HALOGEN CLEAVAGE REACTIONS OF cis-(threo-PhCHDCHD)Mn(CO)$_4$PEt$_3$

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SUMMARY

Halogen cleavage reactions of cis-(threo-PhCHDCHD)Mn(CO)$_4$PEt$_3$ (3) are
studied in detail and are found to proceed either predominantly with retention
or inversion, or non-stereospecifically, depending on reaction conditions.
Reaction mechanisms involving S_E2 (inversion), S_E2 (retention) and S_E (oxidative)
processes are proposed, demonstrating that halogen cleavage reactions of 3
straddle the mechanistic borderline between electrophilic substitution and
oxidation processes of transition metal alkyl compounds

Reactions in which cleavage of transition metal-carbon σ bonds is induced
by electrophilic reagents such as the halogens (1) and mercury(II) compounds (2)
have long been known [1], and have often been useful as aids in the characterizati
of new alkylmetal compounds

$$RML_n + X_2 \rightarrow RX + XML_n \tag{1}$$

$$RML_n + HgX_2 \rightarrow RHgX + XML_n \tag{2}$$
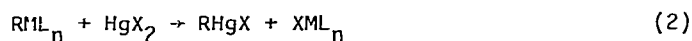
R = alkyl, aryl, X = Cl, Br, I, L = other ligands

Considerable attention has been devoted in recent years to mechanistic
studies of these types of reactions, resulting in the recognition of at least
three major pathways by which an alkylmetal compound may interact with a potential

electrophilic reagent, E   Two of these involve either frontside (**1**) or backside

(**2**) S_E2 attack by E on the α-carbon atom
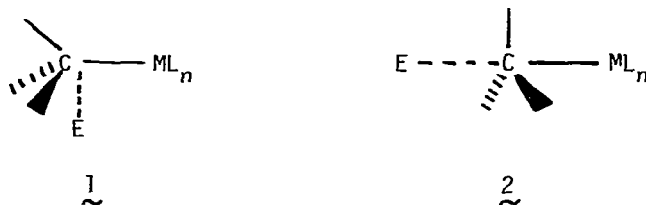
Transition states **1** and **2** result in retention and inversion of configuration

at carbon, respectively, the corresponding mechanisms generally being referred

to as S_E2 (retention) and S_E2 (inversion) [2,3]   Halogens probably cleave alkyl-

mercury [4] and -zirconium [5] compounds by an S_E2 (retention) process, while

mercury(II) compounds appear to cleave alkylcobaloxime compounds by an S_E2

(inversion) process [6-11]   Alkyltin compounds, on the other hand, can be cleaved

by halogens with both retention and inversion of configuration [12-14], indi-

cating that both processes can occur

The third mode of cleavage does not involve the halogen or mercury(II)

behaving as a conventional electrophile, but rather as a one- or two-electron

oxidizing agent   The initial step in halogen cleavage reactions of alkylcobaloximes

$RCo^{III}(DH)_2L$ (R = alkyl group, DH = dimethylglyoximate anion, L = neutral ligand),

for instance, is almost certainly the formation of the cobalt(IV) intermediate,

$[RCo^{IV}(DH)_2L]^+$. Cleavage of the cobalt-carbon bond actually occurs via nucleo-

philic displacement, with inversion of configuration, of the metal from the

α-carbon atom by halide ion [6,7,15-21]   Similar but as yet undefined species

have been implicated in cleavage reactions of compounds of the type $\eta^5\text{-}C_5H_5FeCOLR$

(L = CO, tertiary phosphine) by both the halogens [1,22-24] and mercury(II)

halides [22,24,25]   This general type of reaction will hereafter be referred to

as an S_E(oxidative) process

Stereochemical information has been very important in the elucidation of

the mechanisms of the above reactions, and we have previously utilized the primary

alkyl ligand, _threo_-α,β-dideuterophenethyl (_threo_-PhCHDCHD-) to study the stereo-

chemical changes during a wide variety of alkyl cleavage, transfer and migration

reactions [1,26-28]   In an attempt to further studies of electrophilic cleavage reactions of _cis_-(_threo_-PhCHDCHD)Mn(CO)$_4$PEt$_3$ (3)   A preliminary account of this work has appeared [29]

