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CHLORINATION OF ALKENES BY MANGANESE(III) CHLORIDE SPECIES

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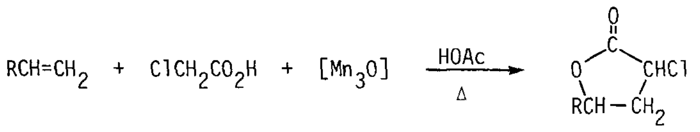
Abstract: Several manganese(III) chloride species have been prepared _in situ_ and used as effective chlorinating agents of alkenes.

α-Chloro-γ-butyrolactones can be prepared via a manganese(III) acetate lactone annulation reaction employing chloroacetic acid, eq. 1.[1] When potassium acetate was added to the reaction mixture, however, this manifold was completely shut down and the 1,2-dichloride became the exclusive product, eq. 2. We felt that chloride ion was produced via S_N2 displacement by the added acetate ion. This chloride ion could then have been oxidatively added across the alkene via some manganese(III) chloride species which eventually resulted in double chlorine addition.


eq. 1

$$RCH{=}CH_2 + ClCH_2CO_2H + [Mn_3O] \xrightarrow[\text{KOAc}, \Delta]{\text{HOAc}} RCH(Cl)CH_2Cl \quad \text{eq. 2}$$

$$[Mn_3O] = \text{Manganese(III) acetate}, [Mn_3O(OAc)_7HOAc]$$

This thinking prompted us to heat an alkene, manganese(III) acetate, and a chloride salt (NaCl or $CaCl_2$) to effect the same reaction.[2] These results are summarized in the first product column of Table I. The method was very efficient for chlorinating nonconjugated alkenes (entries 1-6), and where the opportunity existed the trans addition of the elements of chlorine was strongly favored. The two examples where good yields of dichlorides were not obtained could be rationalized by further reaction of an initial dichloride product. Thus methyl cinnamate (entry 8) gave in addition to the dichloride, the HCl elimination product, Z-PhCH=CClCO$_2$Me (20%). α-Methylstyrene gave no dichloride, but instead only products of elimination or substitution, when treated under these chlorinating conditions, eq. 3.

$$\mathrm{PhMeC{=}CH_2} \longrightarrow \underset{18\%}{\mathrm{Z\text{-}PhMeC{=}CHCl}} + \underset{9\%}{\mathrm{PhC(CH_2Cl){=}CH_2}} + \underset{7\%}{\mathrm{PhCCl(CH_2Cl)_2}} + \underset{19\%}{\mathrm{PhMeC(OAc)CH_2Cl}} \qquad \text{eq. 3}$$

Table I. Manganese(III) Chlorination of Alkenes

Entry	Alkene	[Mn_3O]/$CaCl_2$ 1,2-Dichloride,%[a,b]	$MnCl_3$ HOAc 1,2-Dichloride,%[c]	Chloroacetate, %
1	1-Hexene	81[d]	52	11
2	1-Octene	79	72	7
3	Trans-4-octene	91(2.2:1;meso;dl)	71(11:1; meso:d,l)	5
4	Cyclohexene	61(trans)	48(trans)	4
5	Cyclooctene	83(3.0:1;trans:cis)	85(1.3:1; trans:cis)	4
6	1-Methylcyclohexene	74	18	-
7	α-Methylstyrene	0[e]	62	-
8	Methyl cinnamate	47[f](erythro)	63(63:1; erythro:threo)	-

[a]All yields represent distilled or chromatographed material which was identified by spectral comparison with literature data or authentic samples. [b]Reaction conditions: Manganese(III) acetate (50 meq of Mn(III)), $CaCl_2$ (60 mmol), and an alkene (20 mmol) were heated to reflux in acetic acid (70 mL) until the dark brown color of manganese(III) acetate had disappeared (0.2 - 6 hr). [c]Reaction conditions: Manganese(III) acetate or manganese(III) hydroxide (18 meq of Mn(III)) was added to an ice-cooled mixture of acetic acid/acetyl chloride (2/1, 18 mL) followed by the alkene (8 mmol) five minutes later. The dark purple solution turned colorless (instantly-5 hr). [d]This value is for 1-decene. [e]See text. [f]Plus Z-PhCH=CClCO$_2$Me (20%) and starting material (2%).

