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REACTIONS OF ALKALI METAL DERIVATIVES OF METAL CARBONYLS

XIII*. SOME REACTIONS OF METAL CARBONYL ANIONS WITH DIHALOMETHANES AND RELATED HALIDES

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SUMMARY

Reactions of $ClCH_2I$ with the sodium salts $Na[M(CO)_3C_5H_5]$ ($M = Mo$ and W) in tetrahydrofuran at room temperature give fairly good yields of the corresponding chloromethyl derivatives $ClCH_2M(CO)_3C_5H_5$ ($M = Mo$ and W). A similar reaction of $ClCH_2I$ with the more nucleophilic $Na[Fe(CO)_2C_5H_5]$ gives a rather low yield of the corresponding chloromethyl derivative $ClCH_2Fe(CO)_2C_5H_5$. Reactions of diiodomethane with the sodium salts $Na[M(CO)_3C_5H_5]$ ($M = Mo$ and W) in tetrahydrofuran at room temperature give the very unstable iodomethyl derivatives $ICH_2M(CO)_3C_5H_5$ ($M = Mo$ and W). Reactions of $ClCH_2CH_2I$ with metal carbonyl anions do not give any isolable 2-chloroethyl transition metal derivatives.

INTRODUCTION

Several years ago Green, Ishaq, and Whiteley[2] described the following two-step process for conversion of the metal carbonyl anions $C_5H_5M(CO)_3^-$ ($M = Mo$ and W) and $C_5H_5Fe(CO)_2^-$ to the corresponding halomethyl derivatives $XCH_2M(CO)_3C_5H_5$ (I: $M = Mo$ and W; $X = Cl$ and Br) and $XCH_2Fe(CO)_2C_5H_5$ (II: $X = Cl$ and Br), respectively:

$$NaM(CO)_nC_5H_5 + CH_3OCH_2Cl \rightarrow CH_3OCH_2M(CO)_nC_5H_5 + NaCl$$

$$CH_3OCH_2M(CO)_nC_5H_5 + HX \rightarrow XCH_2M(CO)_nC_5H_5 + CH_3OH$$

The objective of the work described in this paper was to develop a one-step process for conversion of metal carbonyl anions to the corresponding halomethyl derivatives by reactions with appropriately selected methylene halides.

During the past fifteen years[3] reactions of sodium salts of metal carbonyl anions with organic and inorganic halides and other substrates have been carried

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* For Part XII see ref. 1.

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TABLE 1

REACTIONS OF METAL CARBONYL ANIONS WITH DIHALOMETHANES AND DIHALOETHANES

Metal carbonyl anion[a] *(mmoles)*	*Dihaloalkane (mmoles)*	*Reaction time*[b] *(h)*	*Products*[c]
$CpMo(CO)_3^-$ (28)	$ClCH_2I$ (34)	5	$ClCH_2Mo(CO)_3Cp$ (60 to 70%)
$CpW(CO)_3^-$ (40)	$ClCH_2I$ (57)	5	$ClCH_2W(CO)_3Cp$ (60%) + $ICH_2W(CO)_3Cp$ (12%)
$CpFe(CO)_2^-$ (34)	$ClCH_2I$ (57)	$\frac{1}{2}$	$ClCH_2Fe(CO)_2Cp$ (13%)
$Mn(CO)_5^-$ (10.4)	$ClCH_2I$ (20)	5	$Mn_2(CO)_{10}$ (~30%)
$CpMo(CO)_3^-$ (41)	CH_2Br_2 (64)	5	$[CpMo(CO)_3]_2$ + trace $CpMo(CO)_3Br$
$CpMo(CO)_3^-$ (28)	CH_2I_2 (40)	$\frac{1}{4}$	$ICH_2Mo(CO)_3Cp$ (17%)
$CpW(CO)_3^-$ (36)	CH_2I_2 (45)	$\frac{1}{4}$	$ICH_2W(CO)_3Cp$
$CpMo(CO)_3^-$ (53)	$ClCH_2CH_2I$ (60)	$\frac{1}{4}$	$[CpMo(CO)_3]_2$ (~95%) + trace $CpMo(CO)_3X$ (X=Cl, I)
$CpW(CO)_3^-$ (15)	$ClCH_2CH_2I$ (25)	$\frac{1}{2}$	$[CpW(CO)_3]_2$

