6.1 g (0.03 mol) of iodobenzene, 3.6 g (0.03 mol) of *N*-benzylidenemethylamine, and 4 ml (0.03 mol) of nickel carbonyl in 50 ml of benzene was stirred at 70–75° for 20 hr. From the reaction mixture, the following fractions were obtained: (1) 0.98 g, bp 90–94° (50 mm); (2) 0.95 g, bp 110–140° (0.4 mm); (3) 0.87 g, bp 140–160° (0.4 mm); and (4) 2.45 g, bp 160–200° (0.4 mm). Fraction 1 was confirmed to be benzaldehyde by gas chromatographic analysis. Fraction 2 and 3 were found to consist of *N*-methylbenzamide and benzil. Fraction 4 was recrystallized from methanol to give white crystals: mp 113°; ir 1695, 1640 cm^{-1} (CO); nmr τ 7.17 (s, 3 H), 2.65 (m, 15 H), 2.05 (broad, 1 H); mass spectrum *m/e* 329 (M^+), 224, 105. *Anal.* Calcd for $C_{22}H_{19}O_2N$: C, 80.36; H, 5.69; N, 4.30. Found: C, 80.22; H, 5.81; N, 4.25. This compound was confirmed to be *N*-methyl-*N*-(α-phenylphenacyl)benzamide (VII) (53% yield), the coupling product of two of benzoyl group intervening *N*-benzylidenemethylamine.

The Reaction of Iodobenzene with Nickel Carbonyl in Benzene in the Presence of *N*-Benzylideneethylamine.—A solution of 6.1 g (0.03 mol) of iodobenzene, 6 g (0.045 mol) of *N*-benzylideneethylamine, and 4 ml (0.03 mol) of nickel carbonyl in 50 ml of benzene was stirred at 70–75° for 24 hr. From the reaction mixture, the following fractions were obtained: (1) 1.0 g, bp 30–35° (0.5 mm); (2) 1.54 g, bp 124–153° (0.6 mm); and (3) 2.91 g, bp 154–210° (0.6 mm). Fraction 1 was confirmed to be benzaldehyde. Fraction 2 was confirmed to consist of 87 parts of *N*-benzyl-*N*-ethylbenzamide and 13 parts of *N*-ethylbenzamide. Fraction 3 was recrystallized from petroleum ether–benzene to afford white crystals: mp 103°; ir 1685, 1628 cm^{-1} (CO); mass spectrum *m/e* 333 (M^+), 228, 105. *Anal.* Calcd for $C_{23}H_{21}O_2N$: C, 80.69; H, 5.94; N, 4.08. Found: C, 80.44; H, 6.16; N, 3.81. This compound was confirmed to be *N*-ethyl-*N*-(α-phenylphenacyl)benzamide (VIII) (59% yield).

Registry No.—I, 36917-63-2; II, 36917-64-3; IIIa, 36917-65-4; VII, 36917-66-5; VIII, 36895-14-4; iodobenzene, 591-50-4; nickel carbonyl, 13463-39-3; *N*-benzylidene, methylamine 622-29-7; α-(*N*-benzoyl-*N*-methyl)aminostilbene, 16151-51-2; *p*-methyliodobenzene, 624-31-7; *N*-benzylideneethylamine, 6852-54-6.

The Group VI Metal Carbonyl Catalyzed Reaction of Ethers and Acid Halides

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Received August 18, 1972

The reaction of acyclic and cyclic ethers with acid halides in the presence of catalytic quantities of Group VI metal carbonyls [$M(CO)_6$, where M = Cr, Mo, W] was investigated. The catalytic order of effectiveness was found to be $Mo(CO)_6 > W(CO)_6 > Cr(CO)_6$ with $Mo(CO)_6$ being a very useful catalyst for the reaction. The group VA substituted molybdenum carbonyls, $EMo(CO)_5$ [E = $(C_6H_5)_3P$, $(C_6H_5)_3As$] and *cis*-$[(C_6H_5)_3P]_2Mo(CO)_4$, are also good catalysts for the reaction. These catalytic reactions can be carried out either thermally or photochemically (at room temperature). The effects of temperature, of oxygen, and of variation of the halogen in the acid halide on the thermal reaction are noted. Stereochemical studies show that the reaction occurs with partial or complete retention, or net inversion of configuration, subject to the nature of the ether. An ionic mechanism is proposed for these reactions.

Considerable interest has developed recently in the use of Group VI metal carbonyls [$M(CO)_6$, M = Cr, Mo, W] as catalysts[1–8] and as stoichiometric reagents[9–11] for organic synthesis. This paper is concerned with the catalysis of the reaction of ethers and acid halides[12] by these metal carbonyls. The primary objectives of this study were the effectiveness of Group VI metal carbonyls as catalysts compared to other catalysts for the ether–acid halide reaction; the relative catalytic effectiveness within Group VI and possible correlations with the metal–carbon bond strength;[13,14] and the stereochemistry and possible mechanism(s) for the reaction.

Results and Discussion

Acyclic Ethers.—Refluxing the acyclic ethers, neat or in hexane or isooctane solution, with acid chlorides in the presence of molybdenum hexacarbonyl gave esters, organic chlorides, and, in some instances, alkenes.

$$\mathrm{ROR + R'COCl \xrightarrow{Mo(CO)_6} RCl + R'COOR}$$

The results are listed in Table I. For unsymmetrical ethers, the alkyl chloride formed is that derived from the more highly substituted alkoxy carbon atom. Only in the case of benzoin methyl ether was a sluggish reaction observed, probably owing to the presence of the electron-attracting benzoyl group in the reactant ether. When dehydrohalogenation occurs, Saytzeff's rule is usually, but not always, followed. Olefins produced in some of these reactions do not arise from $Mo(CO)_6$-catalyzed dehydrohalogenation of an alkyl chloride, since, for example, 2-chlorooctane was inert to $Mo(CO)_6$ when refluxed in hexane for 1 day.

The alkyl aryl ether, *n*-butyl phenyl ether, reacted with acetyl chloride in the presence of $Mo(CO)_6$ to give only traces of *o*- and/or *p*-*n*-butoxyacetophenone. Here, complexation of the benzene ring of the reactant ether with molybdenum carbonyl may give the less active arene–$Mo(CO)_3$ catalyst.

Cyclic Ethers.—A number of cyclic ethers were subjected to acid halide treatment in the presence of

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[4] M. N. Sheng and J. G. Zajacek, *Advan. Chem. Ser.*, **No. 76**, 418 (1968).

[5] C. H. Bamford, G. C. Eastmond, and F. J. T. Fildes, *Chem. Commun.*, 144, 146 (1970), and references cited therein.

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[9] H. Alper, *Organometal. Chem. Syn.*, **1**, 69 (1971).

[10] H. Alper, *Angew. Chem., Int. Ed. Engl.*, **8**, 677 (1969).

[11] E. Lindner and G. Vitzthum, *ibid.*, **8**, 518 (1969).

[12] R. L. Burwell, Jr., *Chem. Rev.*, **54**, 615 (1954).

[13] D. R. Lloyd and E. W. Schlag, *Inorg. Chem.*, **8**, 2544 (1969).

[14] R. B. King, *Inorg. Nucl. Chem. Lett.*, **5**, 905 (1969).

