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## Reductive Coupling of Carbonyl Compounds to Olefins by Tungsten Hexachloride-Lithium Aluminum Hydride and Some Tungsten and Molybdenum Carbonyls

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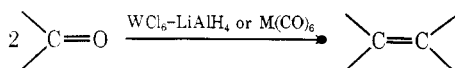
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The  $WCl_6$ -LiAlH<sub>4</sub> system and some zerovalent metal carbonyls such as  $W(CO)_6$ ,  $W(CO)_5L$  (L = PPh<sub>3</sub>, NH<sub>2</sub>C<sub>6</sub>H<sub>11</sub>, CPh(OCH<sub>3</sub>), and Cl), and Mo(CO)<sub>6</sub> have been found to cause reductive coupling of carbonyl compounds. The reactivity of the  $WCl_6$ -LiAlH<sub>4</sub> system is almost the same as that of the  $WCl_6$ -BuLi system. The  $WCl_6$ -LiAlH<sub>4</sub> reagent is also capable of reducing epoxides to olefins. A mechanism involving a carbene-W complex is proposed for the carbonyl coupling.

The reductive coupling of carbonyl compounds by transition metal complexes is an important method for the formation of C-C bonds.<sup>2</sup> Sharpless et al. have reported that a new class of reagents derived from the interaction of tungsten(VI) hexachloride ( $WCl_6$ ) and *n*-butyllithium (BuLi) causes coupling of carbonyl compounds.<sup>3</sup> We were interested in this tungsten-induced coupling for two reasons, because of its synthetic utility and because of its relationship to the significant olefin metathesis reaction caused by VIB group metals, especially tungsten.

We have found that the  $WCl_6$ -LiAlH<sub>4</sub> system and also hexacarbonyltungsten(0) ( $W(CO)_6$ ) show similar reactivities to that of the  $WCl_6$ -BuLi system for coupling.



We have reported that these reagents are also effective for dehalogenative coupling of gem dihalides and related com-

pounds.<sup>4</sup> In this paper we describe the reductive coupling of carbonyl compounds by tungsten compounds and hexacarbonylmolybdenum(0) and also the reductions of epoxides to olefins by tungsten compounds.<sup>5</sup>

### Results and Discussion

**$WCl_6$ -LiAlH<sub>4</sub> System.** The  $WCl_6$ -LiAlH<sub>4</sub>-promoted coupling of carbonyl compounds was carried out using equimolar amounts of  $WCl_6$  and LiAlH<sub>4</sub> and 0.5 equiv of the carbonyl compound in tetrahydrofuran (THF) under nitrogen atmosphere at room temperature. The reaction was rapid and complete within 1 h. The results are summarized in Table I. In contrast to the reaction with  $WCl_6$ -BuLi, it was important to use equimolar amounts of  $WCl_6$  and LiAlH<sub>4</sub> to obtain optimum yield.<sup>3</sup> Substitution of other cocatalysts such as NaAlH<sub>4</sub>, NaBH<sub>4</sub>, LiH, CaH<sub>2</sub>, Mg, or Zn or other solvent systems resulted in inferior yields (Tables II and III). As can be seen from Table I, aliphatic systems underwent coupling in poor yield. The reactivity of this reagent was almost the same

Table I. Coupling of Carbonyl Compounds by  $WCl_6$ -LiAlH<sub>4</sub> or  $W(CO)_6$ <sup>a,d</sup>

Carbonyl compd	Registry no.	Product	Yield, % <sup>b</sup>		Reagent <sup>c</sup>
			E	Z	
Benzaldehyde	100-52-7	Stilbene	73	5	A
			21	21	B
<i>p</i> -Methoxybenzaldehyde	123-11-5	<i>p,p'</i> -Dimethoxystilbene	76	6	A
			39	24	B
<i>p</i> -Chlorobenzaldehyde	104-88-1	<i>p,p'</i> -Dichlorostilbene	63	2	A
			36	26	B
<i>p</i> -Methylbenzaldehyde	104-87-0	<i>p,p'</i> -Dimethylstilbene	57	3	A
			29	14	B
Benzophenone	119-61-9	Tetraphenylethylene	43		A
			3		B
Acetophenone	98-86-2	1,2-Dimethylstilbene	20	13	A
			3	4	B
Propionaldehyde	123-38-6	3-Hexene	18 (E,Z)		A
Cyclohexanone	108-94-1	Cyclohexylidenecyclohexane	55		A
			0.2		B

