is observed at ca. 160 ppm

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Table I. Methyl Chloroglyoxylate–Me_2SO Oxidation of Alcohols to Carbonyl Compounds[a]

alcohol	yield of 2,4-DNP,[5] %	yield, % (GLC)[3] >C=O	>COH	thiomethyl ether
benzyl alcohol	98	100	0	0
1-octanol	99	100	0	0
cyclopentanol	31	32	61	7
cyclohexanol	93	94	6	0

[a] −60 °C in CH_2Cl_2; basification with TEA.[2,3]

downfield from Me_4Si.) The Me_2SO–OC intermediate, however, exhibits a single ^{13}C signal at ca. 49 ppm at −60 °C in CD_2Cl_2–Me_2SO, whereas the ^{13}C NMR signal of Me_2SO in CD_2Cl_2 is at ca. 40.5 ppm under these conditions.

Addition of Me_2SO in CH_2Cl_2 with vigorous stirring to OC dissolved in CH_2Cl_2 at −60 °C results in immediate and vigorous gas evolution with each added drop. Gas evolution is observed until 1 molar equiv of Me_2SO is added to 1 mol of OC; beyond that ratio no gas evolution is noted. Passage of the evolved gas through saturated aqueous barum hydroxide solution causes immediate precipitation of barium carbonate, corresponding to a 95% yield based on a 1:1 Me_2SO–OC reaction.

Finally, if the solution of the Me_2SO–OC intermediate is allowed to warm to room temperature and then worked up, a 97% yield of chloromethyl methyl sulfide ($ClCH_2SCH_3$), the product to be expected from **1b**, can be isolated. All of these facts not only eliminate **1a** as anything but a highly transient intermediate but unequivocally confirm **1b** as the surviving intermediate obtained from Me_2SO and OC and the precursor of the alkoxysulfonium salt formed upon addition of alcohol. The loss of carbon dioxide and monoxide is so favorable energetically that **1a** cannot survive even at −140 °C. This facile decomposition is analogous to that reported in 1963 for chloroglyoxylates[8] and the loss of carbon dioxide from the reaction product of Me_2SO with chloroformates.[9,10]

Intermediate **1b** is not stable at or above about −20 °C. Thus, benzhydrol is oxidized to benzophenone in 98–100% yields at −60 °C, but at −20°C for 30 min only a 34% yield of ketone is obtained; the remainder of the alcohol is converted to benzhydryl chloride.

Methyl chloroglyoxylate ($CH_3OC(O)C(O)Cl$), a compound closely related structurally to OC, also reacts with Me_2SO at −60 °C, but no gas is evolved.[11] The intermediate reacts with alcohols; treatment of the products with TEA yields carbonyl compounds in fair to excellent yields. The initial intermediate is most likely $[Me_2S^+OC(O)C(O)OCH_3]Cl^-$. Table I reports the results of the oxidation of four representative alcohols utilizing the Me_2SO–methyl chloroglyoxylate reagent. The reagent is an efficient one but offers no advantage over OC.

Oxidation of Diverse Alcohols by OC–Me_2SO. The selective oxidation of heteroaromatic and heterocyclic alcohols to carbonyl compounds is often difficult to accomplish with conventional oxidizing agents because of competitive oxidation of the heteroatoms. With the Me_2SO–OC reagent, oxidation to carbonyl compounds in excellent yields (60–100%) is readily accomplished (Table II).[12] No isolable carbonyl compound or 2,4-DNP could be obtained from the last alcohol listed in Table II.

Table II. Heterocyclic Alcohols Oxidized to Carbonyl Compounds by Me_2SO–OC

alcohol	yield of 2,4-DNP,[5] %	yield, % (GLC)[3] >C=O	>COH
2-furanmethanol	61	90	10
2-thiophenemethanol	69	92	8
2-pyridinemethanol	65	70	30
3-pyridinemethanol	95	100	0
4-pyridinemethanol	97	100	0
3-(3-pyridyl)-1-propanol	90	88[a]	12[a]
4-chlorotetrahydrothiophene-3-ol 1,1-dioxide	0	0	0

[a] Relative ratios.

Table III. Diverse Alcohols Oxidized to Carbonyl Compounds by Me_2SO–OC

alcohol	yield of 2,4-DNP,[5] %	yield, % (GLC)[3] >C=O	>COH
chrysanthemyl alcohol (cis and trans)	98	100	0
cyclopropylmethanol	88	98	2
phenethyl alcohol	25	23	39
α-methylphenethyl alcohol	35	38	58
2-phenyl-1-cyclohexanol (trans)	95	96	4
phenoxyethanol	oil	83[a]	17[a]
2-indanol	95	96	4
2-cyclohexen-1-ol	98	95	5
(−)-carveol	70	72	28
(−)-myrtenol	80	82	18
diacetone glucose (1,2:5,6-di-*O*-isopropylidene-D-glucose)		83[b]	
1,2:3,4-di-*O*-isopropylidene-D-galactopyranose		80[b]	
4,5-isopropylidenedioxycyclohex-2-en-1-ol		55[b]	
benzoin		95[b]	
anisoin		90[b]	
furoin		68[b]	
pyridoin		64[b]	
2,2,4,4-tetramethyl-1,3-cyclobutanediol		90[c]	
1,4-cyclohexanediol		95[c]	
1,2-diphenylethanediol		90[c]	
1,4-dithiane-2,5-diol		*d*	

[a] Relative ratios. [b] Yield of isolated carbonyl compound. [c] Yield of isolated dicarbonyl compound. [d] No carbonyl compound was isolated.