TABLE I

REACTION OF ACYCLIC ETHERS WITH ACID CHLORIDES IN THE PRESENCE OF $Mo(CO)_6$

Ether	R'COCl, R' =	Solvent[a]	Reaction time, hr	Products (yield, %)
(+)-2-Ethoxyoctane	CH_3	H	20	$CH_3C(Cl)HC_6H_{13}$ (62), $CH_3CH{=}CHC_5H_{11}$ (31), $CH_3COOC_2H_5$
	C_6H_5	I	24	$CH_3C(Cl)HC_6H_{13}$, $CH_3CH{=}CHC_5H_{11}$, $C_6H_5COOC_2H_5$ (82)
n-Butyl ether	C_6H_5	N	16	$C_6H_5COOC_4H_9$ (73), C_4H_9Cl
Benzoin methyl ether	C_6H_5	I	48	$C_6H_5COC(Cl)HC_6H_5$, $C_6H_5COOCH_3$ (37)
Ethyl triphenylmethyl ether	C_6H_5	H	12	$(C_6H_5)_3CCl$, $C_6H_5COOC_2H_5$ (72)

[a] H = hexane, I = isooctane, N = neat.

TABLE II

REACTION OF CYCLIC ETHERS WITH ACID HALIDES IN THE PRESENCE OF $M(CO)_6$ (M = Cr, Mo, W)

Ether	Acid halide	Solvent[a]	Reaction time, hr	M of $M(CO)_6$	Halo ester (yield, %)	Alkenyl ester (yield, %)
2-Methyltetrahydrofuran	CH_3COCl	H	20	Mo	4-Chloropentyl acetate (80)	3-Pentenyl acetate (7)
	CH_3COCl	H	20	W	4-Chloropentyl acetate (61)	
	CH_3COCl	H	20	Cr	4-Chloropentyl acetate (17)	
	C_6H_5COCl	H	60	Mo	4-Chloropentyl benzoate (54)	3-Pentyl benzoate (27)
	C_6H_5COCl	I	18	Mo	4-Chloropentyl benzoate (78)	3-Pentyl benzoate (12)
	C_6H_5COCl	H	60	W	4-Chloropentyl benzoate (39)	3-Pentenyl benzoate (trace)
	C_6H_5COCl	H	60	Cr	4-Chloropentyl benzoate (11)	3-Pentenyl benzoate (3)
Tetrahydrofuran	CH_3COCl	H	23	Mo	4-Chlorobutyl acetate (78)	
	$C_6H_{11}COCl$	N	18	Mo	4-Chlorobutyl cyclohexanecarboxylate (84)	
	$C_6H_{11}COCl$	N	18	W	4-Chlorobutyl cyclohexanecarboxylate (42)[b]	
	$C_6H_{11}COCl$	N	18	Cr	4-Chlorobutyl cyclohexanecarboxylate (16)	
	C_6H_5COBr	N	23	Mo	4-Bromobutyl benzoate (88)	
2,2,4,4-Tetramethyltetrahydrofuran	CH_3COCl	H	19	Mo		2,2,4-Trimethyl-4-pentenyl acetate (48) 2,2,4-Trimethyl-3-pentenyl acetate (24)
2,5-Dihydrofuran	CH_3COCl	H	20	Mo	4-Chloro-2-butenyl acetate (61)	
	CH_3COCl	H	36	W	4-Chloro-2-butenyl acetate (12)	
	CH_3COCl	H	26	Cr		
7-Oxabicyclo[2.2.1]heptane	CH_3COCl	H	20	Mo	*trans*-4-Chlorocyclohexyl acetate (55)	3-Cyclohexenyl acetate (22)
	CH_3COCl	I	16	W	*trans*-4-Chlorocyclohexyl acetate (57)	3-Cyclohexenyl acetate (10)
	CH_3COCl	H	20	W	*trans*-4-Chlorocyclohexyl acetate (trace)	
	CH_3COCl	H	20	Cr	*trans*-4-Chlorocyclohexyl acetate (trace)	
	C_6H_5COCl	H	36	Mo	*trans*-4-Chlorocyclohexyl benzoate (69)	3-Cyclohexenyl benzoate (13)
	C_6H_5COCl	I	16	Mo	*trans*-4-Chlorocyclohexyl benzoate (54)	3-Cyclohexenyl benzoate (23)
	C_6H_5COCl	H	36	W	*trans*-4-Chlorocyclohexyl benzoate (28)	3-Cyclohexenyl benzoate (12)
	C_6H_5COCl	H	36	Cr	*trans*-4-Chlorocyclohexyl benzoate (9)	3-Cyclohexenyl benzoate (6)
	C_6H_5COBr	I	16	Mo	*trans*-4-Bromocyclohexyl benzoate (72)	3-Cyclohexenyl benzoate (13)
	C_6H_5COF	H	72	Mo		3-Cyclohexenyl benzoate (67)
	C_6H_5COF	H	72	W		
	C_6H_5COF	H	72	Cr		

[a] H = hexane, I = isooctane, N = neat. [b] $C_6H_{11}COO(CH_2)_4O(CH_2)_4Cl$ was also obtained in 18% yield.

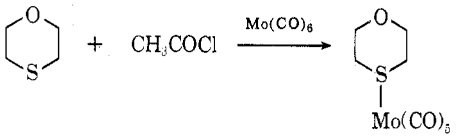
group VI metal hexacarbonyls (Table II). Halo esters and/or elimination products were formed in these reactions. In the reaction of a given acid halide with a specific ether, *e.g.*, tetrahydrofuran (THF) with cyclohexanecarboxylic acid chloride, the yield of halo ester usually decreased in the catalytic order of $Mo(CO)_6 > W(CO)_6 > Cr(CO)_6$. Molybdenum hexacarbonyl is an excellent catalyst for the ether–acid halide reaction, as the yields in Tables I and II indicate (note that no attempt was made to optimize conditions).

Variable amounts of alkenyl ester were also observed in these reactions.

The catalytic order of effectiveness of $Mo(CO)_6 > W(CO)_6 > Cr(CO)_6$ is not in accord with the previously mentioned and generally accepted order of π-back donation of group VI metal carbonyls [Mo–C < Cr–C < W–C].[13,14] This suggests that the cleavage of a metal–carbon bond may not be involved in the rate-determining step of the reaction process.

The presence of an allylic double bond in the reactant ether did not affect the reaction, as 2,5-dihydrofuran gave unrearranged 4-chloro-2-butenyl acetate as the only product on $Mo(CO)_6$- or $W(CO)_6$-catalyzed reaction with acetyl chloride. In contrast, 2,3-dihydropyran, a vinyl ether, reacted with acid chloride and $Mo(CO)_6$ to give no isolable monomeric or dimeric product, but polymeric materials were apparently formed.

The presence of a sulfur atom in the reactant ether resulted in ligand substitution rather than carbon–oxygen bond cleavage; *e.g.*, treatment of 1,4-thioxane (**1**) with acetyl chloride and $Mo(CO)_6$ gave **2**.



1 **2**

Effect of Halogen.—The effect of the halogen, in the acid halide, on the reaction course was determined. Molybdenum carbonyl catalyzed reaction of 7-oxabicyclo[2.2.1]heptane with benzoyl bromide or benzoyl chloride in isooctane gave the halo and alkenyl esters in the ratio of 5.5:1.0 and 2.3:1.0, respectively. Only the elimination product was obtained when benzoyl fluoride was used as the acid halide (Table II).

Temperature Variation.—Several reactions were run in both hexane (bp 68°) and isooctane (bp 101°) in order to see what effect, if any, change in temperature had on the product ratio for a given reaction. While a 2.0:1.0 ratio of halo ester to alkene resulted from the 2-methyltetrahydrofuran–C_6H_5COCl–$Mo(CO)_6$ reaction in hexane, isooctane gave a product ratio of 6.5:1.0. Similarly, carbon–oxygen bond cleavage of 7-oxabicyclo[2.2.1]heptane by C_6H_5COCl in isooctane [$Mo(CO)_6$ catalyst] gave a 2.3:1.0 halo ester–alkenyl ester distribution, which was different than the 5.3:1.0 ratio observed using hexane as solvent. In essence, then, the total product yield is not markedly altered with a change in reaction temperature but the product ratio is affected.

Effect of Oxygen.—It should be emphasized that these $M(CO)_6$ catalyzed reactions can be equally effected in the presence or absence of air (under N_2).