<sup>a</sup> Reaction was performed charging 0.8 mmol of  $WCl_6$ , 0.8 mmol of LiAlH<sub>4</sub>, and 0.4 mmol of the carbonyl compound in 10 mL of THF (for reagent A) or CH<sub>2</sub>Cl<sub>2</sub> (for reagent B) with stirring for 6 h at room temperature under nitrogen atmosphere. <sup>b</sup> Based on the starting carbonyl compound. <sup>c</sup> A, reagent  $WCl_6$ -LiAlH<sub>4</sub>; B, reagent  $W(CO)_6$ . <sup>d</sup> Registry No.— $WCl_6$ , 13283-01-7; LiAlH<sub>4</sub>, 16853-85-3;  $W(CO)_6$ , 14040-11-0.

**Table II. Comparison of Cocatalysts for  $WCl_6$ -Induced Reductive Coupling of Benzaldehyde to Stilbene<sup>a</sup>**

Cocatalyst	Stilbene yield, %	Cocatalyst	Stilbene yield, %
$LiAlH_4$	78	$LiH$	No
$NaAlH_4$	69	$CaH_2$	No
$Zn$	16	$Mg$	No
$NaBH_4$	No		

<sup>a</sup> Reaction was performed under the same conditions as Table I using THF as the solvent.

**Table III. Comparison of Solvents for  $WCl_6$ - $LiAlH_4$ -Induced Coupling of Benzaldehyde to Stilbene<sup>a</sup>**

Solvent	Stilbene yield, %	Solvent	Stilbene yield, %
THF	78	Cyclohexane	Trace
Ethyl ether	23	Benzene	No
Dioxane	13	DMF	No
Acetonitrile	Trace	Pyridine	No
Nitromethane	Trace	Ethanol	No
Methylene chloride	Trace	Carbon tetrachloride	No

<sup>a</sup> Reaction was performed under the same conditions as Table I.

as that of the  $WCl_6$ - $BuLi$  reagent.<sup>3</sup> The role of the cocatalyst  $LiAlH_4$  can be thought to be that it reduces  $W(VI)$  to some lower valent species which is active for coupling since  $WCl_6$  alone is not responsible for the reaction.<sup>3</sup> If this is the case, some zerovalent tungsten compounds such as  $W(CO)_6$  should also be capable of the reaction. We have found that  $W(CO)_6$  and  $Mo(CO)_6$  cause the reductive coupling of carbonyl compounds (Tables I and IV). In Table IV, the solvent effect on the reaction of benzaldehyde with tungsten and molybdenum carbonyls is shown. From the table it is apparent that  $CH_2Cl_2$  and *n*-pentane are the best for  $W(CO)_6$  and  $Mo(CO)_6$ , respectively. But in the case of  $W(CO)_6$ , the solvent dependency is not so high as that of the  $WCl_6$ - $LiAlH_4$  system. Although the different solvent systems are suitable for these reagents, the order of reactivity appears to be  $WCl_6$ - $BuLi$  >  $W(CO)_6$   $\approx$   $Mo(CO)_6$ .

In Table V are shown the reactivities of some zerovalent tungsten carbonyls to coupling of benzaldehyde. The table shows that  $W(CO)_6$  is the most active of the tested complexes and that addition of  $AlCl_3$  to tetraethylammoniumpentacarbonyltungsten(0) chloride increases the yield, probably because  $AlCl_3$  causes elimination of the chloride ligand, furnishing the coordinately unsaturated site. It is interesting that the carbene-W complex, methoxyphenylcarbenepentacarbonyltungsten(0), causes coupling in modest yield. Although these reagents are not capable of coupling aliphatic ketones in good yield, they still have some practical advantage over titanium-induced coupling since they are relatively stable to air. The reagents  $MoCl_5$ ,  $PdCl_2$ , and  $Pd(OAc)_2$  do not cause coupling under similar conditions.

**Mechanism.** Mechanisms involving pinacol type intermediates are suggested in the titanium-induced carbonyl coupling.<sup>2</sup> However, little is known about the tungsten-induced coupling of carbonyl compounds. We assume a carbene-W complex intermediate on the following bases: (i) When benzaldehyde was treated with the  $WCl_6$ - $LiAlH_4$ -THF system in the presence of an enamine, 1-(2-methylpropenyl)pyrrolidine, there was obtained 1-(2,2-dimethyl-3-phenylcyclopropyl)pyrrolidine (1), a cyclopropane,<sup>6</sup> in a 6.2% yield, together with 1.1% yield of stilbene.