With the knowledge that chlorination was possible via a manganese(III) acetate/chloride system, we prepared several known manganese(III) chloride complexes as shown in eq. 4.

$$[\mathrm{Mn_3O}]\ \text{or}\ \mathrm{Mn(OH)_3}^{3} + \mathrm{HCl} \xrightarrow{\text{solvent}} \underset{\text{(purple solution)}}{\mathrm{MnCl_3{\cdot}solvent}} \xrightarrow{\mathrm{M^+\,Cl^-}} \underset{\text{(green solid)}}{\mathrm{M_2[MnCl_5]}} \qquad \text{eq. 4}$$

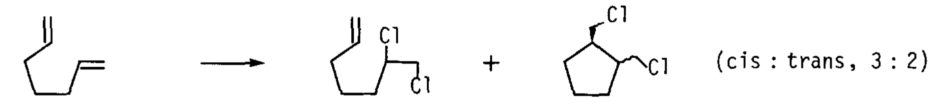
solvent[4] = ether, THF, HOAc, MeCN

$M^+ Cl^-$[5] = NH_4Cl[6], Me_4NCl[6], Et_4NCl[7], PyHCl[8], $PhCH_2NMe_3Cl$[9], $(C_8H_{17})_3NMeCl$[9]

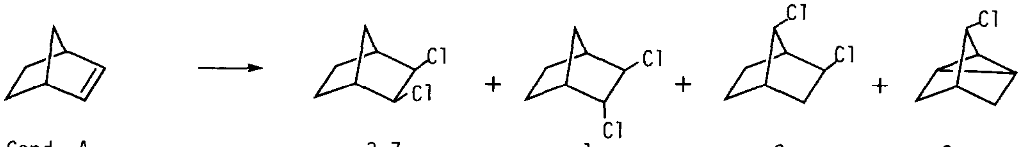
The only reported synthetic chemistry of either the manganese trichloride solvates or the pentachloromanganate salts has been the oxidation of phosphines to phosphine oxides.[10] All the above salts and solvates proved to be active chlorinating species, however the low solubility of all the salts (except $PhCH_2NMe_3^+$ and $(C_8H_{17})_3NMe^+$) precluded these species from further practical consideration. The manganese trichloride solvates could be easily prepared and reacted directly with an alkene. The acetic acid solvate was particularly stable[11] and chlorination results with this complex are included in Table I. Modest to good yields of 1,2-dichlorides were obtained, however small amounts of chloroacetates were also produced. Later experiments have shown that the chloroacetate products were concentration dependent, and that performing the chlorination at higher reactant concentration reduced the amount of chloroacetate to almost negligible levels.

In order to gain some insight into possible reaction intermediates, the reactions in Table II were run. The intermediacy of a secondary radical in the 1,6-heptadiene chlorination would lead to a substantial yield of cyclized dichlorides (k_{cycl} = 1.3 x $10^5 s^{-1}$, 25° C).[12]

Table II. Radical vs. Ionic Intermediates



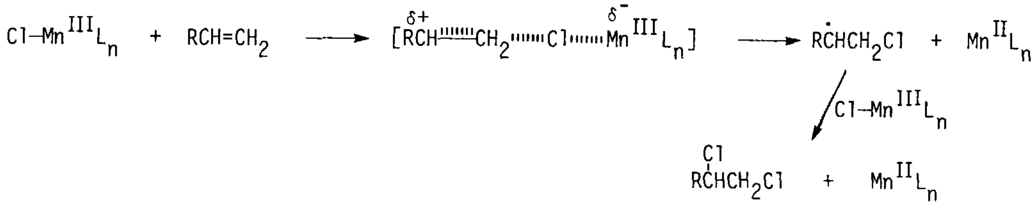
Cond. A	40.9	:	1
Cond. B	1.12	:	1



Cond. A	3.7	:	1	:	0	:	0
Cond. B	3.8	:	1	:	0	:	0

Cond. A : $MnCl_3 \cdot HOAc$, 25°
Cond. B : $[Mn_3O]$, $CaCl_2$, HOAc, 116°

Scheme I



Correspondingly the intermediacy of carbonium or chloronium ions in the chlorination of norbornene would lead to almost entirely rearranged products.[13] The results in Table II imply a substantial radical character to an intermediate under cond. A as well as cond. B. Literature Arrehenius parameters predict $k_{cycl}(116^o) = 35\ k_{cycl}\ (23^o)$;[12] however, neither the concentration of the actual chlorinating species in cond. B, nor the effect of temperature on the rate of chlorination are known at this time. These two unknown effects apparently offset one another because the observed difference in cyclization rates from Table II is 37. Thus the lifetimes of the intermediate radicals produced by both conditions are quite similar. Notably neither set of conditions has any appreciable cationic character. These results lead us to suggest the mechanistic path in Scheme I. Further mechanistic studies are currently underway.

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