Triphenylphosphine and Triphenylarsine Substituted Molybdenum Carbonyls as Catalysts.—Group VA substituted metal carbonyls have been shown to be more or less effective reagents or catalysts than the parent metal carbonyls, in different reactions. For example, triphenylphosphineiron tetracarbonyl does not react stoichiometrically with 2-bromo-4′-phenylacetophenone in refluxing 1,2-dimethoxyethane, while use of iron pentacarbonyl provides a simple preparation of the coupled 1,4-diketone and *p*-phenylacetophenone.[15] In contrast, $Fe(CO)_5$ is a less active catalyst than triphenylphosphineiron tetracarbonyl in generating the trichloromethyl radical by treatment of methyl methacrylate with carbon tetrachloride.[16]

Acetyl chloride was treated with tetrahydrofuran in the presence of Group VA substituted molybdenum carbonyls, and the results are presented in Table III.

TABLE III

REACTION OF TETRAHYDROFURAN AND ACETYL CHLORIDE IN THE PRESENCE OF SUBSTITUTED MOLYBDENUM CARBONYLS

Catalyst	Yield of 4-chlorobutyl, acetate, %
$Mo(CO)_6$	78
$Mo(CO)_5[P(C_6H_5)_3]$	62
cis-$Mo(CO)_4[P(C_6H_5)_3]_2$	79
$Mo(CO)_5[As(C_6H_5)_3]$	84

Substitution of one carbonyl of $Mo(CO)_6$ by triphenylphosphine results in a modest reduction in the yield of chloro ester. However, triphenylarsinemolybdenum pentacarbonyl is a better catalyst than either $Mo(CO)_6$ or $(C_6H_5)_3PMo(CO)_5$ for ring-opening tetrahydrofuran. The disubstituted carbonyl, *cis*-$[(C_6H_5)_3P]_2Mo(CO)_4$, is as effective a catalyst as $Mo(CO)_6$. On the basis of the generally accepted σ-donor and π-acceptor abilities of the ligands, the Mo–C bond strength should decrease in the order *cis*-$Mo(CO)_4[P(C_6H_5)_3]_2 > (C_6H_5)_3PMo(CO)_5 > (C_6H_5)_3AsMo(CO)_5 > Mo(CO)_6$. As in the trend observed within the parent group VI carbonyls, the catalyst effectiveness does not correlate with the metal–carbon bond strength order.

Stereochemistry of the Reaction.—(+)-2-Ethoxyoctane, (−)-menthyl methyl ether, and 3β-ethoxycholest-5-ene were each treated with acetyl chloride in the presence of $Mo(CO)_6$ in order to gain some insight into the stereochemistry and mechanism of the reaction. Comparison[17] of the optical rotation of 2-chlorooctane, obtained from (+)-2-ethoxyoctane, with the values for pure (+)- and (−)-2-chlorooctane showed that this reaction proceeds with net inversion of configuration, although some racemization does occur. The optical purity of the formed (−)-2-chlorooctane was 75%.

The $Mo(CO)_6$-catalyzed reaction of (−)-menthyl methyl ether and acetyl chloride in refluxing hexane gave a 2:1 ratio of menthyl to neomenthyl chloride (73% yield). Hence this ether cleavage reaction occurs with overall retention of configuration. Isomeric menthenes were also isolated, and no doubt produced but not isolated were the low-boiling by-products, methyl acetate and methyl chloride. Menthyl acetate, formed by cleavage of the methyl C–O bond of the reactant ether, was isolated in 10% yield. All of the products were identified by comparison with authentic materials.

It is worthwhile noting that essentially the same ratio of menthyl to neomenthyl chloride was obtained using *n*-butyl chloride instead of CH_3COCl in $Mo(CO)_6$-catalyzed thermal reaction with (−)-menthyl methyl

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(15) H. Alper and E. C. H. Keung, *J. Org. Chem.*, **37**, 2566 (1972).

(16) C. H. Bamford and W. R. Maltman, *Trans. Faraday Soc.*, **62**, 2823 (1966).

(17) (a) E. D. Hughes, F. Juliusberger, S. Masterman, B. Topley, and J. Weiss, *J. Chem. Soc.*, 1525 (1935); (b) E. D. Hughes, C. K. Ingold, and S. Masterman, *ibid.*, 1196 (1937); (c) H. M. R. Hoffmann, *ibid.*, 1249 (1964).

ether. Furthermore, the same results were obtained when the reaction was repeated under room temperature photolytic (2537 Å) rather than thermal conditions. In fact, the photoreaction is apparently at least as useful as the thermal process for effecting the ether–acid halide reaction. Another illustrative example is the formation of 4-chlorobutyl acetate in 80% yield (78% thermal reaction) by irradiation of a hexane solution of tetrahydrofuran and acetyl chloride in the presence of a catalytic quantity of $Mo(CO)_6$. No 4-chlorobutyl acetate was isolated when the photolysis was carried out in the absence of $Mo(CO)_6$. 4-Chlorobutyl acetate was also formed using $(C_6H_5)_3PMo(CO)_5$ as the catalyst and conducting this irradiation at 3000 Å.

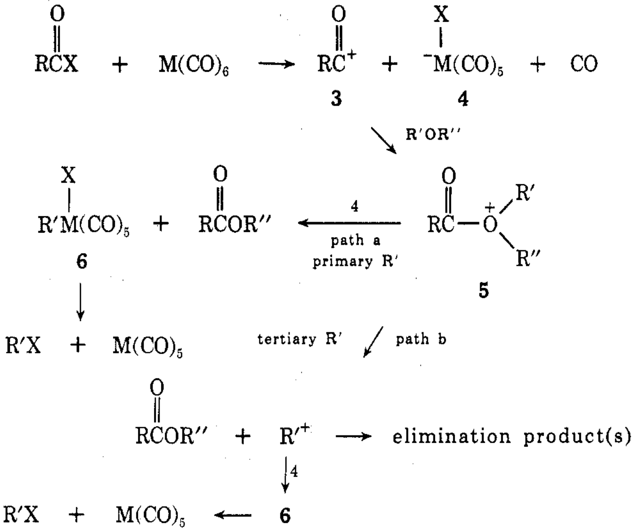
Complete retention of configuration was observed using 3β-ethoxycholest-5-ene as the reactant ether. 3β-Chlorocholest-5-ene was isolated in high yield, accompanied by a small amount of cholesta-3,5-diene.

Mechanism.—Extensive work by Bamford, *et al.*,[5,16] on the oxidation of $Mo(CO)_6$ and other metal carbonyls by several organic halides (*e.g.*, CCl_4) has established the generation of halo alkyl radicals in these reactions. A radical mechanism is apparently not operative in the $M(CO)_6$ [M = Cr, Mo, W] catalyzed ether–acid halide reaction owing to insensitivity of the reaction to oxygen and to a radical initiator. Specifically, treatment of THF with acetyl chloride in hexane in the presence of $Mo(CO)_6$ proceeded qualitatively at the same rate and gave the same product yield whether the reaction was executed under a nitrogen atmosphere, in air, or with added azobisisobutyronitrile.

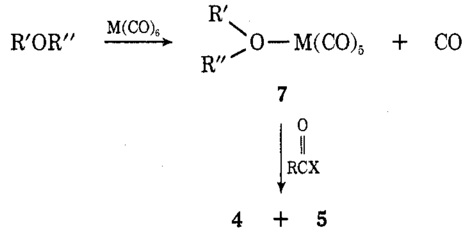
The disappearance of the ir carbonyl stretching absorption of the acid halide and/or appearance of the same type of band for the formed ester was followed for most reactions. Qualitatively, the reaction rate decreased in the order tertiary > secondary > primary carbon (*i.e.*, cleavage of a tertiary carbon–oxygen bond is most facile). For example, the time necessary for complete reaction of acetyl chloride [$Mo(CO)_6$ catalyst] with tetrahydrofuran, 2-methyltetrahydrofuran, and 2,2,4,4-tetramethyltetrahydrofuran was 540, 450, and 105 min, respectively. In addition, the yield of elimination products decreased in the order tertiary > secondary > primary for the same three ethers.

