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### Chlorination of Alkenes with $\text{MnO}_2$ - $\text{MnCl}_2$ -Acetyl Chloride in Dimethyl Formamide

Franco Bellesia<sup>a</sup>, Franco Ghelfi<sup>a</sup>, Ugo M. Pagnoni<sup>a</sup> & Adriano Pinetti<sup>a</sup>

<sup>a</sup> Dipartimento di Chimica, dell'Università, Via Campi 183, I-41100, Modena, Italy

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**CHLORINATION OF ALKENES WITH  $\text{MnO}_2$ - $\text{MnCl}_2$ -ACETYL CHLORIDE  
IN DIMETHYL FORMAMIDE**

Franco Bellesia, Franco Ghelfi, Ugo M. Pagnoni and Adriano Pinetti

Dipartimento di Chimica dell'Università, Via Campi 183, I-41100  
Modena, Italy.

**ABSTRACT:** Chlorination of alkenes was achieved in high yields by  $\text{MnO}_2$ - $\text{MnCl}_2$ -Acetyl Chloride in dimethylformamide. A Mn(III) intermediate and a ligand-transfer process are suggested.

Mn(III) chloride species, prepared by starting from  $\text{Mn}(\text{OAc})_3$  and a chloride donor in acetic acid, can be used in the chlorination of alkenes affording vicinal dichloro alkanes.<sup>1</sup> However, when using chloride salts as halide donors, the reaction has to be heated at reflux, whereas when using acetyl chloride ( $\text{AcCl}$ ), it proceeds at 0°C, but with lower yields and substantial amounts of chloro-acetates.

Recently we found that  $\text{MnO}_2$ -trimethylchlorosilane (TMCS) in tetrahydrofuran (THF) gives rise to a high yield chlorination of

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° to whom correspondence should be addressed

alkenes, suggesting a halogenation accomplished by a Mn(IV)-Cl species.<sup>2,3</sup>

On substituting AcCl for TMCS as chloride carrier, the main transformation was the opening of THF heterocyclic ring. In dimethylformamide (DMF), instead, the MnO<sub>2</sub>-AcCl system smoothly halogenates the alkenes without side reactions. The peculiar ability of DMF to solubilize MnCl<sub>2</sub>, the end product of the MnO<sub>2</sub> reduction, should enable the comproportionation reaction according to the equilibrium  $\text{Mn(II)} + \text{Mn(IV)} \rightleftharpoons \text{Mn(III)} + \text{Mn(III)}$ . Indeed, has been reported that whereas Mn(III) is especially prone to disproportionate in aqueous solution, its complexes are relatively stable in non-aqueous media.<sup>4</sup>

On treating cyclooctene with and without added amounts of MnCl<sub>2</sub> (10 mmoles) or of LiCl (10 mmoles),<sup>5</sup> an autocatalytic process is observed. Since the reaction rate is strongly increased by adding MnCl<sub>2</sub>, while it is reduced by introducing LiCl, the catalytic effect must be assigned to the manganous ion rather than the chloride one.

The addition of MnCl<sub>2</sub> to MnO<sub>2</sub>-AcCl system makes the reaction similar to that effected by Mn(OAc)<sub>3</sub>-AcCl; isomers distribution (the trans:cis ratios are 3.6:1 and 3.4:1 respectively),<sup>6</sup> and reaction rate are indeed very comparable, and the visible absorption spectra of DMF solutions of MnO<sub>2</sub>-MnCl<sub>2</sub>-AcCl (1:1:4) and Mn(OAc)<sub>3</sub>-AcCl (1:3) are superimposable. These experiments indicates that MnCl<sub>2</sub> affords a Mn(III)-Cl species (probably MnCl<sub>3</sub>), by a comproportionation reaction with a Mn(IV) species,

and that this intermediate attacks the alkenes more quickly than  $\text{Mn(IV)-Cl}$ .