The extended versatility of OC as a Me_2SO "activator" can be appreciated by the wide range of functionalized alcohols successfully oxidized to the corresponding carbonyl compounds without overoxidation or interference by other functional groups.

Table III summarizes the results of a study of the oxidation of a group of 21 alcohols. Yields are generally high, often quantitative, with the exception of two phenethyl alcohols (25–35% yields) and 1,4-dithiane-2,5-diol (0% yield). Small ring and allylic alcohols, carbohydrate and allylic ketals, ketols, and diols offer no problem. The carbohydrate ketals require nonaqueous workup as the

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(12) The oxidation of heteroaromatic alcohols to carbonyl compounds, using silver carbonate on celite as the oxidant, was recently reported (Fetizon, M.; Gomez-Parra, F.; Louis, J-M. *J. Heterocycl. Chem.* **1976**, *13*, 525–8). Yields of carbonyl compounds are generally lower than those with Me_2SO–OC.

carbonyl products are water soluble; products are isolated as residues by vacuum evaporation. Yields generally exceed those obtained with Me_2SO–Ac_2O,[13] Me_2SO–P_2O_5,[14] and CrO_3–pyridine.[15]

Allenic alcohols are not oxidized to carbonyl compounds by Me_2SO–OC; no carbonyl compound or recovered alcohol could be isolated in the two cases studied [CH_2=C=CHC≡CCH_2OH and CH_2=C=$CH(CH_2)_2OH$]. As we reported earlier,[3,16] in isolated cases acetylenic alcohols are converted to the corresponding carbonyl compounds in good yields (80–100%) with OC or TFAA, but the majority are not. In some instances unoxidized alcohol can be recovered; in others neither alcohol nor carbonyl compound (or 2,4-DNP) is obtained on workup involving basification with TEA. TEA appears to be responsible for the failure of certain allenic and acetylenic alcohols to be successfully oxidized or recovered. Thus, after reaction of the allenic and/or acetylenic alcohol with the Me_2SO–OC intermediate followed by quenching with water rather than basification with TEA, almost complete recovery of alcohol (85–90%) is achieved. In all of the unsuccessful cases in which TEA is used, syrupy, resinous intractable products result.

We tentatively conclude that during the addition of TEA to the acetylenic or allenic alkoxysulfonium salts destruction of the unstable carbonyl or sulfonium compounds occurs. There appears to be no generally useful mild selective oxidation of acetylenic and allenic alcohols to carbonyl compounds, although special methods exist. For example, nickel peroxide[17] has been used with aromatic acetylenic alcohols (70–80% yields), and the acidic reagents pyridinium chlorochromate,[18] 3,5-dimethylpyrazole-chromium trioxide,[19] and chromium trioxide in acetone[20] have been successful in isolated cases.

Experimental Section[21-23]

Oxidation of Alcohols to Carbonyl Compounds by "Activated" Me_2SO. The procedures have been reported previously.[2,3,5,16] Caution: Reaction of Me_2SO with OC is strongly exothermic with instantaneous gas evolution. No control problems were encountered in oxidizing 10–20 mmol of alcohols.