EXPERIMENTAL

IR spectra were run on a Perkin Elmer 180 Spectrometer, NMR spectra in both CW and FT modes on a Bruker HX60 Spectrometer   Compound 3 was prepared as described in the literature [28], from K[Mn(CO)$_4$PEt$_3$] and _erythro_-PhCHDCHDOTs, while _cis_-PhCH$_2$CH$_2$Mn(CO)$_4$PEt$_3$ labelled at the α-carbon to the extent of 5% with carbon-13 was prepared similarly using labelled tosylate [1], the ^{13}C NMR spectrum exhibits resonances at δ10 9 (d, α-C$\underline{H}_2$, J_{CP} = 11 Hz), δ44 0 (d, β-C$\underline{H}_2$, J_{CP} = 4 Hz), δ18 3 (d, PC$\underline{H}_2$, J_{CP} = 23 Hz), δ7 2 (S, C$\underline{H}_3$), as well as a multiplet in the phenyl region   All solvents were dried and deoxygenated before use
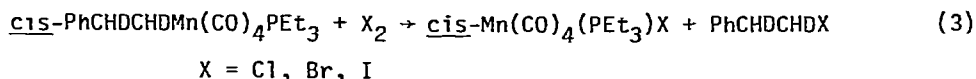
Halogenation reactions were normally carried out by adding a solution of the halogen to a stirred solution of an equimolar amount of 3 under nitrogen at room temperature   The reaction mixtures were generally stirred for 45 min , after which the solvent was removed under reduced pressure   The residue was then dissolved in a small amount of CH$_2$Cl$_2$ and passed through a short alumina column   Elution with 5% CH$_2$Cl$_2$ in petroleum ether gave the phenethyl halide, while elution with CH$_2$Cl$_2$ gave the manganese product, _cis_-Mn(CO)$_4$(PEt$_3$)X Yields of the latter, where calculated, were about 60%

The phenethyl halides were identified on the basis of their ^{1}H NMR spectra [1], the manganese-containing products largely on the basis of their IR spectra in the carbonyl region [30,31]   A sample of the iodide compound, _cis_-Mn(CO)$_3$(PEt$_3$)I analysed correctly (Calc for C$_{10}$H$_{15}$IMnO$_4$P   C, 29 15, H, 3 67   Found   C, 28 88, H, 4 83), while ν_{CO} (petroleum ether) for the chloro (2088,2023,2005,1946), bromo (2086,2021,2003,1948) and iodo (2079,2015,1997,1951) compounds compare very well with values in the literature for very similar compounds [30,31]

RESULTS AND DISCUSSION

In most cases the halogenation reactions proceeded smoothly, as in (3), and the relative amounts of the _threo_- and _erythro_-PhCHDCHDX could be readily

determined   The products from the reactions

$$\underline{cis}\text{-PhCHDCHDMn(CO)}_4\text{PEt}_3 + X_2 \rightarrow \underline{cis}\text{-Mn(CO)}_4(\text{PEt}_3)X + \text{PhCHDCHDX} \qquad (3)$$

$$X = Cl, Br, I$$

are listed in Table 1

TABLE 1

Degree of Retention of Configuration

of the Cleavage Products (%)[a]

Solvent/Reagent	Cl_2	Br_2	I_2	ICl[b]
$n\text{-}C_5H_{12}$	17	33	68	<5
C_6H_6	13	33	70	<5
CS_2	12	22	72	-
CH_2Cl_2	48	42	63	<5
MeCN	49	52	42	<5
$MeNO_2$	61	29	54	-

