Dehalogenation and Condensation Reactions of Molybdenum Carbonyls with Activated Halides

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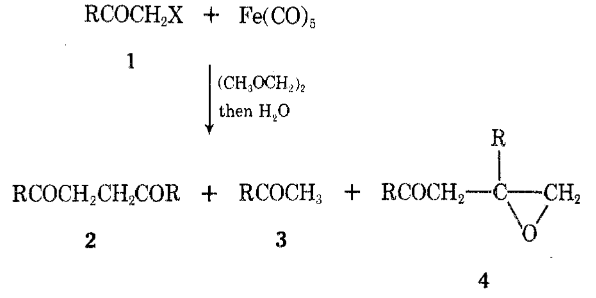
Received August 19, 1975

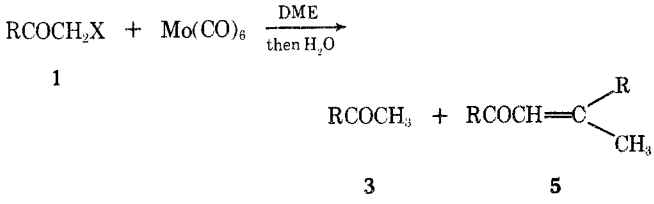
Molybdenum hexacarbonyl reacts with α-halo ketones in 1,2-dimethoxyethane to form monoketones and α,β-unsaturated carbonyls in generally good combined yields. Triphenylphosphine molybdenum pentacarbonyl and tetrabutylammonium pentacarbonyl molybdenate(0) are also useful reagents, but chromium and tungsten hexacarboxyls exhibit low reactivity toward α-halo ketones. Coupling products were obtained by treatment of dichlorodiphenylmethane or 9-bromofluorene with $Mo(CO)_6$.

Reaction of iron pentacarbonyl with α-halo ketones (**1**) affords 1,4-diketones (**2**), monoketones (**3**), and, in several instances, β-epoxy ketones (**4**). 1,4-Diketones were usually the major products of these reactions. Evidence has been presented for initial oxidative addition of the trigonal bipyramidal $Fe(CO)_5$ by the α-halo ketone to give an octahedral intermediate.[1] It was of considerable interest to learn the effect of metal carbonyl configuration on the reaction course. Oxidative addition to octahedral group 6 metal carbonyls such as molybdenum hexacarbonyl [$Mo(CO)_6$] is a much less common process than for $Fe(CO)_5$, since formation of a neutral seven-coordinate intermediate would be required for $Mo(CO)_6$. Rather, treatment of certain halides with $Mo(CO)_6$ under stoichiometric or catalytic conditions results in the generation of radical (from CCl_4, CBr_4, $CCl_3COOC_2H_5$)[2] or ionic (from RCOCl)[3] intermediates. We now wish to report that α-halo ketones react in a different, and interesting, manner with group 6 metal carbonyls as compared to $Fe(CO)_5$.



Results and Discussion

Monoketones (**3**) and α,β-unsaturated ketones (**5**) were obtained by treatment of α-halo ketones with an equimolar amount of $Mo(CO)_6$ in refluxing 1,2-dimethoxyethane (DME, 48 hr) and then with water. The yields, melting points of new compounds, and pertinent spectral data for the reaction products are given in Table I.

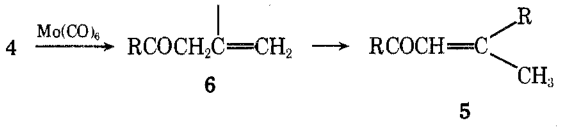


$$\underset{\mathbf{1}}{\mathrm{RCOCH_2X}} + \mathrm{Mo(CO)_6} \xrightarrow[\text{then } \mathrm{H_2O}]{\text{DME}} \underset{\mathbf{3}}{\mathrm{RCOCH_3}} + \underset{\mathbf{5}}{\mathrm{RCOCH{=}C(R)CH_3}}$$

The α-halo ketone–$Mo(CO)_6$ reaction afforded the methyl ketone as the major or only product, except for **1**, R = $p\text{-}NO_2C_6H_4^-$, which gave the chalcone **5**, R = $p\text{-}NO_2C_6H_4$, as the major product. The other group 6 metal carbonyls, chromium hexacarbonyl and tungsten hexacarbonyl, were much less reactive than $Mo(CO)_6$ giving low conversions even after reaction times of 6 days with 2-chloro-2′,3′,4′,5′,6′-pentamethylacetophenone. However, treatment of the latter with triphenylphosphine molybdenum pentacarbonyl resulted in the formation of pentamethylacetophenone in 76% yield.