An ionic mechanism is proposed for the reaction (Scheme I). Initial acid halide–$M(CO)_6$ interaction would give the alkyl or aryloxocarbenium[18] ion (**3**) and metal pentacarbonyl halide anion (**4**).[19] Addition of an ether to **3** would give **5**. For primary and some secondary R′, R″ groups in **5**, SN2 type displacement by **4** (path a) would give the ester and the alkylated pentacarbonyl halide (**6**), which would collapse to organic halide and metal pentacarbonyl. Disproportionation of the latter would regenerate $M(CO)_6$. Alternatively, $M(CO)_6$ may add initially generated CO (dissolved) to give $M(CO)_6$. When **5** contains tertiary or some secondary R′, R″ groups, SN1 type cleavage (path b) would likely occur to give the ester and a carbenium ion, the latter undergoing elimination and/or attack by **4** to eventually produce the alkyl halide.

SCHEME I

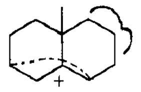


It is also conceivable that $M(CO)_6$ initially interacts with an ether to give **7**[20,21] which could then form **4**



and **5** by reaction with acid halide (**5** would then react *via* path a or b of Scheme I). Unsuccessful attempts were made to isolate, in a pure state, substitution products of type **7** by irradiation of tetrahydrofuran and either $Mo(CO)_6$ or $(C_6H_5)_3PMo(CO)_5$. Similar results have been noted by other investigators.[20,21]

Scheme I can account for the (a) reactivity pattern of the ether carbons (tertiary > secondary > primary); (b) tendency to form elimination products (tertiary > secondary > primary R'^+); (c) effect of halogen (a metal–fluorine bond would be most difficult to break in **4** or **6**); and (d) some of the stereochemical results. Concerning the latter, solvolysis of cholesteryl *p*-toluenesulfonate (carbenium ion generation) and related reactions of cholesteryl derivatives[22] proceed with complete retention of configuration owing to participation of the 5,6-double bond (**8**). Complete retention observed in the 3β-ethoxycholest-5-ene–CH_3COCl–$Mo(CO)_6$ reaction is in accord with these other results and hence suggests the occurrence of pathway b (Scheme I).



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It was previously noted that (−)-2-chlorooctane, of 75% optical purity, was obtained by reaction of

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(18) G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).

(19) E. W. Abel, I. S. Butler, and J. G. Reid, *J. Chem. Soc.*, 2068 (1963).

(20) I. W. Stolz, G. R. Dobson, and R. K. Sheline, *Inorg. Chem.*, **2**, 323 (1963).

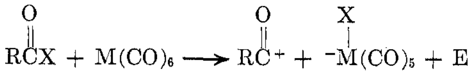
(21) P. H. Pettit, Jr., Ph.D. Thesis, Lehigh University, Bethlehem, Pa., 1969.

(22) (a) S. Winstein and R. Adams, *J. Amer. Chem. Soc.*, **70**, 838 (1948); (b) S. Winstein and A. H. Schlesinger, *ibid.*, **70**, 3528 (1948); (c) C. W. Shoppee, *J. Chem. Soc.*, 1147 (1946).

(+)-2-ethoxyoctane with CH_3COCl and $Mo(CO)_6$. In a definitive paper on solvolysis reactions at secondary carbon atoms, Weiner and Sneen[23] reported that optically pure 2-octyl brosylate, on solvolysis in a 75% dioxane–25% water mixture, gave inverted 2-octanol of 77% optical purity. Here, dioxane participates as a nucleophile in reaction with the brosylate, a process quite analogous to addition of (+)-2-ethoxyoctane to **3**. In Weiner and Sneen's system, the intermediate undergoes displacement by SOH while in the acid halide reaction, displacement occurs on **5** by **4** (path a).

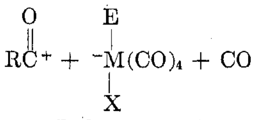
Smith and Wright[24] were able to convert (−)-menthol into retained menthyl chloride of reasonably high optical purity by reaction with Lucas reagent. Huckel and Pietrzok[25] had earlier shown that the same conversion, effected by phosphorus pentachloride, in the presence of ferric or aluminum chloride, also proceeded with partial retention of configuration. These reactions likely occur by an SNi type mechanism. It is possible that an analogous process could take place in the (−)-menthyl methyl ether reaction. Another possibility is that pathways a and b are occurring simultaneously and that the "equatorial"[26] carbenium ion formed *via* path b undergoes preferential equatorial attack by **4**.

When Group VA substituted metal carbonyls are employed as catalysts, either CO or E[16] [E = $P(C_6H_5)_3$ or $As(C_6H_5)_3$] displacement could occur in the first step in Scheme I.



$$R\overset{O}{\overset{\|}{C}}X + M(CO)_6 \longrightarrow R\overset{O}{\overset{\|}{C}}{}^+ + {}^-\overset{X}{\overset{|}{M}}(CO)_5 + E$$

or



$$R\overset{O}{\overset{\|}{C}}{}^+ + {}^-\underset{X}{\underset{|}{\overset{E}{\overset{|}{M}}}}(CO)_4 + CO$$

E = $P(C_6H_5)_3$, $As(C_6H_5)_3$

Anions of different nucleophilicities [*e.g.*, $(C_6H_5)_3AsMo(CO)_4X^- > {}^-MoX(CO)_5$] would accompany CO or E generation. Consequently, the direction of cleavage (E and/or CO) may govern the efficiency of the catalyst.

Since **4** is a proposed intermediate of the ether–acid halide reaction, $(n\text{-}C_4H_9)_4N^+Mo(CO)_5Br^-$ was prepared[21] and used as a catalyst for the neat reaction of benzoyl bromide with tetrahydrofuran. 4-Bromobutyl benzoate was formed in 83% yield, similar to the yield of halo ester (88%) obtained under identical reaction conditions using $Mo(CO)_6$ as the catalyst. Therefore, **4** appears to be an intermediate in the reaction. It may be generated from acid halide or **7**, possibly itself serving as a source for $Mo(CO)_6$ by disproportionation.

We can offer no rationalization for the order of catalytic effectiveness [$Mo(CO)_6 > W(CO)_6 > Cr(CO)_6$].

Experimental Section

General.—Infrared spectra (ir) were recorded using a Perkin-Elmer 457 or 521 infrared spectrometer. Nuclear magnetic resonance spectra were recorded on Varian Associates A-60 or HA-100 spectrometers, with tetramethylsilane as internal standard. Optical rotations were determined using a sodium D line polarimeter. Irradiation experiments were carried out in a Rayonet photochemical reactor at 2537 or 3000 Å. Elemental analyses were performed by Par-Alexander Labs, S. Daytona, Fla., Meade Microanalytical Laboratory, Amherst, Mass., and PCR, Inc., Gainesville, Fla. Melting points were determined using Fisher-Johns melting point apparatus and are uncorrected. Boiling point measurements are also uncorrected.

Solvents were purified by standard techniques. All liquid ethers were dried using lithium aluminum hydride (except tetrahydrofuran, where sodium and benzophenone were used). After fractional distillation from the drying agent, the ether was percolated through a column of Woelm neutral alumina (activity grade I). Acid halides were distilled from $MgSO_4$. Chromium hexacarbonyl was purchased from Pressure Chemical Co. Climax Molybdenum Co. provided molybdenum and tungsten hexacarbonyls. Starting materials which were not commercially available were prepared as follows.