[a] ±7%

[b] Product is predominantly erythro-PhCHDCHDI,
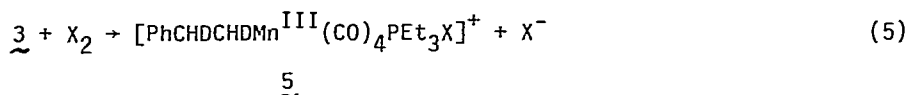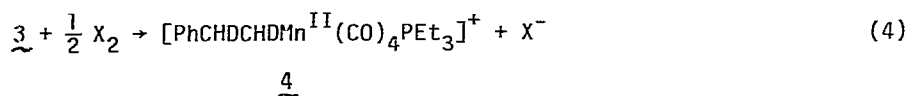with traces of threo-PhCHDCHDCl

As can be seen from the Table, the stereochemistry of the chlorination
and bromination reactions is strongly solvent-dependent, albeit in a somewhat
erratic manner.   Inversion is certainly preferred in the less polar solvents,
but becomes less important in CH_2Cl_2, MeCN and $MeNO_2$ The iodination reactions,
on the other hand, proceed with predominant retention of configuration in non-
polar solvents, and are essentially non-stereospecific in polar solvents   There
is a noticeable increase in the degree of retention in non-polar solvents on
going from chlorine to iodine. The cleavage reactions with ICl, on the other
hand, are highly stereospecific, producing in all cases phenethyl iodide with

essentially complete inversion of configuration and traces of phenethyl chloride with essentially complete retention of configuration

Interestingly, chlorine, bromine and iodine cleavage of $\underset{\sim}{3}$ labelled with carbon-13 in both n-pentane and methylene chloride gave products in which methylene scrambling had <u>not</u> occurred [1]

The wide variation in stereospecificity suggests strongly that halogen cleavage reactions of $\underset{\sim}{3}$ can occur via at least two, and probably more competing pathways, although attempts to rationalize all the data in detail would seem to be futile at present   The lack of scrambling of the methylene carbons is very important (examples chosen would appear to be representative), as it shows that the phenonium ion-like behaviour exhibited by the compound threo-PhCHDCHDFe(CO)$_2$ (η^5-C$_5$H$_5$) in its halogen cleavage reactions [1] does not occur in the manganese system.   The reasons for the difference are not at all obvious, but the PhCHDCHD-group is clearly a "good" primary alkyl ligand for studying the stereochemistry of cleavage reactions of alkylmanganese compounds

The high degree of inversion observed for chlorination and bromination reactions in non-polar solvents is most likely a result of an S_E2(inversion) process, as in $\underset{\sim}{2}$, involving overlap of the filled manganese-carbon σ bond (the HOMO) with the empty σ^* orbital of the halogen (the LUMO) [1]   Although an S_E2 (retention) mechanism (1) may well be responsible for the significant retention of configuration in non-polar solvents, there would appear to be no reason why such a process, involving the same orbitals [1], would become more important for the heavier halogens   The increasing retention of configuration observed for the heavier halogens in non-polar solvents must therefore be indicative of a different mechanism, presumably involving electron transfer, i e   an S_E(oxidative) process such as (4) or (5).

$$\underset{\sim}{3} + \tfrac{1}{2} \; X_2 \rightarrow [PhCHDCHDMn^{II}(CO)_4PEt_3]^+ + X^- \qquad\qquad (4)$$

$$\underset{\sim}{4}$$

$$\underset{\sim}{3} + X_2 \rightarrow [PhCHDCHDMn^{III}(CO)_4PEt_3X]^+ + X^- \qquad\qquad (5)$$

