(5) G. Slomp, Jr., and J. L. Johnson, *J. Am. Chem. Soc.*, **80**, 915 (1958); G. Stork, M. Gregson, and P. A. Grieco, *Tetrahedron Lett.*, 1391 (1969).

(6) NMR spectra ($CCl_4$, 60 MHz) and infrared spectra were obtained for each intermediate and were in every instance in accord with the assigned structure. Chemical shifts are expressed in parts per million downfield from TMS and coupling constants are expressed in hertz. Satisfactory analytical data were obtained.

(7) Yields are for chromatographically pure substances unless otherwise stated.

(8) E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 2000 (1950).

(9) W. H. Watenabe and L. E. Conlon, *J. Am. Chem. Soc.*, **79**, 2828 (1957).

(10) H. Bauer, *Ber.*, **46**, 92 (1913).

(11) The observation that an electron withdrawing ortho-nitro group results in a more facile elimination of the corresponding selenoxide was first reported by Professor K. B. Sharpless. For a report of this work, see K. B. Sharpless and M. W. Young, *J. Org. Chem.*, in press. For an application of this method to the construction of the vernolepin AB-ring system, see P. A. Grieco, J. J. Reap, and J. A. Noguez, *Synth. Commun.*, in press.

(12) Attempts to eliminate the phenyl selenoxide[13] derivative of **15** resulted in less than 4% yield of **16** (50% hydrogen peroxide in THF containing anhydrous magnesium sulfate (24 hr)).

(13) K. B. Sharpless, M. W. Young, and R. F. Lauer, *Tetrahedron Lett.*, 1979 (1973).

(14) Fellow of the Alfred P. Sloan Foundation, 1974–1976.

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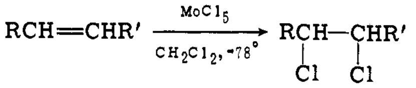
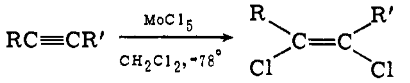
## Chlorination of Alkenes and Alkynes with Molybdenum(V) Chloride[1]

*Sir:*

The reaction of molybdenum(V) chloride with tetrachloroethylene produces hexachloroethane in essentially quantitative yields.[2] The extension of this reaction to other olefins would, if available, constitute a potentially useful procedure for the chlorination of carbon–carbon double bonds. We wish to report that molybdenum(V) chloride reacts with vicinal disubstituted olefins and internal alkynes to produce, inter alia, dichloroalkanes and -alkenes, respectively, in fair to good yields.



$$RCH{=}CHR' \xrightarrow[CH_2Cl_2,\,-78^\circ]{MoCl_5} \underset{Cl}{RCH}{-}\underset{Cl}{CHR'}$$



In a typical experiment, a solution of cyclohexene (2.04 g, 25.0 mmol) in methylene chloride (7 ml) was added over a 15-min period to a vigorously stirred solution of molybdenum(V) chloride[3] (3.40 g, 12.0 mmol) in methylene chloride (5 ml) at −78° with the rigorous exclusions of moisture and oxygen. The resulting mixture was allowed to warm gradually to ambient temperature. After chromatography over alumina, analysis indicated the presence of *cis*-1,2-dichlorocyclohexane (68%), *trans*-1,2-dichlorocyclohexane (2%), cyclohexylcyclohexane (2%), and chlorocyclohexane (14%). Results obtained on treatment of other representative substrates are given in Table I.

This reaction sequence seems applicable to the chlorination of vicinal disubstituted olefins and internal acetylenes; in our hands, terminal, tri-, and tetrasubstituted olefins and terminal acetylenes produced poor yields of dichloro products. The use of methylene chloride or chloroform as solvents results in appreciably higher yields of dichloro products than does pentane. The principal products produced by the reaction of cyclohexene (excess) with molybdenum(V) chloride under similar conditions but in the absence of solvent are chlorocyclohexane (3%) and *cis*-1,2-dichlorocyclohexane (8%).