(+)-2-Ethoxyoctane.—Finely cut sodium (6.25 g) was added to a stirred solution of naphthalene (32.00 g, 0.25 mol) in dry 1,2-dimethoxyethane (250 ml). The solution was stirred for 2 hr, followed by addition of (+)-2-octanol (34.10 g, 0.30 mol). Ethyl bromide (32.70 g, 0.30 mol) was added dropwise to the mixture at *ca.* 5°. The solution was stirred at room temperature overnight. The solvent was removed by flash evaporation, water was added to the residue, and the product was extracted with ethyl ether. The ether extract was dried over anhydrous $MgSO_4$. The residue obtained by removal of ethyl ether was treated with 12 g of phthalic anhydride to react with any unreacted alcohol (the mixture was heated for 8 hr). Distillation of the oil gave (+)-2-ethoxyoctane (9.50 g, 23% yield), bp 45–48° (4.5 mm) [lit.[27] bp 57–58° (10 mm)]; $[\alpha]^{23}{}_D$ +17.80° (C_2H_5OH, 2.510 g/100 ml) (lit.[17b] $[\alpha]^{20}{}_D$ +17.10°).

(−)-Menthyl Methyl Ether.—The ether, bp 82–84° (12 mm), $[\alpha]^{23}{}_D$ −96.6° [lit.[28] bp 83° (12 mm), $[\alpha]^{25}{}_D$ −95.6°], was prepared from (−)-menthol in 82% yield following the procedure of Tarbell and Paulson.[28]

Triphenylphosphine Molybdenum Pentacarbonyl.—A mixture of triphenylphosphine (10.03 g, 38.3 mmol) and $Mo(CO)_6$ [11.62 g, 88.0 mmol] in dry diglyme (100 ml) was refluxed with stirring under nitrogen for 4 hr. The mixture was cooled, and the solvent was distilled under reduced pressure. The crude product was chromatographed on Florisil using methylene chloride as the eluent. Recrystallization from chloroform–petroleum ether (bp 38–52°) gave 12.47 g (65%) of $(C_6H_5)_3PMo(CO)_5$, mp 134.5–135.5° (lit.[29] mp 138–139°). The ir spectrum was in accord with that reported by Magee, *et al.*[29]

Triphenylarsine Molybdenum Pentacarbonyl.—A mixture of triphenylarsine (6.13 g, 20.0 mmol) and $Mo(CO)_6$ (6.07 g, 23.0 mmol) in diglyme (50 ml) was refluxed with stirring under nitrogen for 4.5 hr. The reaction mixture was worked up as for triphenylphosphine molybdenum pentacarbonyl (except for the use of 1:1 chloroform–benzene as chromatographic eluent), and the product was recrystallized from petroleum ether. White crystals, mp 143–145°, of triphenylarsine molybdenum pentacarbonyl were obtained in 65% yield, ir ν_{CO} (hexane) 2080 (s), 1990 (m), 1955 (vs), and 1925 cm^{-1} (sh).

***cis*-Bis(triphenylphosphine)molybdenum Tetracarbonyl.**—A mixture of triphenylphosphine (5.20 g, 17.0 mmol), $Mo(CO)_6$ (2.03 g, 7.70 mmol), and sodium borohydride (0.8 g) in methanol was refluxed for 4 hr. The reaction mixture was then stirred overnight at room temperature. The solution was filtered and the crystals were washed several times with water and finally with ethanol. Recrystallization from methylene chloride–ethanol gave 1.25 g (22%) of product, mp 155° dec. The product

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was assigned the cis configuration on the basis of its ir spectrum[30] [ν_{CO} (CH_2Cl_2) 2025 (s), 1910 (vs), 1885 cm^{-1} (sh)]. No trans isomerr was isolated in contrast to the claim by Chatt and coworkers[31] that *only* the trans isomer is produced following essentially the same procedure.

Tetrabutylammonium Bromopentacarbonyl Molybdenate(0).—The yellow salt was prepared in 80% yield following the general procedure described by Abel, Butler, and Reid.[19] The salt decomposed at 90° (lit.[21] mp 91° dec), ir [(ν_{CO} (CH_2Cl_2)] 2070 (w), 1930 (vs), 1850 cm^{-1} (m) [lit.[21] ν_{CO} ($CHCl_3$) 2063, 1927, 1854 cm^{-1}].

Reaction of Acetyl Chloride with 2-Methyltetrahydrofuran in the Presence of $M(CO)_6$ (M = Cr, Mo, W).—A mixture of 2-methyltetrahydrofuran (31.0 mmol), acetyl chloride (32.2–34.0 mmol), and $Mo(CO)_6$ (2.3 mmol) in hexane (40 ml) was refluxed for 20 hr. The mixture was cooled and concentrated using a flash evaporator. Metal hexacarbonyl was removed by sublimation. Fractional distillation of the sublimation residue gave (a) 4-chloropentyl acetate (80% yield), bp 135–136° (65 mm) [lit.[32] bp 82° (10 mm)]; ir ν_{CO} (CCl_4) 1736 cm^{-1}; nmr (CCl_4) δ 4.06 (m, 3 H, >CHCl and $-CH_2O-$), 1.97 (s, 3 H, CH_3COO-), and 1.49 (d, 3 H, CH_3CClH-); (b) 3-pentenyl acetate (7% yield), bp 105–108° (78 mm) [lit.[33] bp 48° (12 mm)]; ir ν_{CO} (CCl_4) 1741 cm^{-1}; nmr (CCl_4) δ 5.43 (m, 2 H, $CH{=}CH-$), 4.01 (t, 2 H, $-OCH_2-$), 2.07 (s, 3 H, CH_3COO-). The results using $Cr(CO)_6$ and $W(CO)_6$ as catalysts are given in Table II.

Reaction of Benzoyl Chloride with 2-Methyltetrahydrofuran in the Presence of $M(CO)_6$ (M = Cr, Mo, W).—A mixture of 2-methyltetrahydrofuran (46 mmol), benzoyl chloride (36 mmol), and metal carbonyl (2.3 mmol) was refluxed in hexane (35 ml) for 60 hr. The solvent and unreacted ether were removed under reduced pressure, while sublimation recovered $M(CO)_6$. Fractional distillation gave (a) 4-chloropentyl benzoate, bp 129–132° (0.45 mm); ir ν_{CO} (neat) 1716 cm^{-1}; nmr (CCl_4) δ 3.8–4.5 (m, 3 H, >CHCl and $-CH_2O-$), 1.8 (m, 4 H, the remaining methylene protons), 1.47 (d, 3 H, CH_3CHCl-) (*Anal.* Calcd for $C_{12}H_{15}ClO_2$: C, 63.57; H, 6.67. Found: C, 62.98; H, 6.47); (b) 3-pentenyl benzoate, bp 103.5–106.0° (0.55 mm); ir ν_{CO} (CCl_4) 1718 cm^{-1}; nmr (CCl_4) δ 5.46 (m, 2 H, $-CH{=}CH-$), 4.27 (t, 2 H, $-CH_2O-$), δ 2.42 (m, 2 H, $-CH_2CH{=}CH-$), and 1.62 (m, 3 H, $CH_3CH{=}CH-$) (*Anal.* Calcd for $C_{12}H_{14}O_2$: C, 75.79; H, 7.37. Found: C, 75.88; H, 7.05).