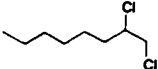
















In a typical experiment the  $\text{AcCl}$  (60 mmol) is poured into a mixture of  $\text{MnO}_2$  (15 mmol),  $\text{MnCl}_2$  (10 mmol) and alkene (10 mmol) in DMF at  $30^\circ\text{C}$ . A strong dark green colour develops immediately and then fades at a rate depending on the substrate structure.

As Table shows, vicinal dichloro compounds are thus prepared in high yields, under mild conditions and with cheap reagents, from differently alkyl-substituted olefines. It is remarkable that the amount of 1,2 dichlorooctane decreases from 84% to 56% without added  $\text{MnCl}_2$ .

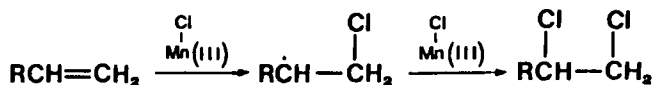
A halogenation through molecular chlorine from  $\text{MnO}_2\text{-MnCl}_2\text{-AcCl}$  is excluded by results on norbornylene, which is a good olefinic probe for free chlorine in reactions with metal chlorides.<sup>7</sup> When, indeed, this substrate is treated with  $\text{Cl}_2$  in DMF,<sup>8</sup> a significantly different products distribution is observed, with a great amount of nortricycyl chloride. As alkyl tri- (items 2,6) and gem-di- (item 9) substituted alkenes give no allylic substitution products, and norbornylene and neo-hexene do not undergo molecular rearrangements, we can also reasonably rule out the intermediacy of a carbocation.

Very comparable results were obtained on substituting 37%  $\text{HCl}$  for  $\text{AcCl}$ . In this case too,  $\text{Cl}_2$  is not the reagent, even though it can be prepared by treating  $\text{MnO}_2$  with hydrochloric acid.<sup>9</sup>

Table

Substrate	Product <sup>a</sup>	Reaction time (h)	Yield %	B.p./°C (mmHg)	M <sup>+</sup>
		6	84	67-71 (4)	182
		2	93	126-128 (760)	140
		4	94	92-94 (70)	154
		4	96	59-65 (14)	152
		3	92 <sup>b</sup>	105-119 (10)	180
		2	94	86-89 (1.5)	166
		1	93 <sup>c</sup>	92-98 (18)	164
		4	92	172-174 (760)	154
		4	95 <sup>d</sup>	162-165 (760)	154

a) products are identified by comparison of their MS spectra to those of authentic samples; b) 78:22, trans:cis; c) 80:20, trans:cis; d) 64:26, eritro:treo.



scheme

The above reported experimental evidences agree with a non-chain radical process (Scheme),<sup>1,10</sup> in which Mn(III)-Cl acts like donor of Cl $\cdot$ .

The treatment of alkynes gave poor results; 1-octyne and phenylacetylene, for instance, are transformed into trans-dichloroderivatives at only about 10%.

### Experimental

**General Reaction Procedure.** In a three-necked flask fitted with a condenser and a dropping funnel DMF (20 ml), MnCl<sub>2</sub> (10 mmoles) and the alkene (10 mmoles) are placed. When the salt has been dissolved, MnO<sub>2</sub> (15 mmoles) is first introduced and then AcCl (60 mmoles) is slowly added (over about five minutes) from the dropping funnel, the suspension being vigorously stirred. The mixture, thermostatted at 30°C, instantly becomes dark green; the substrate transformation is monitored by discolouration and by GC analysis. The mixture is then extracted with light petroleum (b.p. 30-50 °C) (3 x 20 ml) and the organic phase collected are washed with water (1 x 20 ml). After drying (Na<sub>2</sub>SO<sub>4</sub>) and solvent evaporation, the products are isolated and purified by distillation.

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- 5) Reaction conditions (see Experimental Section) are the same in each test, the addition of chloride salts excepted. The alkene consumption is monitored by GC.
- 6) With  $\text{MnO}_2$ -AcCl only, the trans:cis ratio was 4.3:1, thus suggesting that in this test, a species  $\text{Mn(IV)-Cl}$  may also be active.
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- 8) Molecular chlorine is smoothly bubbled in a norbornylene (10 mmoles) solution in DMF (20 ml) at 30°C.
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