**Table I.** Reaction of $MoCl_5$ with Various Olefins and Acetylenes[a]

| Olefin | Dichloride | Yield,[b] % |
|---|---|---|
| Cyclopentene | *cis*-1,2-Dichlorocyclopentane | 66 |
| | *trans*-1,2-Dichlorocyclopentane | <1 |
| Cyclohexene | *cis*-1,2-Dichlorocyclohexane | 68 |
| | *trans*-1,2-Dichlorocyclohexane | <2 |
| Bicyclo[2.2.1]heptene | *exo,cis*-2,3-Dichlorobicyclo[2.2.1]heptane | 27 |
| 2-Hexene | 2,3-Dichlorohexane | 67 |
| 1-Hexene | 1,2-Dichlorohexane | 10 |
| *cis*-3-Hexene | *meso*-3,4-Dichlorohexane | 67 |
| | *d,l*-3,4-Dichlorohexane | <1 |
| *trans*-3-Hexene | *d,l*-3,4-Dichlorohexane | 63 |
| | *meso*-3,4-Dichlorohexane | <1 |
| 1-Methylcyclohexene | 1-Methyl-1,2-dichlorocyclohexane | 4 |
| Tetramethylethylene | 2,3-Dichloro-2,3-dimethylbutane | 9 |
| 4-Octyne[c] | *cis*-4,5-Dichlorooct-4-ene | 36 |
| | *trans*-4,5-Dichlorooct-4-ene | <1 |
| 2-Pentyne[c] | *cis*-2,3-Dichloropent-2-ene | 38 |
| | *trans*-2,3-Dichloropent-2-ene | <1 |

[a] Unless otherwise indicated all additions were carried out in $CH_2Cl_2$ solution at −78° under an inert atmosphere of dry nitrogen. The concentration of molybdenum(V) chloride was ~1.0 *M*. [b] Yields were determined by quantitative vapor phase chromatography and are based on molybdenum(V) chloride. [c] Carried out at room temperature.

Although our understanding of the detailed course of this reaction is still incomplete, several observations permit a description of its general features. First, the products of these reactions provide convincing evidence that the resulting vicinal dichlorides do *not* arise via the ionic or free-radical pathway characteristically observed in the reaction of olefins with molecular chlorine. Specifically, the chlorination of cyclopentene and cyclohexene is essentially unaccompanied by the formation of the corresponding *trans*-1,2-dichlorocycloalkanes.[4] In addition, the treatment of norbornene yields *cis,exo*-2,3-dichloronorbornane with no evidence (<1%) of any *syn*-7-*exo*-2-dichloronorbornane, the principal dichloride obtained from the ionic chlorination of norbornene by molecular chlorine.[5] Similarly, the chlorination of *cis*- and *trans*-3-hexene proceeds stereospecifically to yield respectively *meso*- and *d,l*-3,4-dichlorohexane, again in contrast to the products produced by ionic or free-radical chlorination of these substrates.[4,6,7]

Second, other transition metal chlorides show similar reactivities as chlorinating agents. For example, the tungsten hexachloride produced moderate yields of *cis*-1,2-dichlorocyclohexane (41%) and no (<1%) *trans*-1,2-dichlorocyclohexane when treated with cyclohexene under conditions similar to those detailed above.[8,9] Such a result suggests a general reaction pathway may be common to these systems.

Finally, a similar albeit less stereoselective reaction is observed with certain transition metal bromides. Thus, for example, the addition of cyclohexene to a methylene chloride solution of what is purported to be tungsten(VI) bromide,[10] under conditions equivalent to those cited above, yields a mixture of *cis*-1,2-dibromocyclohexane (40–45%) and *trans*-1,2-dibromocyclohexane (5–10%).

Further observations relating to the mechanism of these reactions will be presented in later papers.