**Table IV. Comparison of Solvents for Coupling of Benzaldehyde to Stilbene by  $W(CO)_6$  or  $Mo(CO)_6$ <sup>a,b</sup>**

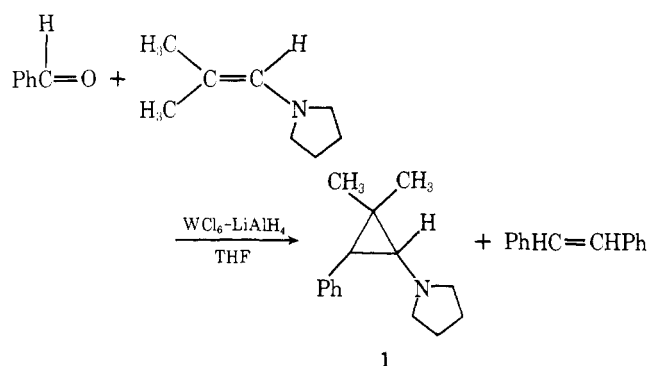
Solvent	Reagent and yield, %	
	$W(CO)_6$	$Mo(CO)_6$
THF	21	10
Ether	14	39
Dioxane	20	13
Benzene	19	39
<i>n</i> -Pentane	17	41
Cyclohexane	20	38
Methylene chloride	42	5
$CCl_4$	27	No
Chlorobenzene	27	
Ethanol	10	No
$Me_2SO$	Trace	No
$CH_3CN$	1	No
Pyridine	No	No
Nitromethane	No	1

<sup>a</sup> Reaction conditions same as Table I. <sup>b</sup> Registry No.— $Mo(CO)_6$ , 13939-06-5.

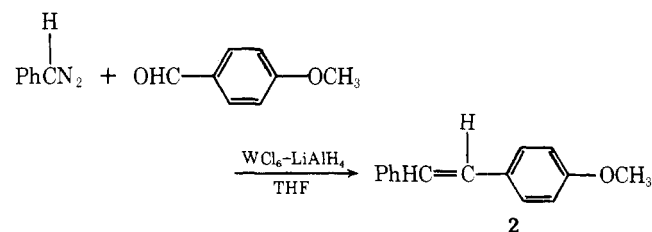
**Table V. Coupling of Benzaldehyde by Tungsten(0) Carbonyls<sup>a</sup>**

W complex	Registry no.	Stilbene yield, %	
		<i>Z</i>	<i>E</i>
$W(CO)_6$		21	21
$W(CO)_5PPh_3$	15444-65-2	9	9
$W(CO)_5NH_2C_6H_{11}$	16969-84-9	7	8
$W(CO)_5C(OCH_3)Ph$	37823-96-4	13	19
$[W(CO)_5Cl]NEt_4$	14780-97-3	4	27
$[W(CO)_5Cl]NEt_4^b$			

<sup>a</sup> Reaction conditions same as Table I. <sup>b</sup> An equivalent amount of  $AlCl_3$  was added.



(ii) When *p*-methoxybenzaldehyde was treated with phenyldiazomethane, a carbene precursor, in the  $WCl_6$ - $LiAlH_4$  system at room temperature, a 12% yield of *p*-methoxystilbene (2) was detected along with *p,p'*-dimethoxystilbene.



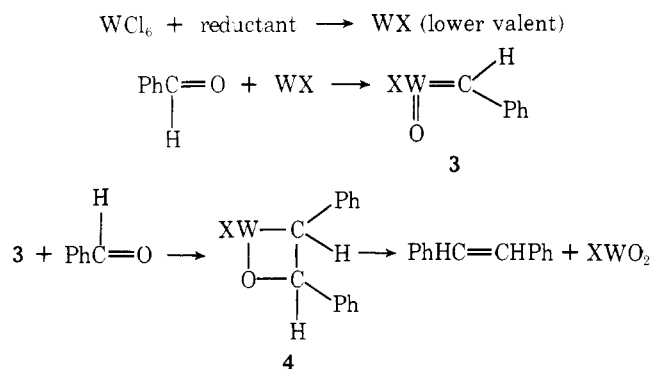
These results i and ii are also observed with the  $W(CO)_6$  reagent. (iii) Carbene-W complexes such as methoxyphenylcarbenepentacarbonyltungsten(0) cause carbonyl coupling in fair yield (Table V). (iv) NMR spectral studies have been performed to detect the carbene-W complex intermediate.

