

REACTIONS OF *cis*-HYDRIDOTETRACARBONYL(TRIPHENYL-PHOSPHINE)MANGANESE WITH SOME ORGANIC HALOGEN COMPOUNDS

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SUMMARY

The hydride *cis*-HMn(CO)₄PPh₃ is an effective reagent for the reduction of a variety of halogenated organic compounds at room temperature. All the available evidence indicates that these reactions occur by a free radical mechanism.

INTRODUCTION

Transition metal hydrides are well known^{1,2} to react with haloalkanes to give the corresponding metal halide with reduction of the haloalkane. We now describe some observations on the reduction of halogenated organic compounds using *cis*-HMn(CO)₄PPh₃ which throw some light on the mechanism of this type of reaction.

RESULTS AND DISCUSSION

The hydride HMn(CO)₄PPh₃, unlike HMn(CO)₅, is an oxidatively stable solid, convenient to handle, and reasonably soluble in a variety of common organic solvents. Previous work² had shown that this hydride readily reduces CCl₄ to CHCl₃, and this present work has shown that this hydride will also reduce a variety of halogenated compounds under mild conditions (Table 1). These reactions were usually carried out in the dark at room temperature either in a flask under an atmosphere of nitrogen or in a sealed tube *in vacuo*. For reactions carried out in sealed tubes it was difficult to be certain when reaction was complete and the reaction times quoted in the Table probably far exceed the actual time required for complete reaction.

By carrying out a series of competition experiments (Table 2) between the hydride and mixtures of CCl₄/CBr₄, CCl₄/CHBr₃, CHI₃/CHCl₃, and CHCl₃/CH₂Br₂ at room temperature in benzene the order of reactivity for the halomethanes has been found to be C-I > C-Br > C-Cl and CX₄ > CHX₃ > CH₂X₂ > CH₃X (where X = Cl, Br or I). Thus the reactivity increases with decreasing bond dissociation energy of the carbon-halogen bond, so, for example, dichloromethane (C-Cl dissociation energy ca. 76 kcal · mol⁻¹) does not react with the hydride after 10 days at room temperature, whereas chloroform (C-Cl bond dissociation energy ca. 72 kcal · mol⁻¹) does. Although it has not been verified experimentally it is predicted on this basis that the C-F bond will be unaffected under these conditions.

TABLE 1

REACTIONS OF *cis*-HMn(CO)₄PPh₃ WITH HALOGENATED COMPOUNDS

Reactant (mmol)	Hydride (mmol)	Temp. (°C)	Solvent	Time (h)	XMn(CO) ₄ PPh ₃ (% yield) ^a	Product (% yield) ^a
CCl ₄ (64.5)	2.5	20		100	90	CHCl ₃ (100)
CHCl ₃ (73.7)	2.34	20		100	85	CH ₂ Cl ₂ (100)
CHBr ₃ (65.3)	2.43	20		100	100	CH ₂ Br ₂ (100)
CBr ₄ (47.5)	2.70	20	Benzene	100	100	CHBr ₃ (100)
CH ₂ Br ₂ ^b		20		100	100	CH ₃ Br (100)
CHI ₃ ^b		20	Benzene	15 min	100	CH ₂ I ₂ (100)
CH ₃ I (147.0)	2.69	20		24	100	CH ₄ (100)
CF ₃ I (54)	2.33	20		22	86	CHF ₃ (100)
CH ₂ =CHCH ₂ Cl (275)	4.7	20		100	20	CH ₃ CH=CH ₂ (20)
		80		6	75	CH ₃ CH=CH ₂ (96)
CH ₂ =CHCH ₂ Br (197)	4.7	20		100	80	CH ₃ CH=CH ₂ (100)
PhCH ₂ Cl (174)	4.65	70		7	83	PhCH ₃ (100)
CF ₂ BrCF ₂ Br (16)	2.33	20	CH ₂ Cl ₂	8 days	81	CF ₂ BrCF ₂ H (100)
CF ₃ CFBrCF ₂ Br (32)	2.33	20	CH ₂ Cl ₂	8 days	50	CF ₃ CF=CF ₂ (50)
$\begin{array}{c} \text{CH}_2\text{CO} \\ \\ \text{CH}_2\text{CO} \end{array} \text{NBr}$	2.33	20	Acetone/ benzene	24	79	$\begin{array}{c} \text{CH}_2\text{CO} \\ \\ \text{CH}_2\text{CO} \end{array} \text{NH} (69)$
1-bromo-2-butene ^c (25)	4.65	20	Toluene	6 days	70	<i>cis</i> -2-butene (21) <i>trans</i> -2-butene (68) 1-butene (11)
3-bromo-1-butene ^d (4.74)	3.49	20	Toluene	6 days	83	<i>cis</i> -2-butene (45) <i>trans</i> -2-butene (42) 1-butene (13)
CH≡CH ₂ Br (130)	4.65	20		24	80	CH ₃ C≡CH (92) CH ₂ =C=CH ₂ (8)
$\begin{array}{c} \text{CH}_2-\text{CHCH}_2\text{Br} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$	5.16	60		6	57	CH ₂ =CHCH ₂ OH (86)
$\begin{array}{c} \text{CH}_2-\text{CHCH}_3 \\ \diagdown \quad \diagup \\ \text{O} \end{array}$						CH ₂ -CHCH ₃ (< 1)
BrCH ₂ CH=CHCH ₂ Br (4.67)	9.3	20	Toluene	7 days	78	<i>cis</i> -2-butene (42) ^e 1-butene <i>trans</i> -2-butene (58)

