Procedure. The nitrogen gas sweep procedure was the same as that previously employed.[7] In the reaction solutions, [2-BuI] = 0.1 M and [base] = 0.25 M. In some reactions, 0.25 M 18-crown-6 was present. Trapped butene products were analyzed by gas chromatography.[4]

Control Experiment. The importance of concomitant solvolysis under the conditions of the base-promoted eliminations was assessed by allowing 2-iodobutane to react with Me_2SO at 50.0 °C in the presence of 1 equiv of 2,6-lutidine. The amount of butenes formed by solvolysis was much less than that produced by reaction of 2-iodobutane with the weakest bases examined.

Registry No. 2-Iodobutane, 513-48-4; 1-butene, 106-98-9; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1.

Effect of a Mercuric Sulfate Precolumn on Chloro Olefin Abstraction[1a]

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Use of a mercuric sulfate–sulfuric acid precolumn removes certain chloro olefins but not others. The reason for this difference has been studied. Lack of correlation with π ionization energies, determined by photoelectron spectroscopy combined with MNDO calculations, indicates that attack on the double bonds is not involved. A high correlation with chlorine lone-pair ionization energies, combined with the fact that only allyl chlorides are removed, implies that removal involves mercury-catalyzed solvolysis, a conclusion supported by ^{35}Cl NQR frequencies.

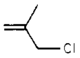
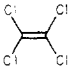
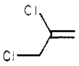
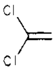
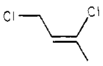
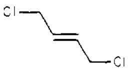
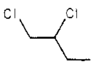
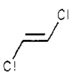
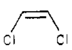
Recently, using a GC/MS technique, we attempted to identify the components of complex reaction mixtures resulting from the chlorofluorination of isobutylene. Most of the components were either four-carbon haloalkanes or haloalkenes. However, it proved difficult to identify the individual components because the fluorochloroalkanes under electron impact gave vanishingly small yields of molecular ions and often fragmented to yield alkene-like mass spectra.[2] It was thought that a precolumn olefin scrubber which would selectively remove unsaturates would greatly assist in the analysis. A comparison of the chromatograms taken with and without the scrubber would then allow GC peaks to be classified as either alkane or alkene.

An olefin scrubbing technique, described some years ago by Francis,[3] was later modified by Innes[4] to meet GC requirements. Innes found that a short precolumn, packed with 20% sulfuric acid impregnated on diatomaceous earth, removed completely the olefin peak from the resulting chromatogram. The olefins ranged from ethylene to 3-heptene.

We therefore constructed a precolumn by packing a short section of Al tubing, 4 in. × 1/4 in. o.d., with 20% mercuric sulfate–20% sulfuric acid loaded on 60/80 mesh Chromosorb P (1 mL of stock solution/g Chromosorb P). The loading was accomplished by rotoevaporating the slurry to dryness. The resulting powder was further dried by heating to 100 °C under vacuum.

This precolumn was, however, found to be generally ineffective in removing F- and Cl-containing olefins from the isobutyl/isobutylene reaction mixtures. The behavior of a number of Cl-containing olefins was therefore studied in the hope of establishing the limitations of this technique.

Table I. Effect of Mercuric Sulfate on Various Chloro Olefins

compd	structure	removal/ nonremoval
I		r
II		nr
III		nr
IV		nr
V[a]		r
VI[b]		r
VII		r
VIII		nr
IX		nr

[a] 4/1 mixture of trans/cis. [b] >95% trans.

For all compounds that were removed by the precolumn, the scrubbing efficiency was 100%; i.e., there was no discernible peak on the chromatogram for a compound that was removed.

The compounds examined, and the effect of the precolumn, are listed in Table I. All of the compounds, with the exception of V, were of greater than 95% purity as determined by GC. All of the compounds gave mass spectra consistent with their structure. Compound V showed two peaks in its chromatogram in the ratio 4/1. NMR showed these peaks to consist of the trans/cis isomer pair. Each of the olefins was examined as a three-compo-

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[1] (a) Presented in part at the National Meeting of the American Chemical Society, Honolulu, Hawaii, Apr. 6, 1979, No. ORGN 487. (b) Robert A. Welch predoctoral fellow.

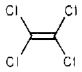
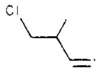
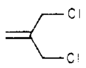
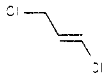
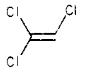
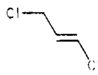
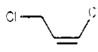
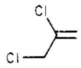
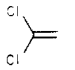
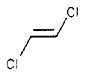
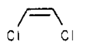
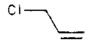
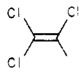
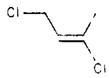
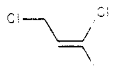
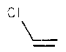
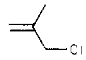
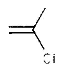
[2] E. R. McCarthy, unpublished results.