Table VI. Reduction of Epoxides by  $WCl_6-LiAlH_4^a$ 

Epoxide	Registry no.	Product	Yield, % <sup>b</sup>	
			Z	E
Styrene oxide	96-09-3	Styrene	49	
(Z)-Stilbene oxide	1689-71-0	Stilbene	4	80
(E)-Stilbene oxide	1439-07-2	Stilbene	1	80
<i>m,m'</i> -Dichlorostilbene oxide ( <i>E-Z</i> = 1:9) <sup>c</sup>		<i>m,m'</i> -Dichlorostilbene	12	88
1-Octene oxide	2984-50-1	1-Octene	75	
(Z)-2-Hexene oxide	6124-90-9	2-Hexene	23	29
(E)-2-Hexene oxide	6124-91-0	2-Hexene	20	36
Cyclohexene oxide	286-20-4	Cyclohexene	27	
Cyclooctene oxide	286-62-4	Cyclooctene	72	

<sup>a</sup> Reaction was performed charging 0.8 mmol of  $WCl_6$ , 0.8 mmol of  $LiAlH_4$ , and 0.8 mmol of the epoxide in 10 mL of THF with stirring for 6 h at room temperature under nitrogen atmosphere. <sup>b</sup> Based on the starting epoxide. <sup>c</sup> Registry No.—*m,m'*-dichlorostilbene oxide (*E* isomer), 65956-99-2; *m,m'*-dichlorostilbene oxide (*z* isomer), 65957-00-8.

Five minutes after the addition of benzaldehyde to a solution of  $WCl_6-LiAlH_4$  in THF, a new peak at  $\tau$  1.20 appeared besides the aldehydic ( $\tau$  0.00) and phenyl protons ( $\tau$  2–3) of benzaldehyde, and this new peak disappeared after 15 min. We assume this new peak at  $\tau$  1.20 to be due to the  $\alpha$  hydrogen of the carbene-W complex **3** since  $\alpha$  protons of metal-carbene complexes have been reported to resonate over a relatively wide range such as  $\tau$  -7 ~ 8.<sup>7</sup> Although these facts are inconclusive we would propose the following mechanism:



Recently Sharpless et al. have proposed a metalocycle intermediate such as **4** in the chromyl chloride oxidation of olefins.<sup>8</sup> The carbene formation from interaction of aldehydes and transition metal systems has also been reported.<sup>9</sup>

**Reductions of Epoxides.** Several transition-metal-induced reductions of epoxides are reported.<sup>10</sup> Sharpless et al. reported that the  $WCl_6-BuLi$  system is effective for the reduction of epoxides to olefins.<sup>3</sup> The  $WCl_6-LiAlH_4$  system has been found to be as effective as the  $WCl_6-BuLi$  system for the reduction. The results are summarized in Table VI. Sharpless et al. have proposed a mechanism involving a metalocycle intermediate such as **4** for this epoxide reduction.<sup>8</sup>

In conclusion, it is shown that  $WCl_6-LiAlH_4$  and  $W(CO)_6$  reagents are capable of coupling of carbonyl compounds, gem dihalides, benzyl halides, and some alcohols<sup>4</sup> and reduction of epoxides to olefins.

### Experimental Section

NMR spectra were obtained with a Japan Electron Optics JNM-4H-100 spectrometer using  $Me_4Si$  as an internal standard.

**Materials.**  $WCl_6$  was purified by sublimation. 1-(2,2-Dimethylvinyl)pyrrolidine was prepared according to the literature.<sup>11</sup> Other starting materials were commercial grade. THF was refluxed and distilled from a dark purple solution of sodium benzophenone dianion under nitrogen. Other solvents were purified by the usual methods.  $W(CO)_6PPh_3$  was prepared from  $W(CO)_6$  and triphenylphosphine according to the literature.<sup>12</sup> Cyclohexylaminepentacarbonyltungsten(0) was prepared from  $W(CO)_6$  and cyclohexylamine.<sup>13</sup> Methoxyphenylcarbenepentacarbonyltungsten(0)<sup>14</sup> and tetraammoniumpentacarbonyltungsten(0) chloride<sup>15</sup> were prepared according to the literature.