^a Based on the hydride taken for the reaction. ^b Not quantitative; yields based on IR spectra only. ^c The starting material consisted of 1-bromo-2-butene (97.2%) and 3-bromo-1-butene (2.8%) as estimated by GLC. ^d The starting material consisted of 1-bromo-2-butene (10.8%) and 3-bromo-1-butene (89.6%) as estimated by GLC. ^e Complete resolution of the peaks due to *cis*-2-butene and 1-butene could not be achieved on the SE 30 GLC column used for this particular analysis, but the fraction was mainly 1-butene.

An attempt has been made to study the kinetics, under *pseudo* first-order conditions, of the reaction of the hydride with some haloalkanes. These reactions were monitored by IR spectroscopy and the results are given in Table 3. A number of peculiar features were apparent. In all the reactions, except that with CH_3I , an induction period of variable length was observed, and this induction period increased in the presence of ethanol.

When the reaction of the hydride with CCl_4 was examined under the same conditions, that is, by mixing the reactants in an IR cell and measuring the spectrum over a period of time, an induction period of ca. 10 min was observed and this was followed by an extremely rapid reaction which was too fast to measure. If, however, the reaction was carried out at 30° in a Pyrex vessel, after an induction period, reaction proceeded smoothly over a period of 5 min and could be measured by recording the spectra of samples withdrawn over this period. The reason for this difference in behaviour is not clear.

TABLE 2

COMPETITION EXPERIMENTS WITH HALOGENATED METHANE DERIVATIVES^a

Reactants (mmol)	Hydride (mmol)	Time (h)	Product (% yield) ^b	
CHI_3 (5.92)	CHCl_3 (29.4)	2.64	24	$\text{IMn}(\text{CO})_4\text{PPh}_3^c$
CCl_4 (11.9)	CBr_4 (11.8)	2.32	100	$\text{BrMn}(\text{CO})_4\text{PPh}_3$ (76)
CCl_4 (15.9)	CHBr_3 (16.0)	2.82	100	$\text{BrMn}(\text{CO})_4\text{PPh}_3$ (80)
CHCl_3 (20.5)	CH_2Br_2 (20.0)	2.53	100	$\text{BrMn}(\text{CO})_4\text{PPh}_3^d$ (50)

^a Reactions were carried out in benzene solvent at room temperature in a darkened flask. ^b Based on the amount of hydride taken. ^c This was the only product formed as indicated by IR spectroscopy but the yield was not recorded. ^d Elemental analysis indicated that this product may have been contaminated with the chloro derivative, but no evidence for this could be obtained from the IR spectrum.