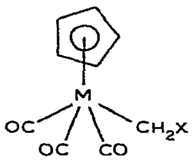
[a] These anions were employed as their sodium salts in tetrahydrofuran solution (see Experimental Section); Cp=cyclopentadienyl. [b] These reactions were carried out at room temperature for the indicated times. [c] The yields of the indicated products are given in parentheses.

out in tetrahydrofuran solution using dichloromethane as the extraction solvent for the crude residue obtained after evaporation of the tetrahydrofuran upon completion of the reaction. No chloromethyl transition metal derivatives were ever obtained from such reactions even in cases where subsequent work showed that the metal carbonyl anion had not reacted with the substrate and thus was still present in the crude mixture being extracted with the dichloromethane. This indicated that dichloromethane was too unreactive to form chloromethyl derivatives with metal carbonyl anions but suggested that a chloromethyl group might be stable in the presence of metal carbonyl anions.

The apparent inertness of carbon–chlorine bonds in dihalomethanes to substitution with metal carbonyl anions still left unanswered the question as to whether the weaker bonds of carbon to the heavier halogens bromine and iodine when present in dihalomethanes could undergo nucleophilic displacement reactions with metal carbonyl anions. The mixed dihalomethane $ClCH_2I$[4] offered a particularly interesting possibility for reactions with metal carbonyl anions in which the carbon–iodine bond is broken but the stronger carbon–chlorine bond is retained thereby providing a direct synthesis of transition metal chloromethyl derivatives according to the following equation:

$$NaM(CO)_nC_5H_5 + ClCH_2I \rightarrow ClCH_2M(CO)_nC_5H_5 + NaI$$

This paper describes the reactions of $ClCH_2I$ as well as a few other methylene halides with the more common metal carbonyl anions.



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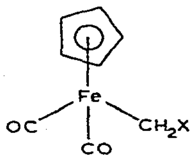

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EXPERIMENTAL

Materials

The sodium salts of the metal carbonyl anions $NaM(CO)_3C_5H_5$ (M = Mo and W), $NaFe(CO)_2C_5H_5$, and $NaMn(CO)_5$ were prepared and handled in tetrahydrofuran solutions under nitrogen using procedures adequately described elsewhere[5,6]. The halides $ClCH_2I$[4] and $ClCH_2CH_2I$[7] were prepared by the cited published procedures.

General procedure for the reactions of metal carbonyl anions with dihalomethanes and dihaloethanes (Table 1)

A freshly prepared tetrahydrofuran solution of the sodium salt of the metal carbonyl anion was stirred with the dihaloalkane at room temperature. The quantities and reaction times are indicated in Table 1. After completion of the reaction the tetrahydrofuran was removed in vacuum at or below room temperature. Nitrogen was admitted to the residue which was then extracted with several portions of pentane until the pentane extracts were no longer colored. Concentration of the pentane extracts in vacuum at room temperature followed by cooling in a −78° bath gave

TABLE 2

A COMPARISON OF THE PROPERTIES OF THE HALOMETHYL COMPOUNDS OF MOLYBDENUM AND TUNGSTEN

Compound	*Infrared spectrum (cm^{-1})*		*^{1}H NMR spectrum (τ (ppm))*		
	Solvent	*ν(CO)*[c]	*Solvent*	*π-C_5H_5*	*CH_2*
$ClCH_2Mo(CO)_3C_5H_5$[a] orange	c-C_6H_{12}	2037, 1961, 1947	CCl_4	4.35	5.78
$BrCH_2Mo(CO)_3C_5H_5$[b]	Nujol	2032, 1945, 1920	CS_2	4.85(?)	6.28
$ICH_2Mo(CO)_3C_5H_5$ yellow	Pentane	2040, 1957, 1938	CCl_4	4.36	7.08
$ClCH_2W(CO)_3C_5H_5$ yellow	c-C_6H_{12}	2026, 1955, 1938	CCl_4	4.40	5.78
$BrCH_2W(CO)_3C_5H_5$[b]	CS_2	2030, 1937	CS_2	4.46	6.14
$ICH_2W(CO)_3C_5H_5$ yellow	c-C_6H_{12}	2031, 1951, 1940	CCl_4	4.35	6.86