There are several important differences in the behavior of iron and molybdenum carbonyls toward α-halo ketones: (1) monoketones (**3**), usually the major products formed using $Mo(CO)_6$, were generally obtained as minor products with $Fe(CO)_5$; (2) coupling to 1,4-diketones is the major reaction pathway for $Fe(CO)_5$, while $Mo(CO)_6$ affords α,β-unsaturated carbonyls and no 1,4-diketones; (3) the $Mo(CO)_6$–**1** reaction can be effected in the presence of a nitro group, while such a functionality undergoes reduction on treatment with $Fe(CO)_5$;[4] (4) substitution of a carbon monoxide ligand by triphenylphosphine in the reactant $Mo(CO)_6$ results in increased product yields, while α-halo ketones were inert to triphenylphosphine iron tetracarbonyl.[1]

The different reactivity patterns, products, and product distributions for the iron and molybdenum carbonyl–α-halo ketone reactions suggest that these reactions are likely occurring via different pathways. However, the mechanistic details, for the group 6 metal carbonyl reactions, are not clear. It seemed conceivable that the α,β-unsaturated ketones (**5**) could arise by deoxygenation of a β-epoxy ketone (**4**) to the β,γ-unsaturated ketone **6**, followed by isomerization to **5**. The major reaction pathway, however, for epoxide–$Mo(CO)_6$ reactions is rearrangement rather than deoxygenation.[5] Conversion of an α-halo ketone such as **1**, R = $p\text{-}C_6H_5C_6H_4^-$, to **3** and **5** was also observed using tetrabutylammonium bromopentacarbonyl molybdenate [$(C_4H_9)_4N^+Mo(C)_5Br^-$]. The latter did not effect aldol condensation of **3** to **5**.[8]



$$\mathbf{4} \xrightarrow{\mathrm{Mo(CO)_6}} \underset{\mathbf{6}}{\mathrm{RCOCH_2C(R){=}CH_2}} \longrightarrow \underset{\mathbf{5}}{\mathrm{RCOCH{=}C(R)CH_3}}$$

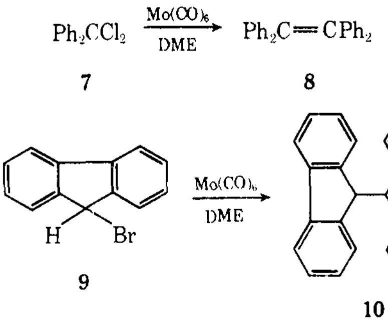
Molybdenum hexacarbonyl did effect coupling of several other types of activated halides. Tetraphenylethylene (**8**) was formed in 65% yield by treatment of dichlorodiphenylmethane (**7**) with $Mo(CO)_6$. No chlorodiphenylmethane, diphenylmethane, or 1,2-dichloro-1,1,2,2-tetraphenylethane was isolated in this reaction. Tetraphenylethylene was also obtained by treatment of 1,2-dichloro-1,1,2,2-tetraphenylethane with $Mo(CO)_6$. Iron pentacarbonyl also reacts with **7** or with 1,2-dichloro-1,1,2,2-tetraphenylethane to give tetraphenylethylene.[1]

Treatment of 9-bromofluorene (**9**) with $Mo(CO)_6$ gave bisfluorenyl (**10**) in 40% yield, but no fluorene. The lack of

Table I. Products Obtained from Reaction of Group 6 Metal Carbonyls with α-Halo Ketones in DME[a]