TABLE 3

RATE CONSTANTS FOR THE REACTIONS OF $\text{HMn}(\text{CO})_4\text{PPh}_3$ WITH SOME HALOGENATED METHANE DERIVATIVES

Reactant (mmol)	Hydride (mmol)	Initiation period (min)	$10^{-4} \times k$ (sec^{-1})
CHCl_3 (53.8)	0.26	25	(1) 3.84 (2) 3.97
CHBr_3 (94.1)	0.41	3	36.8
CH_3I (71.5)	0.19		3.07
CHCl_3 (183) + 1% w/w $\text{C}_2\text{H}_5\text{OH}$	0.60	160	2.94
CHCl_3 (28.2) + $\text{C}_2\text{H}_5\text{OH}$ (24.8)	0.23	240	4.48

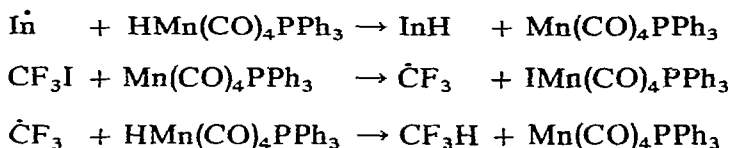
The kinetics of the reaction of the hydride with CCl_4 have also been studied in various solvents (Table 4), but the results were inconclusive. One surprising feature was that the reaction in cyclohexanol occurred at a rate which was too fast to measure. The reduced reaction rates in nitromethane and tetrahydrofuran probably reflect the lower stability of the hydride in these solvents, since separate experiments have shown that the hydride slowly decomposes in both these solvents with a greater rate of decomposition in tetrahydrofuran than in nitromethane. Some peculiar features were also observed when the reaction of CCl_4 was carried out at various temperatures. Up to and including a temperature of 40° good first order plots were obtained, but above this temperature straight line plots were obtained for the initial stages of the reaction and then the rate increased almost exponentially. From the limited data available the activation energy for this reaction was found to be ca. $6 \text{ kcal}\cdot\text{mol}^{-1}$, but obviously too much reliance cannot be placed on this figure.

Although the kinetic data were not very conclusive the general reaction features, namely, the observation of an induction period, the absence of any obvious solvent effects, and the low activation energy, are more in keeping with a radical reaction rather than an ionic or four-centre mechanism. In an attempt to confirm these tentative conclusions the effect of radical inhibitors and initiators on the reaction of the hydride with CCl_4 were investigated. Benzoquinone reacted with the hydride to precipitate an unidentified green solid, whereas Terpene B* appeared to accelerate reaction rather than inhibit it as expected. When a small amount of the radical α,α -diphenylpicrylhydrazyl was added to a solution of the hydride in CCl_4 at room temperature the characteristic violet colour of the radical disappeared after 10 min and the hydride was found to have reacted completely to give *cis*- $\text{ClMn}(\text{CO})_4\text{PPh}_3$. However, in a separate experiment in which the hydrazyl radical was added to a solution of the hydride in benzene (1/1 molar ratio of reactants) it was shown by IR spectroscopy that reaction occurs to give a colourless, unstable complex, but this could not be isolated. The addition of benzoyl peroxide to the reaction mixture of the hydride and CCl_4 did not increase the rate of reaction significantly. However, reaction of the hydride with dichloromethane at 80° in the presence of azobis(isobutyronitrile) gave a 30% yield of *cis*- $\text{ClMn}(\text{CO})_4\text{PPh}_3$ after 8 h; no reaction occurred in the absence of the initiator under identical conditions. Similarly, UV irradiation of a mixture of the hydride and dichloromethane in a quartz cell gave a 30% yield of the chloromanganese complex after 3 h; irradiation for a longer period only resulted in decomposition of the reaction products.

