Tetrahedron Letters No. 37, pp 3427 - 3430.
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0040-4039/78/0908-3427$02.00/0

IN SITU-GENERATED MOLYBDENUM (VI) REAGENT FOR *CIS*-CHLORINATION OF ALKENES

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The reaction of olefins with elemental chlorine occurs via a selective *trans* addition so that a procedure for selective *cis* chlorination of olefins is of considerable interest. Vemura and coworkers[1a] and more recently San Felippo[1b] have reported the formation of *cis*-dichloroalkanes upon treatment of the corresponding alkenes with $MoCl_5$. However, this reaction as applied to mono-, tri-, and tetrasubstituted olefins suffers from low (1-10%) yields[1b,2]. We now report a procedure which offers improved yields without requiring low temperatures and also discuss some mechanistic aspects of this interesting reaction. An improved preparation of tetrabutylammonium octamolybdate[3], I, is also reported.

In a typical procedure 0.73 g (6.48 mmol) trans-4-octene was treated with 3.84 g (14.3 mg-atom Mo) of I in 50 ml CH_2Cl_2. Fifteen minutes after adding 5 ml acetyl chloride the suspension had turned yellow and homogeneous but no dichloride could be detected by glc. The solution suddenly discharged to red and then green after which stirring was continued for 2 hr. Ether was added to precipitate Mo-containing products and the solution was washed with 3M NaOH and water Evaporating the dried organic phase afforded product which was somewhat yellow. Elution of this material over a short column of Woelm alumina with pentane afforded 1.08 g (91%) of 4,5-dichlorooctane which was >98% d,l-isomer by glc.

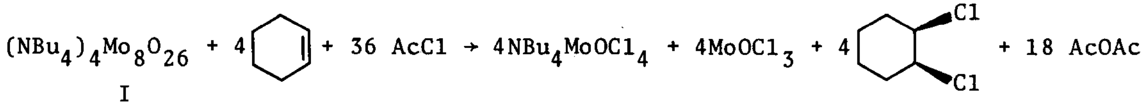
Yields for several other olefins are summarized in Table I. The products gave satisfactory elemental analyses and in each case <2% of the product was that resulting from trans-chlorination.

TABLE I. Isolated Yields for Reaction of Alkenes with I and Acetyl Chloride in CH_2Cl_2

Alkene	Product	Yield %
1-Hexene	1,2-dichlorohexane	85
1-Octene	1,2-dichlorooctane	86
cis-3-Octene	(meso)-3,4-dichlorooctane[a]	91
trans-4-Octene	(d,l)-4,5-dichlorooctane[a]	91
Cyclohexene	cis-1,2-dichlorocyclohexane[a]	94
Cycloheptene	cis-1,2-dichlorocycloheptane[a]	83
Tetramethylethylene	2,3-dichloro-2,3-dimethylbutane[b]	35

a) Contains <2% of product from trans addition.
b) Purified by sublimation.

The stoichiometry of this reaction was the following:



Thus addition of ether to the product mixture precipitated approximately half of the molybdenum as the known[4] complex NBu_4MoOCl_4. Treatment of the remaining solution with triphenylphosphine oxide allowed isolation of the remaining molybdenum as the known[5] $(Ph_3PO)_2MoOCl_3$.

Replacement of acetyl chloride with BCl_3[6] allowed a much faster reaction which proceeded essentially as a titration and affords some mechanistic insight into the reaction. Thus upon treatment[7] of cyclohexene with I and BCl_3 in the proportions olefin:Mo:BCl_3 = 1:2:2 the cyclohexene was recovered unreacted.[8] As additional BCl_3 was dropped in as a CH_2Cl_2 solution the conversion of the olefin to cis-1,2-dichlorocyclohexene was observed to a limit of 1 mmol olefin per 2 mg-atom Mo.

The apparent requirement of Cl/Mo > 2 in the active reagent is noteworthy in light of studies on chlorinations using authentic chloro molybdenum compounds as summarized in Table II.[9] Thus MoO_2Cl_2 was itself completely ineffective as a chlorination agent but upon addition of acetyl chloride did afford some dichloride.