**General Procedure for Coupling of Carbonyl Compounds by  $WCl_6-LiAlH_4$ .** Into a flame-dried 50-mL centrifuge tube containing a magnetic stirring bar was added 10 mL of THF by syringe, and the tube was sealed with a No-Air stopper. After the tube had been flushed with nitrogen it was cooled to  $-78^\circ C$  and then  $WCl_6$  (0.8 mmol) and  $LiAlH_4$  (0.8 mmol) were added under nitrogen. The solution changed from green to dark brown. Then 0.4 mmol of the carbonyl compound was added by syringe and the mixture was stirred for 6 h at room temperature under nitrogen. The reaction mixture was quenched with 20% aqueous NaOH. The organic materials were extracted with ether. The combined ether layers were washed with water, dried over  $MgSO_4$ , filtered, and concentrated. The products were analyzed by GLC. The products were identified by mixture melting point, IR, NMR, and retention time comparison with authentic samples. The authentic *p,p'*-dichlorostilbene,<sup>16</sup> *p,p'*-dimethoxystilbene,<sup>17</sup> *p,p'*-dimethylstilbene,<sup>17</sup> cyclohexylidene cyclohexane,<sup>18</sup> and 1,2-dimethylstilbene<sup>19</sup> were prepared according to the procedures in the literature.

**General Procedure for Coupling of Carbonyl Compounds by Metal Carbonyls.** Into the same centrifuge tube as described above was added 10 mL of  $CH_2Cl_2$  (in the case of  $Mo(CO)_6$ , *n*-pentane was the solvent) and tungsten carbonyl (0.4 mmol) and the tube was sealed with a No-Air stopper. After the tube had been flushed with nitrogen 0.2 mmol of the carbonyl compound was added by syringe. The mixture was stirred for 6 or 24 h at room temperature under nitrogen, then the tube was cooled to  $-78^\circ C$  and the precipitated metal complexes were removed by filtration. To the mother liquor was added ether and the ethereal layers were washed, dried with  $Na_2SO_4$ , and concentrated. The products were analyzed and isolated by GLC. Identities of the products were proved by the same procedures as above.

**Trapping of Carbene Intermediate.** Into a flame-dried 50-mL centrifuge tube containing a magnetic stirring bar and 40 mL of THF were added 3.2 mmol of  $WCl_6$  and  $LiAlH_4$  (equal amount) and the tube was sealed with a No-Air stopper. After the tube had been flushed with nitrogen, 3.2 mmol of benzaldehyde and 10 mL of 1-(2,2-dimethylvinyl)pyrrolidine were added. The mixture was allowed to warm to room temperature and stirred for 6 h at room temperature under nitrogen. After work-up as described above, the products were analyzed by GLC and shown to contain 1-(2,2-dimethyl-3-phenylcyclopropyl)pyrrolidine (**1**) and stilbene in 6.2 and 1.1% yields, respectively. The cyclopropane derivative **1** was identified by comparison with a sample of which preparation and physical properties were already described.<sup>4</sup>

**General Procedure for Reduction of Epoxides by  $WCl_6-LiAlH_4$ .** The epoxides were reduced in the same procedure described in the section of the coupling of carbonyl compounds by this reagent, charging 0.8 mmol of  $WCl_6$ , 0.8 mmol of  $LiAlH_4$ , and 0.8 mmol of the epoxide in 10 mL of THF with stirring for 6 h under nitrogen atmosphere. All the products formed were identified by comparison with authentic samples. The results are listed in Table VI.

**Reaction of Phenylhydrazomethane with *p*-Methoxybenzaldehyde in the Presence of  $WCl_6-LiAlH_4$ .** Into a centrifuge tube containing a magnetic stirring bar,  $WCl_6$  (0.8 mmol),  $LiAlH_4$  (0.8 mmol), *p*-methoxybenzaldehyde (0.4 mmol), and THF (10 ml) was added an ethereal solution of phenylhydrazomethane (0.6 mmol) prepared from oxidation of phenylhydrazone with  $HgO$ . The mixture was stirred until the solution changed from dark red to dark brown, and then the mixture was quenched with 20% aqueous NaOH. After work-up as usual, the residue was analyzed by GLC to give *p*-methoxystilbene<sup>20</sup> (12% yield based on phenylhydrazomethane) and *p,p'*-dimethoxystilbene.<sup>19</sup>

## References and Notes

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## Oxidation of Long-Chain and Related Alcohols to Carbonyls by Dimethyl Sulfoxide "Activated" by Oxalyl Chloride<sup>1</sup>

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Dimethyl sulfoxide "activated" by oxalyl chloride at low temperatures in methylene chloride reacts rapidly with alcohols to give alkoxysulfonium salts, convertible to carbonyls in high to quantitative yields upon addition of triethylamine. Oxalyl chloride is the most efficient and generally useful Me<sub>2</sub>SO "activator" thus far reported. The mild, high yield oxidation of long-chain saturated, unsaturated, acetylenic, and steroidal alcohols to carbonyls utilizing Me<sub>2</sub>SO "activated" by oxalyl chloride is described.