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Registry No. 1b, 23372-58-9; Me_2SO, 67-68-5; CO, 79-37-8; methyl chloroglyoxylate, 5781-53-3; benzyl alcohol, 100-51-6; 1-octanol, 111-87-5; cyclopentanol, 96-41-3; cyclohexanol, 108-93-0; 2-furanmethanol, 98-00-0; 2-thiophenemethanol, 636-72-6; 2-pyridinemethanol, 586-98-1; 3-pyridinemethanol, 100-55-0; 4-pyridinemethanol, 586-95-8; 3-(3-pyridyl)-1-propanol, 2859-67-8; *cis*-chrysanthemyl alcohol, 18383-59-0; *trans*-chrysanthemyl alcohol, 18383-58-9; cyclopropylmethanol, 2516-33-8; phenethyl alcohol, 60-12-8; α-methylphenethyl alcohol, 698-87-3; 2-phenyl-1-cyclohexanol, 2362-61-0; phenoxyethanol, 122-99-6; 2-indanol, 4254-29-9; 2-cyclohexen-1-ol, 822-67-3; (-)-carveol, 99-48-9; (-)-myrtenol, 6712-78-3; diacetone glucose, 53735-98-1; 1,2:3,4-di-*o*-isopropylidene-D-galactopyranose, 4064-06-6; 4,5-isopropylidenedioxycyclohex-2-en-1-ol, 65173-67-3; benzoin, 119-53-9; anisoin, 30587-18-9; furoin, 552-86-3; pyridoin, 1141-06-6; 2,2,4,4-tetramethyl-1,3-cyclobutanediol, 3010-96-6; 1,4-cyclohexanediol, 556-48-9; 1,2-diphenylethanediol, 492-70-6; benzaldehyde, 100-52-7; octanal, 124-13-0; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; 2-furancarboxaldehyde, 98-01-1; 2-thiophenecarboxaldehyde, 98-03-3; 2-pyridinecarboxaldehyde, 1121-60-4; 3-pyridinecarboxaldehyde, 500-22-1; 4-pyridinecarboxaldehyde, 872-85-5; 3-(3-pyridyl)-1-propanone, 1802-16-0; *cis*-2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxaldehyde, 20104-06-7; *trans*-2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxaldehyde, 20104-05-6; cyclopropanecarboxaldehyde, 1489-69-6; benzeneacetaldehyde, 122-78-1; α-methylbenzeneacetaldehyde, 93-53-8; 2-phenylcyclohexanone, 1444-65-1; phenoxyacetaldehyde, 2120-70-9; 2-indanone, 615-13-4; 2-cyclohexen-1-one, 930-68-7; (-)-carvone, 6485-40-1; (-)-myrtenal, 18486-69-6; 1,2:5,6-bis[*o*-(1-methylethylidene)]hexulose, 71606-94-5; 1,2:3,4-di-*o*-isopropylidene-α-D-*galacto*-hexadialdo-1,5-pyranose, 4933-77-1; 4,5-isopropylidenedioxycyclohex-2-en-1-one, 71606-78-5; diphenylethanedione, 134-81-6; bis(methoxyphenyl)ethanedione, 33037-21-7; di-2-furanylethanedione, 492-94-4; di-2-pyridylethanedione, 492-73-9; 2,2,4,4-tetramethyl-1,3-cyclobutanedione, 933-52-8; 1,4-cyclohexanedione, 637-88-7; benzaldehyde (2,4-dinitrophenyl)hydrazone, 1157-84-2; octanal (2,4-dinitrophenyl)hydrazone, 1726-77-8; cyclopentanone (2,4-dinitrophenyl)hydrazone, 2057-87-6; cyclohexanone (2,4-dinitrophenyl)hydrazone, 1589-62-4; 2-furancarboxaldehyde (2,4-dinitrophenyl)hydrazone, 2074-02-4; 2-thiophenecarboxaldehyde (2,4-dinitrophenyl)hydrazone, 24383-66-2; 2-pyridinecarboxaldehyde (2,4-dinitrophenyl)hydrazone, 71606-79-6; 3-pyridinecarboxaldehyde (2,4-dinitrophenyl)hydrazone, 1834-93-1; 4-pyridinecarboxaldehyde (2,4-dinitrophenyl)hydrazone, 71606-80-9; 3-(3-pyridyl)-1-propanone (2,4-dinitrophenyl)hydrazone, 71606-81-0; *cis*-2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxaldehyde (2,4-dinitrophenyl)hydrazone, 71606-82-1; *trans*-2,2-dimethyl-3(2-methylpropenyl)-cyclopropanecarboxaldehyde (2,4-dinitrophenyl)hydrazone, 71630-64-3; cyclopropanecarboxaldehyde (2,4-dinitrophenyl)hydrazone, 36873-36-6; benzeneacetaldehyde (2,4-dinitrophenyl)hydrazone, 2074-04-6; α-methylbenzeneacetaldehyde (2,4-dinitrophenyl)-hydrazone, 5530-36-9; 2-phenylcyclohexanone (2,4-dinitrophenyl)-hydrazone, 24385-72-6; 2-indanone (2,4-dinitrophenyl)hydrazone, 51758-37-3; 2-cyclohexen-1-one (2,4-dinitrophenyl)hydrazone, 1459-31-0; (-)-carvone (2,4-dinitrophenyl)hydrazone, 2121-89-3; (-)-myrtenal (2,4-dinitrophenyl)hydrazone, 71606-83-2; thiomethyl ether, 75-18-3.

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(21) Consult ref 3 for spectral and other apparatus used and GLC techniques. Reference 2 describes reactants, product isolation, and determination of the composition of crude reaction products. Most alcohols were the best commercial grades and were used directly. We thank Dr. Grant R. Krow, Temple University, for a generous sample of 4,5-isopropylidenedioxycyclohex-2-en-1-ol and -1-one. The allenic alcohols 4,5-hexadien-2-yn-1-ol[22] and penta-3,4-dien-1-ol[23] were prepared according to literature procedures. Low-temperature and conventional ^{13}C NMR spectra were obtained with a modified XL-Varian spectrometer; we thank Michael Frey for technical assistance. We also thank Dr. J. Schiffer, Temple University, for the use of his low-temperature IR equipment.
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