Thermal and Photolytic Reactions of Acetyl Chloride with Tetrahydrofuran in the Presence of $Mo(CO)_6$.—The reaction was carried out as described for 2-methyltetrahydrofuran (reflux 23 hr in hexane) to give 4-chlorobutyl acetate: bp 59–60° (1.8 mm) [lit.[34] bp 92–93° (22 mm)]; ir ν_{CO} (neat) 1740 cm^{-1}; nmr (CCl_4) δ 4.05 (s, 2 H, $-CH_2O-$), 3.55 (t, 2 H, CH_2Cl), 1.99 (s, $COCH_3$). A 42% yield of 4-chlorobutyl acetate has been reported when the reaction was carried out in the absence of a catalyst.[34]

An 80% yield of 4-chlorobutyl acetate was obtained by irradiation of a hexane solution of the CH_3COCl–THF–$Mo(CO)_6$ mixture at 2537 Å for 28 hr at room temperature. Repetition of the photoreaction in the absence of $Mo(CO)_6$ gave no 4-chlorobutyl acetate.

Reaction of Cyclohexanecarboxylic Acid Chloride with Tetrahydrofuran in the Presence of $M(CO)_6$ (M = Cr, Mo, W).—A mixture of the acid chloride (15.5 mmol) and $M(CO)_6$ (1.14 mmol) in THF (25 ml) was refluxed for 18 hr. The solution was cooled and filtered, and unreacted tetrahydrofuran was removed from the filtrate by flash evaporation at room temperature. Distillation at 1.3 mm gave 4-chlorobutyl cyclohexanecarboxylate: bp 139–141°; ir ν_{CO} (neat) 1735 cm^{-1}; nmr (CCl_4) δ 4.06 (t, 2 H, CH_2O), 3.55 (t, 2 H, $-CH_2Cl$), 2.25 (m, 1 H, $>CHC({=}O)O$), and 1.20–2.00 (m, 10 H, methylene protons of cyclohexane ring). *Anal.* Calcd for $C_{11}H_{19}ClO_2$: C, 60.40; H, 8.76. Found: C, 60.22; H, 9.05. Halo ester yields are given in Table II. In the absence of a catalyst, a reaction run under identical conditions gave a 9% yield of 4-chlorobutyl cyclohexane carboxylate.

Reaction of Acetyl Chloride with 2,2,4,4-Tetramethyltetrahydrofuran in the Presence of $Mo(CO)_6$.—Reaction and work-up following the procedure used for 2-methyltetrahydrofuran gave a 2:1 mixture (based on nmr) of (a) 2,2,4-trimethyl-4-pentenyl acetate and (b) 2,2,4-trimethyl-3-pentenyl acetate (72% total yield): bp 78–79° (13 mm) [lit.[35] bp (a) 71.5–73.0° (10 mm), lit.[36] bp (b) 69.0–70.0° (9 mm)]; ir ν_{CO} (neat) 1710 cm^{-1}; nmr (CCl_4) δ 5.06 (m, 2 H, olefinic proton of b), 4.87 and 4.63 (m, 2 H, olefinic protons of a), 3.83 [s, 2 H, $-CH_2O$ (b)], 3.76 [s, 2 H, $-CH_2O$ (a)]. A mass spectrum showed the expected fragments.

Reaction of 2,5-Dihydrofuran with Acetyl Chloride in the Presence of $M(CO)_6$ (M = Cr, Mo, W).—A mixture of 2,5-dihydrofuran (2.42 g, 34.6 mmol), acetyl chloride (5.50 g, 70.0 mmol), and $M(CO)_6$ (2.7 mmol) was refluxed in hexane (20 ml) for 20 or 36 hr (Table II). Metal hexacarbonyl was precipitated in a Dry Ice–acetone bath and filtered. The filtrate was evaporated under reduced pressure. Distillation of the residue at 8 mm afforded 4-chloro-2-butenyl acetate: bp 85–86° [lit.[37] bp 82.0–84.5° (9 mm)]; ir ν_{CO} (CCl_4) 1744 cm^{-1}; nmr (CCl_4) δ 5.78 (m, 2 H, olefinic protons), 4.63 (m, 2 H, $-CH_2O-$), 4.14 (m, 2 H, CH_2Cl), 2.01 (s, 3 H, CH_3CO-).

Reaction of Acetyl Chloride and 7-Oxabicyclo[2.2.1]heptane in the Presence of $M(CO)_6$ (M = Cr, Mo, W).—The hexane or isooctane solution containing the acid chloride, the ether, and metal hexacarbonyl was allowed to react and worked up following the procedure described for 2-methyltetrahydrofuran. One or both of the following products were obtained: (a) *trans*-4-chlorocyclohexyl acetate, bp 133.0–135.0° (40 mm) [lit.[38] bp 83.5–83.7° (4.5 mm)]; ir ν_{CO} (neat) 1736 cm^{-1}; nmr (CCl_4) δ 4.75 (m, 1 H, >CHO–), 4.05 (m, 1 H, >CHCl), 1.96 (s, 3 H, $CH_3C{=}O$), and 1.3–2.4 (m, 8 H, methylene protons); (b) 3-cyclohexenyl acetate, bp 112–114° (40 mm) [lit.[39] bp 75° (25 mm)]; ir ν_{CO} (neat) 1730 cm^{-1}; nmr (CCl_4) δ 5.58 (m, 2 H, olefinic protons), 4.87 (m, 1 H, >CHO–), and 1.96 (s, 3 H, $CH_3C{=}O$). The product yields are given in Table II.

Reaction of Benzoyl Chloride and 7-Oxabicyclo[2.2.1]heptane in the Presence of $M(CO)_6$ (M = Cr, Mo, W).—The procedure for 2-methyltetrahydrofuran was followed. Distillation at 0.15 mm afforded 3-cyclohexenyl benzoate: bp 93–95° [lit.[40] bp 149–150° (12 mm)]; ir ν_{CO} (neat) 1713 cm^{-1}; nmr (CCl_4) δ 5.62 (m, 2 H, olefinic protons), 5.21 (q, 1 H, >CHO), 1.6–2.5 (m, 6 H, methylene protons). *Anal.* Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.97. Found: C, 77.53; H, 6.87.

The distillation residue was chromatographed on Florisil. Elution with petroleum ether and subsequent recrystallization gave *trans*-4-chlorocyclohexyl benzoate: mp 52.5–54.0°; ir ν_{CO} (KBr) 1708 cm^{-1}; nmr (CCl_4) δ 5.04 (m, 1 H, >CHO–), 4.08 (m, 1 H, >CHCl), 1.5–2.5 (m, 8 H, methylene protons). *Anal.* Calcd for $C_{13}H_{15}ClO_2$: C, 65.39; H, 6.33. Found: C, 65.64; H, 6.32. Pertinent data for these reactions are given in Table II.

Reaction of Benzoyl Bromide with 7-Oxabicyclo[2.2.1]heptane in the Presence of $Mo(CO)_6$.—A mixture of benzoyl bromide (3.70 g, 20.0 mmol), ether (2.16 g, 22.0 mmol), and $Mo(CO)_6$ (1.9 mmol) in isooctane (25 ml) was refluxed for 16 hr. Work-up of the reaction in the usual manner gave (a) *trans*-4-bromocyclohexyl benzoate (72% yield), mp 63.5–64.0° [lit.[41] bp 170° (1 mm)]; ir ν_{CO} (KBr) 1714 cm^{-1}; nmr (CCl_4) δ 5.05 (m, 1 H, >CHO), 4.25 (m, 1 H, >CHBr), and 1.3–2.4 (methylene protons) (*Anal.* Calcd for $C_{13}H_{15}BrO_2$: C, 55.15; H, 5.34; Br, 28.22. Found: C, 55.24; H, 5.21; Br, 28.55); (b) 3-cyclohexenyl benzoate (13% yield).

Reaction of Benzoyl Fluoride and 7-Oxabicyclo[2.2.1]heptane in the Presence of $M(CO)_6$ (M = Cr, Mo, W).—Under standard conditions, $Mo(CO)_6$ as catalyst gave 3-cyclohexenyl benzoate in 67% yield. No reaction occurred when $Cr(CO)_6$ or $W(CO)_6$ were employed as catalysts.