[a] M.p. 136–137°. [b] Data of ref. 2. [c] All of the indicated ν(CO) frequencies were strong.

crystals (generally yellow) of the haloalkyl transition metal derivative. The crude product was purified by repeated low temperature crystallizations from pentane. The chloromethyl derivatives $ClCH_2M(CO)_3C_5H_5$ (I) could also be purified by vacuum sublimation at 100°/0.1 mm (M = Mo) or 60°/0.5 mm (M = W). The haloalkyl transition metal derivatives were identified from their infrared and proton NMR spectra (Table 2).

The residues from the pentane extractions contained any bimetallic cyclopentadienylmetal carbonyls {*e.g.* $[C_5H_5M(CO)_3]_2$ (M = Mo and W) and $[C_5H_5Fe(CO)_2]_2$} and cyclopentadienylmetal carbonyl halides formed in the reactions. These residues were extracted with dichloromethane. If more than one transition metal organometallic derivative appeared to be in this dichloromethane solution based on an examination of its infrared ν(CO) frequencies, these components were separated by chromatography on neutral alumina. The compounds $[C_5H_5M(CO)_3]_2$ and $C_5H_5M(CO)_3X$ were identified by their infrared spectra in the ν(CO) region.

DISCUSSION

The reactions of $ClCH_2I$ with the sodium salts $NaM(CO)_3C_5H_5$ (M = Mo and W) gave fairly good yields ($\approx$60%) of the corresponding chloromethyl derivatives $ClCH_2M(CO)_3C_5H_5$ (I: M = Mo and W) arising from selective replacement of the iodine atom in $ClCH_2I$ with the $C_5H_5M(CO)_3$ group. The reaction of $ClCH_2I$ with $NaFe(CO)_2C_5H_5$ also gave some of the corresponding chloromethyl derivative $ClCH_2Fe(CO)_2C_5H_5$, but the yield was much lower ($\approx$13%) apparently owing to the increased possibility for side reactions arising from the extremely high nucleophilicity[8] of $C_5H_5Fe(CO)_2^-$ relative to $C_5H_5M(CO)_3^-$ (M = Mo and W). The reaction of $ClCH_2I$ with $NaMn(CO)_5$ appeared to give only the coupling product $Mn_2(CO)_{10}$. The reactions of $ClCH_2I$ with metal carbonyl anions thus appear to be useful for the preparation of the chloromethyl derivatives $ClCH_2M(CO)_3C_5H_5$ (I: M = Mo and W) but not for the preparation of other chloromethyl derivatives.

Some attempts were made to prepare the haloalkyl derivatives $XCH_2M(CO)_3C_5H_5$ (I: X = Br and I; M = Mo and W) by similar reactions of $NaM(CO)_3C_5H_5$ (M = Mo and W) with other appropriate dihalomethanes. However, reaction of dibromomethane with $NaMo(CO)_3C_5H_5$ gave none of the desired bromomethyl derivative $BrCH_2Mo(CO)_3C_5H_5$. Instead only the coupling product $[C_5H_5Mo(CO)_3]_2$ was obtained. On the other hand, the reactions of diiodomethane with the sodium salts $NaM(CO)_3C_5H_5$ (M = Mo and W) gave the corresponding yellow iodomethyl derivatives $ICH_2M(CO)_3C_5H_5$ (I: X = I; M = Mo and W). These observations suggest that a carbon–iodine bond is necessary for reaction of a dihalomethane with $NaM(CO)_3C_5H_5$ (M = Mo and W) to give the corresponding haloalkyl derivative $XCH_2M(CO)_3C_5H_5$ (I: M = Mo and W).