α-Halo ketone (1)	Registry no.	Metal carbonyl	Registry no.	Products[b]	Registry no.	New compd mp,[c] °C	Yield, %	Ir, ν_{CO},[d] cm^{-1}	NMR (CH_3),[e] δ, p.p.m.	MS, m/e, M+
2-Bromo-4′-phenylacetophenone	135-73-9	$Mo(CO)_6$	13939-06-5	3, R = p-$C_6H_5C_6H_4$	92-91-1		51	1685	2.60	196
				5, R = p-$C_6H_5C_6H_4$	57196-64-2	196–197	16	1650	2.56	374
2-Chloro-2′,3′,4′,5′,6′-pentamethylacetophenone	57196-63-1	$Mo(CO)_6$		3, R = 2,3,4,5,6-$(CH_3)_5C_6$	2040-01-9		51	1680	2.44	190
				5, R = 2,3,4,5,6-$(CH_3)_5C_6$	57196-65-3	177–178	<1	1662		362
		$W(CO)_6$	14040-11-0	3, R = 2,3,4,5,6-$(CH_3)_5C_6$			12[f]			
		$Cr(CO)_6$	13007-92-6	None						
		$(C_6H_5)_3PMo(CO)_5$	14971-42-7	3, R = 2,3,4,5,6-$(CH_3)_5C_6$			76			
2,4′-Dibromoacetophenone	99-73-0	$Mo(CO)_6$		3, R = p-BrC_6H_4-	99-90-1		25	1683	2.58	
				5, R = p-BrC_6H_4-	7509-25-3		14	1655	2.54	380
2-Bromo-4′-methoxyacetophenone	2632-13-5	$Mo(CO)_6$		3, R = p-$CH_3OC_6H_4$-	100-06-1		46	1678	2.54	150
				5, R = p-$CH_3OC_6H_4$-	16197-83-4		18	1652	2.51	282
2-Bromo-4′-nitroacetophenone	99-81-0	$Mo(CO)_6$		3, R = p-$NO_2C_6H_4$-	100-19-6		20	1682	2.67	165
				5, R = p-$NO_2C_6H_4$-	7509-21-9		26	1660	2.70	312
1-Adamantyl bromomethyl ketone	5122-82-7	$Mo(CO)_6$		3, R = 1-adamantyl	1660-04-4		14	1712	2.07	
				5, R = 1-adamantyl	57196-66-4	185–186	6	1680	1.97	338

[a] 1:1 ratio of $Mo(CO)_6$:1. Reaction time of 48 hr. [b] Satisfactory (±0.4%) analytical (C, H) data were obtained for new compounds. [c] The melting point or boiling point and spectral data for known products were in good agreement with literature data. [d] Chloroform as solvent. [e] $CDCl_3$–Me_4Si as internal standard. [f] Reaction time of 6 days. after 48 hr reaction, 3, R = 2,3,4,5,6=$(CH_3)_5C_6$, was formed in 2% yield.



formation of fluorene indicates that 9 (and 7) are generating different intermediates than those produced in α-halo ketone–$Mo(CO)_6$ reactions. For 9 and 7, halogen atom transfer may be occurring to form a radical, which then undergoes coupling.[2]

Experimental Section

General. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were carried out by Drs. F. and E. Pascher, Bonn, West Germany, and by Galbraith Laboratories Inc., Knoxville, Tenn. Infrared spectra were obtained on a Beckman IR20A spectrometer. NMR spectra were obtained on a Varian T-60 spectrometer, with tetramethylsilane used as the internal standard. Mass spectra were recorded on a Varian MS902 spectrometer.

We are grateful to the Climax Molybdenum Co. for providing generous quantities of molybdenum hexacarbonyl. This metal carbonyl was sublimed prior to use. Tungsten and chromium hexacarbonyls were purchased from Pressure Chemical Co. and used as received. Mr. C. C. Huang supplied us with a sample of triphenylphosphine molybdenum pentacarbonyl.[3] The organic reactants were commercial products and were recrystallized or distilled prior to use. Solvents were dried and purified by standard techniques. All reactions were run under an atmosphere of dry nitrogen.

Reaction of $Mo(CO)_6$ with α-Halo Ketones. A mixture of the α-halo ketone (8–10 mmol) and an equimolar amount of $Mo(CO)_6$, in dry DME (40–70 ml), was heated with stirring at 85–90° (oil bath temperature) for 48 hr. The solution was cooled and filtered (inorganic material) into 200–350 ml of ice water. The resulting precipitate was filtered and dried. Work-up was effected for the particular reactions as follows (see Table I for yields and pertinent physical data for the products).

A. 1 (R = p-$C_6H_5C_6H_4$). Continuous extraction (Soxhlet) of the solid with petroleum ether (bp 30–60°) afforded the methyl ketone 3, R = p-$C_6H_5C_6H_4$. The α,β-unsaturated ketone 5, R = p-$C_6H_5C_6H_4$, was isolated by treatment of the Soxhlet residue with chloroform, filtration, and evaporation of the filtrate.