TABLE II. Yields of 1,2-Dichlorooctane from 1-Octene and Various Molybdenum Species by GLC.[a]

	% Yield Dichloride at Mo/Octene Ratio		
Mo Species	1	2	3
$MoOCl_4$	15	16	6
$MoCl_5$	12	6	6
MoO_2Cl_2	0	0	0
MoO_2Cl_2 + AcCl[b]	29	37	39
I + AcCl[b]	44	76	96
WCl_6	<2[c]	<2[c]	<2[c]

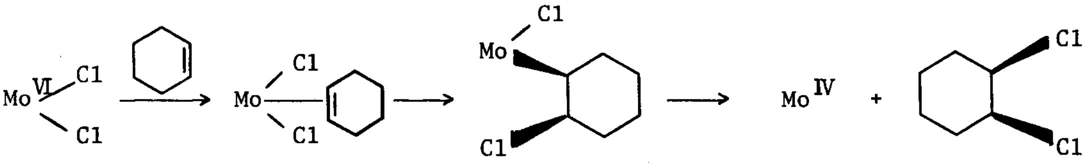
a) For 0.611 mmol 1-octene in 8 ml CH_2Cl_2 at 25°C.

b) Reaction additionally containing 1 ml acetyl chloride.

c) Somewhat greater yields of the other isomeric vicinal dichlorooctanes were observed apparently reflecting scrambling of the starting olefin.

We suggest that the active reagent is a polychloromolybdenum species. The effectiveness of BCl_3 and acetyl chloride in this process is presumed to reflect the Lewis acid character of these chlorine sources[10] which aids in interaction with the Mo^+-O^- functionality of I. The ready reactivity of I reflects its solubility in CH_2Cl_2; the less soluble MoO_3 and Na_2MoO_4 are not useful reagents for this reaction.[11]

Our observations are best accommodated by a mechanism similar to that proposed by Sharpless for side-product formation during chromyl chloride oxidations.[12]



Such a scheme involves formal cis-insertion of the olefin into the Mo-Cl bond[13] of a polychlorinated Mo^{VI} species followed by reductive elimination. A coproportionation process ($Mo^{IV} + Mo^{VI} \rightarrow 2Mo^{V}$) would then account for the observed Mo^V products. The observation of a high yield analog of well known homogeneous hydrogenation processes is noteworthy since it suggests that stereospecific introduction of other functionality to olefins may be possible by similar routes.

Compound I was prepared by treatment of 43 g of technical ammonium molybdate in 100 ml H_2O with 50 g of 40% NBu_4OH solution.[14] A white precipitate immediately formed which was washed with ether and dried *in vacuo* at 100°C for 5 hr, yield 32.8 g (80%). The product was identified as the α-isomer of I by IR[3] and exhaustive elemental analysis.[15]

REFERENCES

1. a) S. Uemura, A. Onoe, and M. Okano, Bull. Chem. Soc. Jpn., 47, 3121 (1974).
   b) J. San Filippo, Jr., A. F. Sowinski, and L. J. Romano, J. Am. Chem. Soc., 97, 1599 (1975).
2. Low yields of dichlorides from terminal olefins apparently results from a competing polymerization process; J. San Filippo, Jr., private communication
3. W. G. Klemperer and W. Shum, J. Am. Chem. Soc., 98, 8291 (1976) and references therein.
4. O. Piovesana and C. Furlani, Inorg. Nucl. Chem. Lett., 3, 535 (1967).
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6. With BBr_3 the cis and trans isomers of 1,2-dibromocyclohexane were obtained in a 1:2 ratio.
7. The boron containing products were not investigated but a reasonable possibility is that the known thermally stable trichloroboroxole, $Cl_3B_3O_3$, is

formed, see R. F. Porter and S. K. Gupta, J. Phys. Chem., 68, 280 (1964).

8. During the addition transient formation of the (red) active species is apparently observed due to locally high concentrations of BCl_3.
9. Requirement for a 3:1 Mo/olefin ratio in small scale (glc) reactions is not fully understood but is apparently related to greater warming of the (exothermic) preparative scale reactions.
10. With $AlCl_3$, BF_3, $SnCl_4$ or Me_3SiCl products of cis halogenation were not obtained.
11. Low yields of cis-dichlorides were observed with NBu_4ReO_4 and NBu_4NOsO_3.
12. Yields of up to 12% cis-chlorination products were observed with CrO_2Cl_2 at -78°C. K. B. Sharpless, A. Y. Teranishi, and J. E. Backvall, J. Am. Chem Soc., 99, 3120 (1977).
13. We wish to point out that precedent for this process exists in the reaction of WCl_6 with nitriles, cf. G. W. A. Fowles, D. A. Rice, and K. J. Shanton, J. Chem. Soc. Dalton, 1977, 1212.
14. Use of a NBu_4OH/Mo ratio either above or below that indicated resulted in reduced yields or no product.
15. Calcd. for $C_{64}H_{144}Mo_8N_4O_{26}$: C, 35.70; H, 6.74; Mo, 35.64; N, 2.60; O, 19.32. Found: C, 36.36; H, 6.79; Mo, 35.89; N, 2.80; O, 19.60.

(Received in USA 5 June 1978; received in UK for publication 7 July 1978)