$$\underset{\sim}{5}$$

Intermediate $\underset{\sim}{4}$ would be analogous to and isoelectronic with that which is believed to occur during halogenation reactions of alkylcobaloximes [6,7,15-21], and would similarly be expected to yield phenethyl halide with inversion of configuration via nucleophile displacement of, presumably, a manganese(0) species by halide ion. Intermediate $\underset{\sim}{5}$ is analogous to that which is believed to occur during halogenation and mercuration reactions of compounds of the type $\eta^5-C_5H_5FeCOLR$ [1,22-26] It could yield phenethyl halide with retention of configuration via a reductive elimination process [1], or with inversion of configuration via nucleophilic displacement of cis-$Mn(CO)_4PEt_3X$ by free halide ion Reductive elimination from $\underset{\sim}{5}$ would appear to be the best explanation for the observations under consideration, although it is not obvious why the heavier halogens would tend to prefer an electron transfer process over either of the more conventional S_E2 processes Steric factors are likely unimportant, but it seems possible that, as the halogens become larger and their σ^* orbitals more diffuse, overlap with the metal-carbon σ orbital should decrease, making an S_E2 process less favourable. It is also likely that solvation problems would be less severe for an ionic iodide complex intermediate than for similar chloride or bromide complexes Nucleophilic attack by X^- on the α-carbon atom of $\underset{\sim}{5}$ can be ruled out as the process leading to predominant inversion during chlorination and bromination reactions in non-polar solvents, as nucleophilic properties of the halides decrease in the order $I^- > Br^- > Cl^-$, in contrast to the observed trend Similarly, chain radical processes as contributors to observations of non-stereospecificity may possibly be ruled out, as chain processes should be most important for chlorination reactions, again in contrast to observations (Radical processes are often difficult to prove or disprove in this type of chemistry, however [1], and a more definitive statement must await the results of planned kinetics studies) Thus, in non-polar solvents, halogenation reactions seem to occur mainly by two competing processes, S_E2(inversion) and oxidation to $\underset{\sim}{5}$, followed by reductive elimination

The general increase in the degree of retention of configuration for the chlorination and bromination reactions in more polar solvents (CH_2Cl_2, MeCN, $MeNO_2$) most likely occurs because of an increase in importance of the S_E(oxidative)

process, (5), as reactions involving ionic intermediates are generally favoured in polar solvents   There certainly is no obvious reason why an S_E2(retention) process should become more important than an S_E2(inversion) process on going to more polar solvents, and epimerization of product PhCHDCHDX by exchange with free halide ion can be ruled out because such exchange reactions are found to be very slow for phenethyl chloride and bromide   Interestingly bromination in CH_2Cl_2 in the presence of a ten-fold excess of bromide ion (as the tetraethyl-ammonium salt) does not lead to increased inversion but, rather, to a slight increase in retention, again suggesting that nucleophilic attack by halide ion on an oxidized intermediate is relatively unimportant

In the case of iodination reactions in the same polar solvents, the observed lack of stereospecificity may be a result of stabilization of the intermediate, [threo-PhCHDCHDMn(CO)$_4$PEt$_3$I]I, by the polar solvents   The results could then be rationalized if bimolecular nucleophilic displacement of cis-Mn(CO)$_4$(PEt$_3$)I from the α-carbon atom by the ionic iodide ion were to become competitive (as described above for alkylcobaloximes)   Some epimerization via exchange with free iodide ion could also occur, although this does not generally appear to be a significant factor

The cleavage reactions with ICl are unique in being highly stereospecific for both the major product, PhCHDCHDI (inversion) and the minor product, PhCHDCHDCl (retention), although again interpretation of the data remains ambiguous   The complete lack of solvent dependence suggests that some unique property of ICl may be dominating the course of the reaction, and we suggest that the key factor with the interhalogen may be its polarization   The relatively electropositive iodine atom of ICl should be more electrophilic, and the observed product distribution is consistent with the major pathway involving an S_E2(inversion) process in which the iodine end of the ICl approaches the backside of the α-carbon atom   While it might seem contradictory that ICl prefers an S_E2(inversion) process while I_2 does not, reaction of the interhalogen would probably be aided by contraction of the radial function of the component of the σ^* orbital on iodine by the electronegative chlorine atom, thus allowing significant overlap with the filled manganese-carbon σ orbital