[3] A. W. Francis and S. J. Lukasiewicz, *Ind. Eng. Chem., Anal. Ed.*, 17, 703 (1945).

[4] W. B. Innes, W. E. Bambrick, and A. J. Andreatch, *Anal. Chem.*, 35, 1198 (1963).

0022-3263/79/1944-4109$01.00/0

Table II. First Ionization Potentials (eV)

compd	removal/ nonremoval	MNDO	exptl *a*	*b*	*c*	*d*	*e*	*f*
		10.74		9.58				
	r	10.72						10.42
		10.72						10.28
	r	10.71						10.27
		10.65		9.75				
		10.63	9.70					
		10.62	9.70					
	nr	10.62						10.09
	nr	10.57		10.16		10.00	10.00	
	nr	10.56		9.91		9.80	9.93	
	nr	10.50		9.93		9.80	9.93	
		10.48			10.38			
	nr	10.48						
	r	10.44						9.62[g]
	r	10.43						9.62[g]
		10.39	10.30	10.29	10.01	10.15		
	r	10.26						9.90
		10.21						9.76

[a] Reference 9a. [b] Reference 9b. [c] Reference 9c. [d] Reference 9d. [e] Reference 9e. [f] Values reported in this work. [g] Mixture of cis and trans isomers.

nent mixture consisting of cyclohexane (80%), *trans*-2-heptene (10%), and the chloro olefin (10%). Cyclohexane was unaffected by the precolumn and so served as a diluent. *trans*-2-Heptene was removed completely and was therefore added as a check on precolumn efficiency. Individual compounds and the three-component mixtures were examined on a HP 5750 gas chromatograph using an 8 ft × $^1/_4$ in. 5% SE-52 column. All compounds were found to elute below a column temperature of 100 °C.

The removal of a simple olefin by the column is presumably due to reaction with the mercuric sulfate–sulfuric acid solution, resulting in addition to the C=C bond. Such additions are believed to involve electrophilic attack by mercuric ion on the olefin to form a π complex[5] which then reacts with a nucleophile. Since mercury has no d electrons available for back-coordination,[5] the ease of such π-complex formation should be greater the lower the ionization potential of the olefin. The fact that some of the chloro olefins (I, V, VI, VII) were removed by the column, and the others not, could therefore be easily understood if the ionization potentials of the former lay below, and of the latter above, some critical value.

Ionization potentials are best measured by photoelectron spectroscopy (PES). Since such data were available for only about half the compounds listed in Table I, we obtained PES spectra for most of the rest (see Figure 1), at ambient temperature, using a spectrometer similar to one previously described.[6] Table II shows the first ionization

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(5) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C71 (1951).

(6) P. K. Bischoff, M. J. S. Dewar, D. W. Goodman, T. B. Jones, *J. Organomet. Chem.*, **82**, 89 (1974).