## References and Notes

(1) Supported by the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(2) T. M. Brown and E. L. McCann, *Inorg. Chem.*, **7**, 1227 (1968); D. L. Kepert and R. Mandyczewsky, *ibid.*, **7**, 2091 (1968); E. L. McCann and T. M. Brown, *Inorg. Synth.*, **12**, 181 (1970).

(3) A. J. Leffler and R. Penque, *Inorg. Synth.*, **12**, 187 (1970).

(4) M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 4285 (1965).

(5) M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 4293 (1965).

(6) E. S. Huyser, *Synthesis*, 7 (1970), and references therein.

(7) Although generally acknowledged as yielding trans substituted dichlorides, cis addition of molecular chlorine to phenanthrene (P. B. D. de la Mare, N. V. Klassen, and R. Koenigsberger, *J. Chem. Soc.*, 5285 (1961)) and acenaphthalene (S. J. Crislol, F. R. Stermitz, and P. S. Ramey, *J. Am. Chem. Soc.*, **78**, 4939 (1956)) has been noted. Cis addition is also suspected in the cases of 1-phenylpropene (R. C. Fahey and C. Schubert, *ibid.*, **87**, 5172 (1965)) and stilbene (S. J. Cristol and R. S. Bly, *ibid.*, **82**, 142 (1960)). More recently the addition of chlorine to cyclopentadiene has been observed to produce, inter alia, a 24% yield of the dichloride *cis*-3,4-dichlorocyclopentene (V. L. Heasley et al., *J. Org. Chem.*, **39**, 736 (1973)). The reaction of iodobenzene dichloride with several olefins is also reported to produce *cis*-dichloroalkanes: H. J. Lucas and E. R. Kennedy, "Organic Syntheses", Coll. Vol. 3, Wiley, New York, N.Y., 1955, p 482, and references therein.

(8) Tetrachloroethylene is reported to react with rhenium(V) chloride to produce hexachloroethane and rhenium(IV) chloride: A. Brignole and F. A. Cotton, *Chem. Commun.*, 706 (1971).

(9) Halogenation of olefins with copper(II) bromide and chloride leads to trans substituted dihalides and apparently involves molecular halogens: W. C. Baird, Jr., J. H. Surridge, and M. Buza, *J. Org. Chem.*, **36**, 3324 (1971).

(10) W. Hieber and E. Romberg, *Z. Anorg. Chem.*, **221**, 321 (1935).

(11) Exxon Summer Research Fellow, 1974.

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## Anodic Oxidation of Aziridines

*Sir:*

Our extensive studies of the generation and reactions of nitrenium ions[1] have utilized various routes to this highly reactive, divalent, electron-deficient nitrogen species. In principle, removal of a hydride, or of a proton and two electrons from a secondary amine, should produce a nitrenium ion. The latter of these possibilities would appear to be theoretically feasible through electrochemical processes. However, electrochemical studies reported thus far on simple aliphatic amines indicated that various modes of reaction were found to occur, which did not necessarily require the intermediacy of nitrenium ions.[2] With these facts in mind, we undertook a study of the electrolysis of aziridines, in order to determine whether chemical behavior consistent with the intermediacy of a singlet nitrenium ion could be observed. We now wish to present a preliminary report of the results of this study.[3]