The most convincing evidence that these reactions occur by a radical pathway comes from a study of the products obtained on reaction of the hydride with other organohalogen compounds (Table 1). Reaction of the hydride with CF_3I at room temperature gives $\text{IMn}(\text{CO})_4\text{PPh}_3$ and trifluoromethane. This result is inexplicable on the basis of a four-centre or a bimolecular nucleophilic mechanism, both of which would be expected to give the stable compound $\text{CF}_3\text{Mn}(\text{CO})_4\text{PPh}_3$ and HI. The possibility that $\text{CF}_3\text{Mn}(\text{CO})_4\text{PPh}_3$ may be formed initially but react with HI to give the observed products was checked by monitoring the reaction by IR spectroscopy. As a further check the reaction was repeated using pyridine as a solvent and was found to give identical results. The observed products are, however, consistent with a radical mechanism (Scheme 1).

* A 50/50 mixture of 4-isopropenyl-1-methylcyclohexene and 4-isopropylidene-1-methylcyclohexene.

SCHEME 1

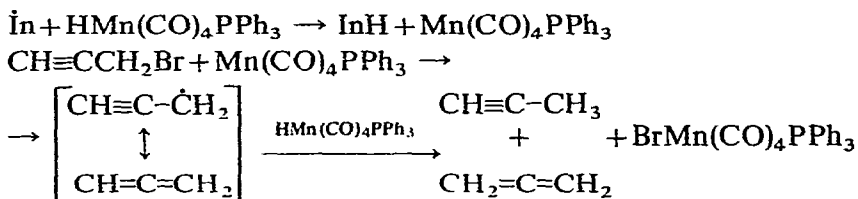


Some evidence in support of this mechanism was obtained by repeating the reaction using methyl methacrylate as a solvent whereupon some polymerisation (0.25%) was found to occur.

Further evidence for a radical mechanism comes from a comparison of the reduction products from 1-bromo-2-butene and 3-bromo-1-butene. It is noticeable that the ratio of 2-butene/1-butene obtained from these reactions is identical within experimental error, although there are some differences in the *cis-trans*-2-butene ratios. Once again this result is incompatible with a four-centre reaction, and can only be explained by an ionic reaction if the ratio $k(S_N2)/k(S_N2')$ for 1-bromo-2-butene is identical to $k(S_N2')/k(S_N2)$ for 3-bromo-1-butene. This is obviously improbable and indeed, Hughes and England³ have shown that for the reaction of LiBr in dry acetone the ratio of the rate constants are widely different.

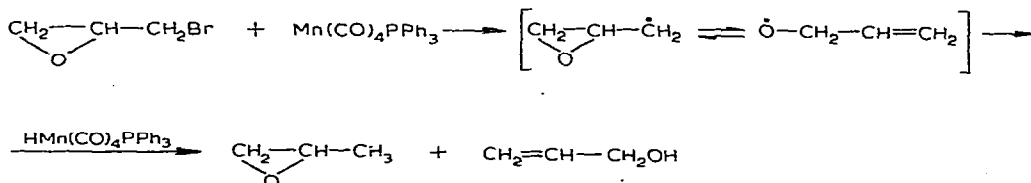
The formation of allene as the minor product from reduction of propargyl bromide is also of interest in that a bimolecular nucleophilic displacement should give the allene as the major reaction product by comparison with the reaction of LiAlH₄ with *n*-C₃H₇CHClC≡CH which is reported⁴ to give *n*-C₃H₇CH=C=CH₂ and *n*-C₃H₇CH₂C≡CH in a ratio of > 7/1. The low yield of allene is explicable by a radical mechanism if the reasonable assumption is made that the canonical form (CH=C=CH₂) makes less contribution to the resonance hybrid than the other major contributing canonical form ($\dot{\text{C}}\text{H}_2\text{C}\equiv\text{CH}$) (Scheme 2); some evidence in support of this assumption has been obtained from the photosensitized decomposition of allene⁵.

SCHEME 2



Similarly, it is difficult to explain the formation of allyl alcohol as the major product from the reduction of epibromohydrin other than by a radical reaction (Scheme 3), since both a four-centre reaction and an S_N2 mechanism would be expected to give mainly propene oxide.

SCHEME 3



Several other minor products were also detected in this last reaction, but they could not be identified. Some of these products were shown to arise by reaction of $\text{BrMn}(\text{CO})_4\text{PPh}_3$ with epibromohydrin while others undoubtedly arose by further reaction of the radical intermediates.