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Reaction of Benzoyl Chloride and 2,3-Dihydropyran in the Presence of $Mo(CO)_6$.—A mixture of benzoyl chloride (4.36 g, 31.0 mmol), dihydropyran (3.87 g, 46.0 mmol), and $Mo(CO)_6$ (2.3 mmol) in hexane (40 ml) was refluxed for 3 days. The solution was cooled and filtered, and the filtrate was evaporated *in vacuo* to remove solvent and unreacted ether. The residue from evaporation could not be distilled at temperatures as high as 230° and a pressure of 0.2 mm. Intense ir absorption was observed at 1720 cm^{-1} (neat), presumably due to a carbonyl stretching vibration. The nmr spectrum (CCl_4) gave only a broad singlet absorption at δ 4.2. The product seemed to be polymeric.

Reaction of Acetyl Chloride and 1,4-Thioxane in the Presence of $Mo(CO)_6$.—A mixture of 1,4-thioxane (3.23 g, 31.0 mmol), acetyl chloride (2.85 g, 36.3 mmol), and $Mo(CO)_6$ (8.14 g, 31.0 mmol) in hexane (30 ml) was refluxed under nitrogen for 84 hr. Unreacted $Mo(CO)_6$ was removed by filtration. The filtrate was concentrated under reduced pressure. The residue was dissolved in ether–petroleum ether, filtered, and chromatographed on Florisil (under N_2). Elution with ether gave a very air-sensitive yellow solid,[21,42] ir ν_{CO} (neat) 2075 (m), 1940 (s), 1920 cm^{-1} (sh). Under catalytic conditions, thioxane–molybdenum pentacarbonyl was also produced along with recovered starting materials.

Reaction of Acetyl Chloride with *n*-Butyl Phenyl Ether in the Presence of $Mo(CO)_6$.—Using standard reaction (24 hr) and work-up conditions, trace amounts of *o*- and/or *p*-*n*-butoxyacetophenone were obtained.

Reaction of Benzoyl Chloride and *n*-Butyl Ether in the Presence of $Mo(CO)_6$.—A mixture of benzoyl chloride (4.36 g, 31.0 mmol) and $Mo(CO)_6$ (2.3 mmol) in *n*-butyl ether (25 ml) was refluxed for 16 hr. Fractional distillation afforded the unreacted ether and 4.02 g (73%) of *n*-butyl benzoate, bp 120° (4 mm) (lit.[43] bp 250.3°). The ir and nmr spectra of the product were identical with spectra for authentic material. No attempt was made to isolate *n*-butyl chloride.

Reaction of Ethyl Triphenylmethyl Ether and Benzoyl Chloride in the Presence of $Mo(CO)_6$.—Standard reaction conditions gave, on work-up, ethyl benzoate in 72% yield and triphenylmethyl chloride. Identification was made by comparison with authentic samples.

Reaction of Benzoyl Chloride with Benzoin Methyl Ether in the Presence of $Mo(CO)_6$.—Methyl benzoate (37% yield) and desyl chloride were obtained by treating benzoyl chloride (10 mmol), benzoin methyl ether (10 mmol), and $Mo(CO)_6$ (1.3 mmol) in refluxing isooctane (25 ml) for 48 hr.

Reaction of Acetyl Chloride with Tetrahydrofuran in the Presence of $Mo(CO)_5E$ [$E = P(C_6H_5)_3$ or $As(C_6H_5)_3$] or *cis*-$Mo(CO)_4[P(C_6H_5)_3]_2$.—A mixture of acetyl chloride (3.93 g, 50.0 mmol), tetrahydrofuran (2.16 g, 30.0 mmol), and group VA substituted molybdenum carbonyl (2.0 mmol) in hexane (30 ml) was refluxed for 22–23 hr. The solution was filtered, and the filtrate was evaporated at *ca.* 30 mm. Distillation of the residue from evaporation of the filtrate gave 4-chlorobutyl acetate. See Table III for yields using different catalysts. 4-Chlorobutyl acetate was also obtained when the reaction [$(C_6H_5)_3PMo(CO)_5$ as catalyst] was effected photolytically at 3000 Å.

Reaction of Acetyl and Benzoyl Chlorides with (+)-2-Ethoxyoctane in the Presence of $Mo(CO)_6$.—Reaction (acetyl chloride) in hexane (20 hr) under standard conditions gave ethyl acetate, 2-octene (31%), and (−)-2-chlorooctane (62%), bp 61.0–63.0° (14 mm) [lit.[43] bp 75° (28 mm)], $[\alpha]_D$ −23.5° (ethanol). Using benzoyl chloride as the acid chloride and isooctane as solvent (24 hr) gave the same three products. Yields are given in Table I.

Reaction of Acetyl Chloride with (−)-Menthyl Methyl Ether in the Presence of $Mo(CO)_6$.—A mixture of acetyl chloride (2.34 g, 30.0 mmol), (−)-menthyl methyl ether (2.55 g, 15.1 mmol), and $Mo(CO)_6$ (1.2 mmol) was refluxed in hexane (20 ml) for 24 hr. The solution was cooled and flash evaporated, and $Mo(CO)_6$ was recovered by sublimation. The residue was chromatographed on Florisil. Elution with petroleum ether and subsequent distillation afforded (a) menthenes, bp 62.0–65.0° (4.9 mm) (lit.[43] bp 168°); nmr (CCl_4) δ 5.33 and 5.50 (m, 2 H, olefinic protons); (b) menthyl and neomenthyl chloride (1.85 g, 73%), bp 53–55° (4.9 mm) (lit.[24] bp 101.0–101.5° (21 mm)]. The nmr spectrum of the mixture was superimposable with the spectra published by Glaze and Selman[44] for menthyl and neomenthyl chlorides. Based on nmr integration, the ratio of menthyl to neomenthyl chloride is 2:1.

Elution with ether gave menthyl acetate to (0.22 g, 10%) which was identified by comparison of physical properties with those of authentic material prepared by treating (−)-menthol with acetyl chloride.

Reaction of *n*-Butyryl Chloride with (−)-Menthyl Methyl Ether in the Presence of $Mo(CO)_6$.—Menthene, menthyl and neomenthyl chlorides, and menthyl *n*-butyrate were obtained following the previous procedure. The ratio of menthyl to neomenthyl chloride was 2:1. Menthyl *n*-butyrate was identified by comparison with an authentic sample prepared by treating (−)-menthol with *n*-butyryl chloride.

A 2:1 ratio of menthyl to neomenthyl chloride also resulted when the same reaction was effected photolytically (2537 Å, hexane solution, 41 hr).

Reaction of 3β-Ethoxycholest-5-ene and Acetyl Chloride in the Presence of $Mo(CO)_6$.—A mixture of the steroidal ether (4.15 g, 10.0 mmol), acetyl chloride (1.26 g, 16.0 mmol), and $Mo(CO)_6$ (0.8 mmol) in hexane (20 ml) was refluxed with stirring for 21 hr. The solution was cooled and flash evaporated at room temperature, and $Mo(CO)_6$ was recovered by sublimation. The sublimation residue was chromatographed on Florisil. Elution with petroleum ether gave a small amount of cholesta-3,5-diene, mp 77.5–79.0° (lit.[43] mp 80°). Elution with benzene gave 4.01 g of crude 3β-chlorocholest-5-ene, which was recrystallized from ethanol to give pure material, mp 95–96° (lit.[43] mp 96°), identical with an authentic sample.