B. 1 (R = 2′,3′,4′,5′,6′-$(CH_3)_5C_6$). Compound 3, R = 2,3,4,5,6-$(CH_3)_5C_6$, was obtained by continuous extraction of the precipitate with petroleum ether. Extraction of the residue in the thimble with ether or ether–chloroform gave a trace amount of 5, R = 2,3,4,5,6-$(CH_3)_5C_6$.

C. 1 (R = p-BrC_6H_4-). Continuous extraction of the solid with petroleum ether gave 3, R = p-BrC_6H_4-. The nonextractable material was then continuously extracted with chloroform to give 5, R = p-BrC_6H_4. Pure 5 was obtained by recrystallization from petroleum ether–benzene.

D. 1 (R = p-$CH_3OC_6H_4$-). Extraction of the aqueous filtrate (no precipitate formed here) with ether gave an oil which was chromatographed on Florisil. Elution with benzene–petroleum ether gave 3, R = p-$CH_3OC_6H_4$. Elution with benzene or benzene–chloroform (4:1) afforded pure 5, R = p-$CH_3OC_6H_4$.

E. 1 (R = p-$NO_2C_6H_4$-). The milky aqueous filtrate was extracted with ether, dried (Na_2SO_4), and evaporated to give a yellow semisolid. p-Nitroacetophenone (3, R = p-$NO_2C_6H_4$) was obtained by treating the semisolid mixture with 100 ml of petroleum ether–benzene (1:1) and decanting the solution, which was then evaporated in vacuo. Crystallization of the petroleum ether–benzene insoluble oil from hexane afforded 5, R = p-$NO_2C_6H_4$.

F. 1 (R = 1-Adamantyl). The solid was dissolved in petroleum ether and chromatographed on Florisil. Elution with petroleum ether–benzene (2:1) gave 3, R = 1-adamantyl. Elution with benzene afforded the unsaturated carbonyl 5, R = 1-adamantyl.

Reaction of 2-Chloro-2′,3′,4′,5′,6′-pentamethylacetophenone with $W(CO)_6$. A mixture of 1, R = pentamethylphenyl (1.80 g, 8.00 mmol), and W(CO)$_6$ (2.81 g, 8.00 mmol) in DME (40 ml) was heated to 90° for 48 hr. Work-up as described for the reaction of the same α-chloro ketone with Mo(CO)$_6$ gave **3**, R = pentamethylphenyl, in 2% yield, along with recovered starting materials. Using a reaction time of 6 days resulted in the formation of methyl ketone in 12% yield.

Reaction of 2-Chloro-2′,3′,4′,5′,6′-pentamethylacetophenone with Triphenylphosphine Molybdenum Pentacarbonyl. A DME (60 ml) solution of $(C_6H_5)_3PMo(CO)_5$ (2.611 g, 5.20 mmol) and α-chloro ketone (1.17 g, 5.20 mmol) was heated at 85–90° for 46 hr. The solution was cooled and filtered into ice–water. The resulting precipitate was filtered and dried. Continuous extraction of the solid with petroleum ether gave reasonably pure methyl ketone [$(C_6H_5)_3PMo(CO)_5$ as impurity] which could be furthur purified by column chromatography on Florisil using petroleum ether as eluent. No α,β-unsaturated carbonyl was obtained by treatment of the nonextractable material with ether–chloroform.

Reaction of 2-Bromo-4′-phenylacetophenone with Tetrabutylammonium Pentacarbonyl Molybdenate(0). A mixture of tetrabutylammonium pentacarbonyl molybdenate(0)[6] (0.918 g, 2.10 mmol) and 2-bromo-4′-phenylacetophenone (0.578 g, 2.10 mmol) in DME (45 ml) was heated at 90° for 48 hr. The reaction mixture was worked up as described in procedure A to give **3** and **5**, R = p-$C_6H_5C_6H_4$.

Reaction of Dichlorodiphenylmethane (7) with Mo(CO)$_6$. A mixture of dichlorodiphenylmethane (1.90 g, 8.00 mmol) and Mo(CO)$_6$ (4.20 g, 16.0 mmol) in dry DME (40 ml) was heated at 85–90° for 48 hr. The solution was cooled and poured into cold water. The resulting solid was filtered to give crude tetraphenylethylene (**8**). Chromatography of the latter on silica gel, using benzene as eluent, gave 0.864 g (65%) of pure **8**: mp 223.5–225.0° (lit.[1] mp 226–227°); mass spectrum m/e 332 (M$^+$).