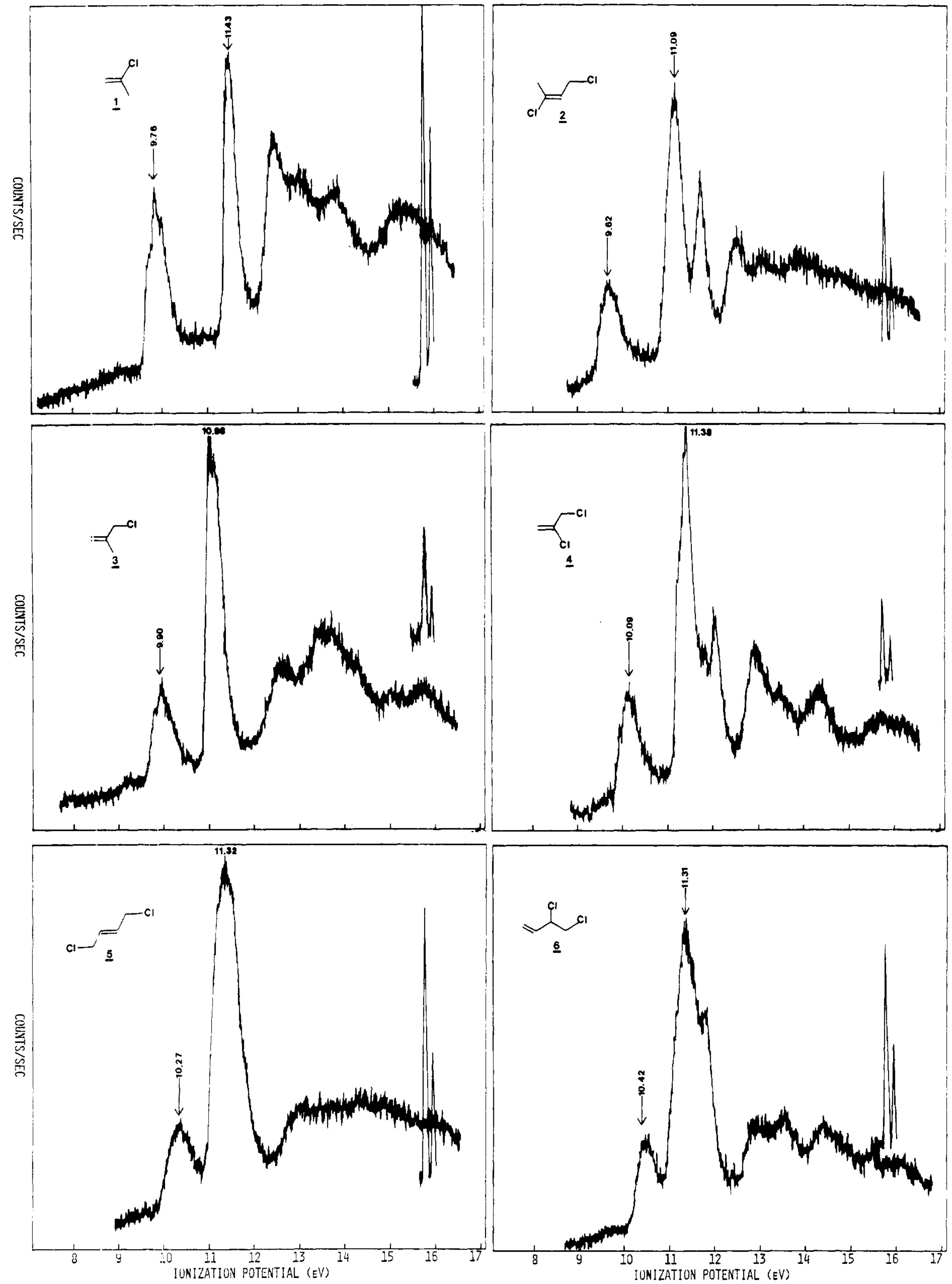

Figure 1. Photoelectron spectra of 2-chloropropene (1), 1,3-dichloro-*cis*-2-butene (2), 2-(chloromethyl)propene (3), 2,3-dichloropropene (4), 1,4-dichloro-*trans*-2-butene (5), 3,4-dichloro-1-butene (6).

potentials found in this way, together with an indication of whether or not the compounds were removed by the column. It will be seen that the effect of the column bears no relation to the observed ionization potentials.

The possibility remained that the first ionization potentials of these compounds might not always correspond to loss of a π electron from the C=C bond but rather from a chlorine lone pair.

As a check, we therefore decided to carry out MNDO[7] calculations for the series of chloro olefins. MNDO has been shown to give good estimates of the ionization energies of molecules by using Koopman's theorem. In par-

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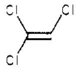
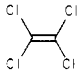
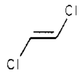
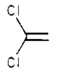
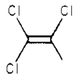
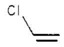
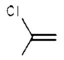
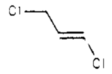
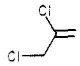
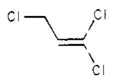
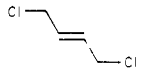
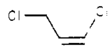
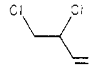
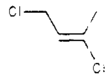
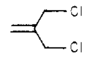
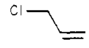
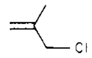
[7] (a) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899, 4907 (1977); (b) M. J. S. Dewar, H. S. Rzepa and M. L. McKee, *ibid.*, **100**, 3607 (1978).

Table III. Second Ionization Potentials (eV)

compd	removal/ nonremoval	MNDO	exptl					
			a	*b*	*c*	*d*	*e*	*f*
		12.85		11.71				
		12.84		11.59				
	nr	12.72		11.80		11.82	12.14	
	nr	12.72		11.70		11.64	11.90	
	nr	12.64		11.65		11.62	11.66	
	nr	12.62						
		12.43	11.70	11.73	11.67	11.61		
		12.35						11.43
		12.33	11.08					
	nr	12.32						11.38
	r	12.31						11.09[g]
	r	12.23						11.32
		12.22	10.90					
	r	12.18						11.31
	r	12.17						11.09[g]
		12.15						11.10
		12.04			11.21			
	r	12.01						10.98

[a] Reference 9a. [b] Reference 9b. [c] Reference 9c. [d] Reference 9d. [e] Reference 9e. [f] Values reported in this work. [g] Mixture of cis and trans isomers.

ticular, it nearly always gives the various ionizations in the right order.