The formation, with essentially complete retention of configuration, of the minor product, PhCHDCHDCl, in the ICl reactions is consistent with an S_E(oxidative) process, as in (5), followed by reductive elimination from small amounts of the oxidized intermediate [PhCHDCHDMn(CO)$_4$(PEt$_3$)Cl]I. Furthermore, since the major product, erythro-PhCHDCHDI, could also be formed by nucleophilic attack of the ionic iodide on the postulated chloro complex, with displacement of cis-Mn(CO)$_4$(PEt$_3$)Cl, then an S_E(oxidative) process appears to rationalize formation of erythro-PhCHDCHDI as well as does an S_E2(inversion) process

The general pattern of results in Table 1, however, leads us to favour the latter As stated above, the iodination reactions appear to be dominated by the S_E(oxidative) process of (5), reductive elimination of phenethyl iodide from 5 (X=I) being very competitive with nucleophilic attack of iodide on 5 followed by elimination of cis-Mn(CO)$_4$(PEt$_3$)I It seems highly unlikely therefore, that reductive elimination from an intermediate such as [PhCHDCHDMn (CO)$_4$(PEt$_3$)Cl]I would be insignificant

Cleavage reactions with interhalogens have been investigated previously, and it is interesting to note that complexes of the type η^5-C$_5$H$_5$FeCOLR, which are believed to react via an S_E(oxidative) process, are cleaved by ICl to yield predominantly alkyl chloride [1,24], while complexes of the type [RCr(H$_2$O)$_5$]$^{2+}$, which are believed to react via an S_E2(inversion) process, are cleaved by IBr to yield exclusively alkyl iodide [32] Our results thus appear to be quite consistent with observations on the chromium system.

Our results are also consistent with a very brief report by Johnson and Pearson [33], who showed that bromine cleavage of optically active Me*CH(CO$_2$Et)Mn(CO)$_5$ in tetrahydrofuran proceeds with partial retention of configuration On the other hand, the high stereospecificity we observe at the manganese is probably not significant The cis isomers are expected to be the thermodynamically preferred products, while Wojcicki et al [34] have shown that halogen cleavage reactions of cis-Mn(^{12}CO)$_4$(^{13}CO)Me result in a statistical distribution of the labelled carbonyl group in the halide products, XMn(^{12}CO)$_4$(^{13}CO) Thus the intermediate(s) in this type of reaction may be fluxional, as has been previously suggested for compounds of the type η^5-C$_5$H$_5$FeCOLR [1,23-24].

The propensity for mechanistic diversity exhibited by 3 in its halogen cleavage reactions is also reminiscent of the iron system [1,24,25] The fact that electrophilic reagents seem to attack both carbon and manganese with equal facility adds an interesting dimension to our earlier suggestion [1] that such attack should occur at the HOMO of the metal complex and, since the HOMO is usually an essentially non-bonding metal d orbital, that electrophilic attack should _normally_ occur at the metal (i e an S_E(oxidative) process)   In the case of compounds of the type $\eta^5-C_5H_5Fe(CO)_2R$, studied previously in great detail [1,22-26], electrophilic attack seems to take place exclusively at the metal rather than at the iron-carbon σ bonding orbital, consistent with the rather large difference of 1 44 eV (~33 kcal/mole) between the latter orbital and the HOMO [35]   In the case of the manganese system, however, photoelectron data for the parent methyl compound, $MeMn(CO)_5$ [36,37], suggest that the energy difference between the HOMO and the manganese-carbon σ bonding orbital is only 0.84 eV (~19 kcal/mole)   Although the effects of phosphine substitution on this energy difference are not known, the metal-carbon σ bonding orbital is very likely more "available" for interactions with electrophilic reagents than is the corresponding orbital in the iron series

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