Reaction of 1,2-Dichloro-1,1,2,2-tetraphenylethane with Mo(CO)$_6$. A mixture of 1,2-dichloro-1,1,2,2-tetraphenylethane (2.02 g, 5.00 mmol) and Mo(CO)$_6$ (2.37 g, 9.00 mmol) in DME (40 ml) was heated at 85–90° for 42. hr. Work-up as described for **7** gave tetraphenylethylene in 81% yield.

Reaction of 9-Bromofluorene with Mo(CO)$_6$. A solution of 9-bromofluorene (2.14 g, 8.60 mmol) and Mo(CO)$_6$ (2.29 g, 8.65 mmol) in DME (30 ml) was heated at 90–95° for 45 hr. The solution was cooled and filtered (inorganic) into ice water to give a white solid which was subsequently filtered. Recrystallization from benzene–ethanol gave 0.580 g (40%) of bisfluorenyl (**10**), mp 246–248° (lit.[7] mp 246°). Spectral data for **10** were in accord with data for authentic material.

Acknowledgments. We are grateful to the National Research Council of Canada for support of this work. We are indebted to Messrs. Jake Blair and Raj Capoor for mass spectral and NMR spectral determinations, respectively.

Registry No.—**7**, 2051-90-3; **8**, 632-51-9; **9**, 1940-57-4; tetrabutylammonium bromopentacarbonyl molybdenate, 32592-48-6; 1,2-dichloro-1,1,2,2-tetraphenylethane, 1600-30-2.

References and Notes

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(8) **Note Added in Proof.** Methylmanganese pentacarbonyl has recently been shown to induce aldol condensation of benzyl methyl ketone [R. L. Bennett and M. I. Bruce, *Aust. J. Chem.*, **28**, 1141 (1975)].

Kinetics of the Reaction of n-Butyllithium with 4-Methylmercaptoacetophenone in Benzene[1]

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Received August 13, 1975

Kinetics of the reaction of 4-methylmercaptoacetophenone (**2**) with excess n-butyllithium in benzene at 25.0 °C have been studied by ir and uv stopped-flow spectrophotometric techniques. The observed first-order rate constant increases rapidly as the concentration of n-butyllithium is increased from 0.014 to ca. 0.1 M, but the rate is not greatly enhanced by further increases in the concentration of alkyllithium. The rate of the reaction is increased by the presence of alkoxides in the alkyllithium reagent; addition of 0.001 M of the product alcohol to 0.1 M n-butyllithium increases the measured first-order rate constant by a factor of about 2. Some mechanistic implications of these observations are outlined.

The reaction of the ketone 2,4-dimethyl-4′-methylmercaptobenzophenone (**1**) with methyllithium in diethyl ether has been shown[2] to be first order in ketone and one-fourth order in methyllithium. These data are consistent with a mechanism for addition proceeding through monomer in equilibrium with tetrameric methyllithium. Other examples of reactions occurring through monomeric organolithium, which is in equilibrium with higher aggregates in ethereal solvents, include the addition of n-butyllithium[3] and phenyllithium[3] to benzonitrile, the addition of methyllithium to transition metal carbonyls,[4] the initiation of vinyl polymerization,[5,6] and the metalation of triphenylmethane.[7] The addition of alkyllithium reagents to styrene[8–10] and to 1,1-diphenylethylene[11,12] in aromatic solvents is also believed to proceed through monomeric species; however, for the addition of n-butyllithium to butadiene[13] and ethyllithium to 1,1-diphenylethylene[14] in aromatic solvents, monomer may not be the sole reactive species. In aliphatic solvents, alkyllithium reagent aggregates species appear to react with isoprene[15–17] and ethylene.[18]

The addition of lithium halides to diethyl ether solutions of methyllithium has been shown[2] to retard the rate of addition to ketone **1**. This is the expected result because the incorporation of lithium halides into methyllithium aggregates lowers the fraction of the organolithium present in monomeric form.[2]

In contrast to the rate-depressing effect of lithium halides in diethyl ether on the addition to ketones, alkoxides have been reported to either increase or decrease the reactivity of alkyllithium reagents in hydrocarbons. For example, the initiation of styrene polymerization in aromatic solvents,[19–21] the propagation of olefin polymerizations,[15,16,19,21,22] and the alkylation of naphthalene[23] are depressed by lithium alkoxides, while in contrast alkoxides