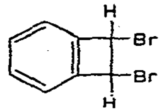
The chloromethyl derivatives $ClCH_2M(CO)_3C_5H_5$ (I: X = Cl; M = Mo and W) and $ClCH_2Fe(CO)_2C_5H_5$ (II: X = Cl) are known compounds and could be unambiguously identified by comparison of their infrared and proton NMR spectra with those given in the literature[2]. The iodomethyl derivatives $ICH_2M(CO)_3C_5H_5$ (I: X = I; M = Mo and W) are new compounds and appear to be the first known compounds containing both a transition metal–carbon σ-bond and a carbon–iodine bond. They formed yellow crystalline solids which began to decompose at room temperature within a few minutes. This decomposition appears to be accelerated by light. This instability of the iodomethyl derivatives $ICH_2M(CO)_3C_5H_5$ at room temperature prevented us from obtaining elemental analyses. However, the following spectroscopic observations (Table 2) make their identification unequivocal:

(1). The pattern of infrared ν(CO) frequencies was similar to that of the other halomethyl derivatives $XCH_2M(CO)_3C_5H_5$ (I: X = Cl and Br; M = Mo and W) as well as other $RM(CO)_3C_5H_5$ compounds.

(2). Their proton NMR spectra exhibited singlet cyclopentadienyl and methylene resonances of the correct relative intensities (5/2). The chemical shift of the methylene resonance in the halomethyls $XCH_2M(CO)_3C_5H_5$ (I: M = Mo and W) increases monotonically from chlorine through bromine to iodine in accord with the expected electronegativity effects.

Several reactions of the chloromethyl derivatives $ClCH_2M(CO)_3C_5H_5$ (I: X = Cl; M = Mo and W) were investigated. Most of these reactions suggested relative inertness to nucleophilic substitution of the carbon–chlorine bonds in these compounds although the instability of these chloromethyl derivatives limited the vigor of the reaction conditions that could be used. Thus the molybdenum compound $ClCH_2Mo(CO)_3C_5H_5$ was recovered unchanged after reaction with either methyllithium or diethylamine at room temperature. However, the molybdenum compound $ClCH_2Mo(CO)_3C_5H_5$ underwent a complex reaction with sodium iodide in acetone solution at room temperature over a two day period to give $C_5H_5Mo(CO)_3I$, $Na[C_5H_5Mo(CO)_3]$, and $ClCH_2I$ identified from the NMR spectra of the reaction mixture. The formation of $Na[C_5H_5Mo(CO)_3]$ and $ClCH_2I$ from this reaction indicates that the molybdenum–carbon bond to the chloromethyl group is more readily attacked by nucleophilic reagents than the carbon–chlorine bond. Our observations as well as the earlier observations of Green, Ishaq, and Whitley[2] indicate that the halomethyl derivatives $XCH_2M(CO)_3C_5H_5$ are unsuited as sources of $CH_2Mo(CO)_3C_5H_5$ groups in synthetic reactions.

The reactions of $ClCH_2CH_2I$ with the sodium salts of metal carbonyl anions gave no evidence for formation of stable 2-chloroethyl transition metal derivatives. Reactions of 1,2-dihaloethanes with metal carbonyl anions [*i.e.* $C_5H_5M(CO)_3^-$ (M = Mo and W) and $C_5H_5Fe(CO)_2^-$] consistently led instead to oxidation of the metal carbonyl anion to the corresponding bimetallic derivative apparently with ethylene evolution. This contrasts with the previously reported[1] reaction of 7,8-dibromobenzocyclobutene (III), effectively a substituted 1,2-dihaloethane, with $NaFe(CO)_2C_5H_5$ to give a stable bimetallic derivative $C_8H_6[Fe(CO)_2C_5H_5]_2$ (IV). However, in the case of the formation of (IV) from (III) and $C_5H_5Fe(CO)_2^-$, the alternate pathway involving oxidation of the metal derivative with concurrent olefin formation is very unfavorable because of the instability of benzocyclobutadiene, the olefin which would be formed from III.



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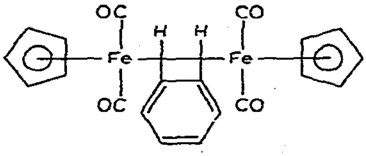

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