Reaction of Benzoyl Bromide with Tetrahydrofuran in the Presence of $Mo(CO)_6$ or $(C_4H_9)_4N^+Mo(CO)_5Br^-$.—A mixture of benzoyl bromide (5.55 g, 30.0 mmol) and metal carbonyl (5 mmol) in tetrahydrofuran (12 ml) was heated at 60° for 23 hr. After standard work-up, 4-bromobutyl benzoate, bp 128–130° (1.5 mm) [lit.[34] bp 155–157° (9 mm)], was isolated in 88% yield using $Mo(CO)_6$ and in 83% yield using $(C_4H_9)_4N^+Mo(CO)_5Br^-$: ir ν_{CO} (neat) 1723 cm^{-1}; nmr (CCl_4) δ 4.25 (m, 2 H, $-CH_2O$), 3.38 (t, 2 H, CH_2Br), and 1.89 (m, 4 H, other methylene protons).

Registry No.—$Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_5[P(C_6H_5)_3]$, 14971-42-7; $Mo(CO)_5[As(C_6H_5)_3]$, 19212-22-7; *cis*-$Mo(CO)_4[P(C_6H_5)_3]_2$, 16742-93-1; $(C_4H_9)_4N^+Mo(CO)_5Br^-$, 32592-48-6; CH_3COCl, 75-36-5; C_6H_5COCl, 98-88-4; $C_6H_{11}COCl$, 2719-27-9; C_6H_5COBr, 618-32-6; C_6H_5COF, 455-32-3; tetrahydrofuran, 109-99-9; 2-methyltetrahydrofuran, 96-47-9; 2,2,4,4-tetramethyltetrahydrofuran, 3358-28-3; 4-chloropentyl acetate, 36978-15-1; 3-pentenyl acetate, 36978-16-2; 4-chloropentyl benzoate, 36978-17-3; 3-pentenyl benzoate, 36978-18-4; 4-chlorobutyl acetate, 6962-92-1; 4-chlorobutyl cyclohexanecarboxylate, 36978-20-8; 2,2,4-trimethyl-4-pentenyl acetate, 3420-44-8; 2,2,4-trimethyl-3-pentenyl acetate, 4194-23-4; 2,5-dihydrofuran, 1708-29-8; 4-chloro-2-butenyl acetate, 35125-19-0; 7-oxabicyclo[2.2.1]heptane, 279-49-2; *trans*-4-chlorocyclohexyl acetate, 19556-77-5; 3-cyclohexenyl acetate, 10437-78-2; 3-cyclohexenyl benzoate, 36978-27-5; *trans*-4-chlorocyclohexyl benzoate, 36978-28-6; *trans*-4-bromocyclohexyl benzoate, 36994-52-2; 2,3-dihydropyran, 110-87-2; 1,4-thioxane, 15980-15-1; *n*-butyl phenyl ether, 1126-79-0; *n*-butyl ether, 142-96-1; ethyl triphenylmethyl ether, 968-39-8; benzoin methyl ether, 3524-62-7; (+)-2-ethoxyoctane, 36978-30-0; (−)-2-chlorooctane, 18651-57-5; (−)-menthyl methyl ether, 1565-76-0; *n*-butyl chloride, 141-75-3; 3β-ethoxycholest-5-ene, 986-19-6; 4-bromobutyl benzoate, 36978-34-4.

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Acknowledgments.—This research was supported by grants from the Petroleum Research Fund, administered by the American Chemical Society, and from the Research Foundation of the State of New York. We are pleased to acknowledge gifts of generous quantities of molybdenum and tungsten hexacarbonyls from Climax Molybdenum Co. We are grateful to Ms. R. Cartmell for running spectra on the Varian HA-100 nmr spectrometer. We are indebted to Mr. E. C. H. Keung for carrying out some preliminary experiments.

Selective Metalations of Methylated Pyridines and Quinolines. Condensation Reactions[1a]

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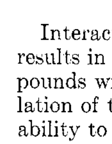
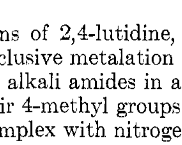
Received July 27, 1972

Interactions of 2,4-lutidine, 2,4,6-collidine, and 2,4-dimethylquinoline with *n*-butyllithium in ether–hexane results in exclusive metalation of their 2-methyl groups. In contrast, treatment of these active hydrogen compounds with alkali amides in ammonia or with lithium diisopropylamide in ether–hexane gives exclusive metalation of their 4-methyl groups. Such differences are interpreted in terms of metallic cations and their relative ability to complex with nitrogen atoms, either of the heterocycles or of the solvent or coreagent. Similar selective metalations are not realized on 2,6- or 2,7-dimethylquinolines, presumably because of lack of resonance delocalization of carbanions on the 6- and 7-methyl groups, respectively. All of the carbanions formed, particularly those on the 4-methyl groups, have been condensed with various electrophiles in fair to excellent yields.

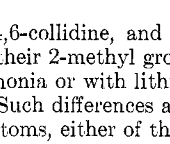
2- and 4-picolyl organometallic reagents, prepared from interaction of the parent picolines with a variety of bases, have been studied rather extensively.[2a,b] However, the related carbanions derived from 2,4-lutidine (**1a**) and 2,4,6-collidine (**1b**) have but rarely been prepared and their reactions are thus relatively unknown. For example, 2-lithiomethyl derivatives **2a,b** have been obtained in a few cases by treatment of **1a,b** with lithiohydrocarbons like phenyllithium; subsequent condensations with various carbonyl compounds are known.[3a-c] On the other hand, 4-alkalimethyl derivatives **3a,b** have been realized only upon treatment of **1a,b** with alkali metal amides in liquid ammonia.[4a,b] Compound **3a** has been methylated in unspecified yield,[4a] and both **3a,b** have been nitrated by alkyl nitrates in good yields to afford the corresponding nitromethyl derivatives.[4b]



1a, R = H
b, R = CH_3



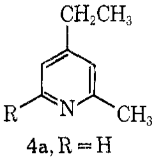
2a, R = H
b, R = CH_3



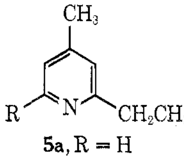
3a, R = H
b, R = CH_3

However, the picture is far from clear, as illustrated by the report by Chichibabin that **1b** is converted to **2b**, not **3b**, by various alkali metal amides.[5] Thus, our involvement with compounds **1a,b** arose not only because of the paucity of data on the 4-lutidyl (**3a**) and 4-collidyl (**3b**) anions, but also on our initial skepticism (and confusion) concerning the above purported different sites of metalation within these molecules (4-methyl *vs.* 2-methyl) as a function of the base (alkali amides *vs.* organolithiums). To our knowledge, such a remarkable dependence upon base had previously not been recognized. Usually, of course, ionization of molecules containing more than a single kind of similarly activated hydrogen atom has resulted in the same hydrogen atom being abstracted regardless of the base employed, though the relative rates of reaction have often been different.

First, to unequivocally ascertain the site of metalation as a function of the base, **1a,b** were allowed to react with three different base systems and the resulting carbanions were subsequently identified by condensations with certain electrophiles. Thus, interaction of **1a,b** with sodium or potassium amides in liquid ammonia (method A) or with lithium diisopropylamide in ether (or THF)-hexane (method B) afforded the 4-alkali methyl derivatives **3a,b** since methylation with methyl iodide gave methylethylpyridines **4a,b** respectively. Similar treatment of **1a,b** with *n*-butyllithium in ether–hexane (method C) gave the 2-metallomethyl derivatives **2a,b**, since methylation afforded the isomeric methylethylpyridines, **5a,b** respectively. Incidentally, authentic **4b** was prepared by an unequivocal ring closure, thereby providing a standard compound for nmr spectroscopic determinations of other structures.



4a, R = H
b, R = CH_3



5a, R = H
b, R = CH_3

Methods A and B were then employed to synthesize various other substituted pyridines arising from alkylation of the 4-methyl groups of **1a,b**. Thus, **3a** was *n*-propylated, *n*-butylated, and benzylated to

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[1] (a) Supported in part by the Petroleum Research Fund, administered by the American Chemical Society, on Grant 3710-A, and by the National Science Foundation on Grant GY-7281; (b) NSF Undergraduate Research Participant.

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