It must be concluded, therefore, that $\text{HMn}(\text{CO})_4\text{PPh}_3$, and most probably other similar transition metal hydrides, react with organic halogen compounds by a free radical mechanism analogous to that postulated to occur in the similar reactions of trialkyltin hydrides⁶.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer model 257 instrument.

GLC analyses were carried out using either a Pye 104 or a Pye 105 instrument. *cis*-Hydridotetracarbonyl(triphenylphosphine)manganese was prepared as reported previously⁷ and purified by repeated chromatography on deactivated alumina using dichloromethane as eluent. 3-Bromo-1-butene and 1-bromo-2-butene were purified by preparative GLC (SE 30 at 50°), and epibromohydrin and propargyl bromide were commercial samples purified by fractional distillation and analysed by GLC; 1,4-dibromo-2-butene was also a commercial sample purified by chromatography on deactivated alumina. All solvents were purified and dried by the standard procedures and deoxygenated before use. Products were identified either by IR spectroscopy alone or for more complex reactions by IR spectroscopy and GLC analysis using DNP, SE 30 or ethylene glycol/silver nitrate columns.

Reactions of the hydride with halomethane derivatives

(a). *Quantitative experiments.* These reactions were carried out in a blackened flask at room temperature under an atmosphere of nitrogen using the quantities given in Table 1. The volatile products were removed under vacuum and analysed by GLC, leaving the halogenomanganese derivative which was washed with light petroleum and in some cases chromatographed before identification by IR spectroscopy.

(b). *Competition experiments.* In a typical experiment carbon tetrachloride (4.0 g, 11.8 mmol) and carbon tetrabromide (1.8 g, 11.8 mmol) in benzene were added to a solution of the hydride (1.0 g, 2.32 mmol) in benzene and the reactants were kept at room temperature under nitrogen in the dark for 100 h. The volatile products were removed under vacuum, and the residual solid washed with light petroleum, and chromatographed on deactivated alumina (25% diethyl ether/light petroleum eluent) to give bromotetracarbonyltriphenylphosphinemanganese (1.14 g, 2.24 mmol, 76%) identified by IR spectroscopy and elemental analysis for C, H and P. The other experiments were carried out in a similar manner and the results are given in Table 2.

(c). *Kinetic experiments.* In some cases the kinetics were followed by placing a solution of the hydride in the haloalkane in an 0.1 mm IR cell at 28° and measuring the disappearance of the highest frequency metal carbonyl band in the spectrum of the hydride: the results of these experiments are given in Table 3.

The kinetics of the reactions with carbon tetrachloride were measured by taking a solution of the hydride in dry, freshly distilled "Analar" carbon tetrachloride under an atmosphere of nitrogen in a blackened flask fitted with a serum-capped side arm. The flask was kept in a thermostatted bath at 30° and samples were withdrawn at

intervals by means of a syringe. The IR spectra of these samples were immediately recorded and the reaction was followed by the disappearance of the highest frequency metal carbonyl band of the hydride and the appearance of a band at 2092 cm^{-1} due to the halogeno complex. The reaction was repeated in various solvents and the results are summarised in Table 4.

TABLE 4

EFFECT OF SOLVENTS ON THE RATE OF REACTION OF CARBON TETRACHLORIDE WITH *cis*-HMn(CO)₄PPh₃

<i>CCl</i> ₄ (mmol)	<i>Hydride</i> (mmol)	<i>Solvent</i> (mmol)	$10^{-7} \times k$ (sec ⁻¹)
0.47	1.43		12.8
0.21	1.41	Benzene (0.21)	13.2
0.21	1.41	Cyclohexanol (0.21)	Instantaneous
0.21	1.46	Nitromethane (0.21)	9.5
0.21	1.46	Tetrahydrofuran (0.22)	3.7

Reaction of the hydride with other halogenated organic compounds

These reactions were all carried out in tubes sealed under vacuum. The volatile reaction products were removed under vacuum, and were separated from unreacted starting material and solvent by fractional distillation *in vacuo* before analysis by GLC. The solid residue was chromatographed and identified by IR spectroscopy.

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