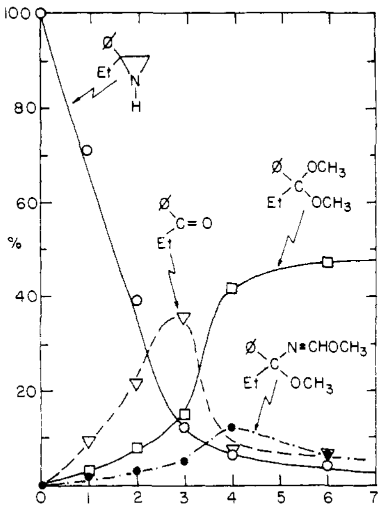
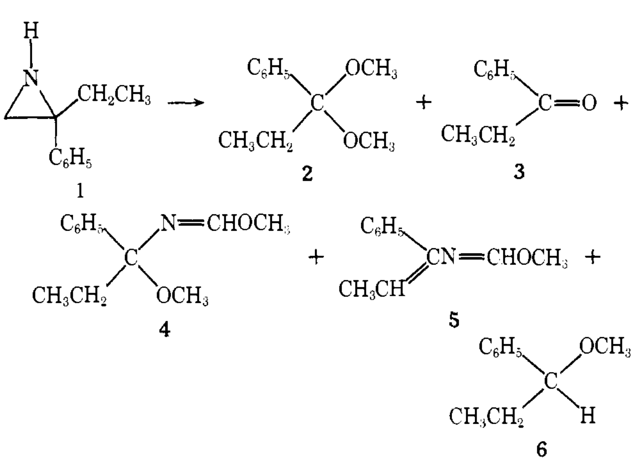
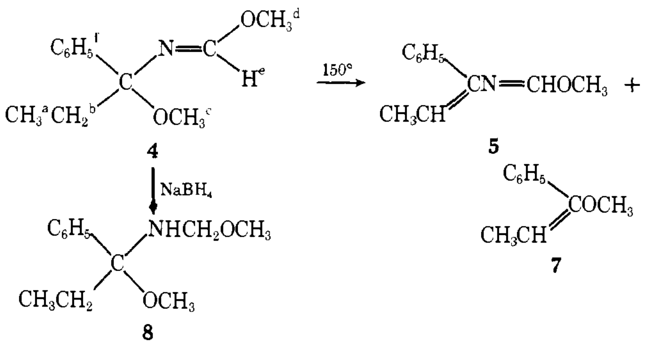


**Figure 1.** Plot of percentage composition (determined by VPC analysis) of the reaction mixture as a function of the number of faradays passed per mole of 2-phenyl-2-ethylaziridine.



1 2 3 4 5 6

2-Phenyl-2-ethylaziridine (1)[6] was electrolyzed in anhydrous methanol at 0° under a nitrogen atmosphere in a divided cell utilizing platinum electrodes, sodium perchlorate as electrolyte, and sodium carbonate as buffer. Passage of 4 F of current per mole of starting material at an applied voltage of 10-15 V and a constant current of 0.5 amps gave **2** (50%), **3** (6%), **4** (12%), **5** (1%), and **6** (<1%). Workup of the electrolysis mixture with aqueous acid resulted in considerable hydrolysis of **2** and **4**. All of the products were isolated by preparative VPC and identified either *via* comparison with independently prepared samples (for **2**, **3**, and **6**) or through their spectral properties. The structure of **4** was assigned on the basis of its spectral and chemical properties. The ir spectrum of **4** showed strong absorptions at 5.98 (C=N) and 9.53 (C—O) $\mu$; the NMR spectrum of **4** showed absorptions at $\tau$ 9.32 (3 H, t, $H_a$), 8.18 (2 H, q, $H_b$), 7.10 (3 H, s, $H_c$), 6.20 (3 H, d, $J_{de} = 0.7$ Hz, $H_d$), 2.40-3.00 (5 H, m, $H_f$), and 2.32 (1 H, q, $J_{de} = 0.7$ Hz, $H_e$[7]). Irradiation of the methoxyl group collapsed the quartet, observed for $H_e$, to a singlet. The mass spectrum of **4** failed to show a parent peak. Instead it showed a base peak (and *apparent* parent peak) at *m/e* 178 which represents the loss of the ethyl group from **4**.[8] In contrast to the failure of normal mass spectrometric methods to give the true parent ion, chemiionization mass spectrometry[9] established the molecular weight of **4** to be 207. Chemical evidence for the structure of **4** was obtained from its pyrolysis at 150° to give **5** (loss of $CH_3OH$) and **7** (loss of $HN{=}CHOCH_3$) in the ratio of 2:1. In the presence of sodium borohydride, **4** was reduced slowly to give a product, which was spectroscopically identified as **8**.



4 5 7 8