Long-chain aldehydes (in masked form) are of importance in biological systems, such as plasmalogens, found in many organs of the body, e.g., heart, muscle, liver, kidney, pituitary gland, and cerebellum white and gray matter.<sup>2</sup> In the synthesis of plasmalogens, long-chain saturated and unsaturated aldehydes are necessary intermediates.

No satisfactory and universally applicable method for the preparation of long-chain carbonyls by the mild, selective oxidation of the corresponding long-chain saturated and unsaturated alcohols has been reported. Earlier work<sup>3</sup> involved the preparation of a sulfonate ester (mesylate or tosylate) of the alcohol followed by reaction with dimethyl sulfoxide (Me<sub>2</sub>SO) at 160 °C for 5–10 min in the presence of sodium bicarbonate (yields 60–72%). The use of Me<sub>2</sub>SO–acetic anhydride or Me<sub>2</sub>SO–sodium bicarbonate at room temperature with the sulfonate esters was unsuccessful.

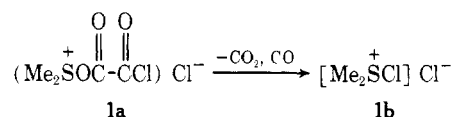
The oxidation of long-chain primary alcohols to aldehydes by the dipyridine–chromic anhydride complex was recently reported<sup>4</sup> but a sixfold excess of oxidant to alcohol is required. Yields are good, however, and range from 83–94%. No evidence (by infrared) of cis–trans isomerization of double bonds was observed in the preparation of mono-, di-, or triunsaturated aldehydes. Isomerization of double bonds is observed when more acidic oxidizing agents are employed.<sup>5–8</sup>

"Activated" Me<sub>2</sub>SO has been used extensively by us to oxidize many classes of alcohols to carbonyls in excellent yields under mild conditions via the intermediate alkoxysulfonium salts.<sup>9–11</sup> In this paper we report our studies of "activated" Me<sub>2</sub>SO as an oxidant for the mild, high-yield oxidation of long-chain saturated, unsaturated, acetylenic, and steroidal alcohols at low temperatures to carbonyls utilizing the newly discovered and most successful "activator" developed in our

laboratory, namely, oxalyl chloride.<sup>11</sup> The results were compared with those obtained at room temperature with pyridinium chlorochromate<sup>7</sup> and pyridine–SO<sub>3</sub>–Me<sub>2</sub>SO,<sup>12</sup> two other well-known oxidants, and Me<sub>2</sub>SO "activated" by trifluoroacetic anhydride (TFAA).<sup>9,10</sup>

### Results and Discussion

Oxalyl chloride reacts violently and exothermically with Me<sub>2</sub>SO at room temperature; therefore successful "activation" of Me<sub>2</sub>SO by oxalyl chloride requires the use of low temperatures (–60 °C) to form intermediate 1. The structure of intermediate 1 from oxalyl chloride and Me<sub>2</sub>SO is unknown; intermediates 1a and 1b are both possible. Intermediate 1b



is the same as that reported by Corey and Kim for the low-temperature reaction of dimethyl sulfide with chlorine (Me<sub>2</sub>S–Cl<sub>2</sub>),<sup>6</sup> also a useful intermediate in alcohol oxidations.

The oxidation of long-chain saturated and unsaturated alcohols by Me<sub>2</sub>SO "activated" by oxalyl chloride is summarized in Table I, acetylenic alcohols are summarized in Table II, and steroidal alcohols are summarized in Table III. The TFAA "activated" Me<sub>2</sub>SO oxidation of several long-chain saturated alcohols is summarized in Table IV.

The oxalyl chloride "activated" Me<sub>2</sub>SO oxidation of long-chain saturated alcohols to the corresponding aldehydes proceeds virtually quantitatively (Table I) and is limited only by the solubility of the alcohol in the solvent system