The calculations were carried out by the standard MNDO procedure,[7] the geometries being calculated as usual[7] by minimizing the total energy without making any assumptions. The HOMO of each molecule corresponded predominantly to the C=C π MO, implying that the first ionization in each case does indeed involve loss of a C=C π electron. Table I lists the first ionization energies deduced from the HOMO energies by using Koopman's theorem.

It will be seen that the calculated ionization energies are systematically too large by ca. 1 eV. A similar error appears in all cases[8] for MOs composed largely, or partly, of chlorine 3p AOs and is probably due[8] to the neglect of 2p–3p interactions in MNDO. However, since the error is fairly uniform and since the gaps between the first and second ionization potentials (see below) are quite large, there seems little doubt that the first ionizations of all these compounds do indeed correspond to loss of electrons from their olefinic π MOs. It therefore seems very unlikely that their removal by the precolumn involves attack on C=C double bonds.

Mercuric ion can, however, catalyze other reactions as well as addition. In particular, it catalyzes the S_N1 solvolysis of chlorides, RCl, particularly where R^+ is a relatively stable cation. Allyl chloride falls in this category, and it will be seen that the compounds removed by the precolumns are all substituted allyl chlorides. This suggests that removal of chlorides by the precolumn is related to the ease of their S_N1 solvolyses.

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(8) M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, **100**, 784 (1978).

Figure 2. Illustration of the hyperconjugative interaction present in (a) allyl cation and (b) allyl chloride which increases the electron density on chlorine.

The resonance interaction between C=C and C$^+$ that stabilizes the allyl cation (Figure 2a) is also present in allyl chloride, in the form of a hyperconjugative interaction between the C=C π bond and the C–Cl σ bond (Figure 2b).[9f] A semiquantitative estimation of the amount of hyperconjugation due to the C–Cl bond in allyl chloride has been made by Schweig et al.[9f] In this estimation the C–Cl bond is found to have a hyperconjugative effect about equivalent to that of the C–H bond. If one considers an analogous treatment of our 2,3-dichloropropene/2-chloropropene/vinyl chloride system, the hyperconjugative effect of the C–Cl bond is found to be almost 1.5 times that of the C–H bond. We believe this relationship to be very reasonable especially since in our system more hyperconjugation should be possible due to the conjugative interaction of the vinyl chloride. This hyperconjugative interaction results in a transfer of negative charge to chlorine which manifests itself by a decrease in the lone-pair ionization potential of chlorine[9] and by a decrease in the ^{35}Cl nuclear quadrupole resonance frequencies.[10,11]

Since conjugative interactions between Cl and the double bond in a vinyl chloride lead to a positive charge on chlorine and so to an increase in the lone-pair ionization potential, the second ionization potential of a chlorinated allyl chloride should correspond to ionization of a lone pair of the allylic chlorine. Removal by the precolumn would then be expected to occur only for compounds whose second ionization potentials lie below some critical value.

Table III shows calculated (MNDO) and observed (PES) second ionization potentials for the compounds studied here. It will be seen that they do indeed correspond to the predicted pattern. All chlorides with a second ionization potential below 11.35 eV (observed) or 12.32 eV (calculated) were removed by the column but none with values above these limits.

Use of nuclear quadrupole resonance (NQR) data is less direct in this connection because the conjugative interactions in vinyl chlorides also lower the ^{35}Cl NQR frequencies. Moreover, data are available for only two of the allyl chlorides in Table I, i.e., III (34.69 MHz[10]) and VI (34.11 MHz[11]). However, these are consistent with our interpretation, VI being removed by the precolumn whereas III was not. On this basis one would expect the precolumn also to remove benzyl chloride (33.63 MHz[11]) even though it is not an olefin derivative.

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Registry No. 1, 557-98-2; I, 563-47-3; II, 21400-25-9; III, 78-88-6; IV, 75-35-4; *cis*-V, 10075-38-4; *trans*-V, 7415-31-8; *cis*-VI, 1476-11-5; *trans*-VI, 110-57-6; VII, 760-23-6; VIII, 156-60-5; IX, 156-59-2; tetrachloroethene, 127-18-4; 3-chloro-2-(chloromethyl)-1-propene, 1871-57-4; trichloroethene, 79-01-6; *cis*-1,3-dichloro-1-propene, 10061-01-5; 3-chloro-1-propene, 107-05-1; chloroethene, 75-01-4; mercuric sulfate, 7783-35-9.

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Efficient Peroxyoxalate Chemiluminescence from Reactions of *N*-(Trifluoromethylsulfonyl)oxamides with Hydrogen Peroxide and Fluorescers[1]

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Chemilumescence quantum yields above 0.11 einstein mol^{-1} (11%) were obtained from six *N*-(trifluoromethylsulfonyl)oxamides substituted on nitrogen by electronegatively substituted aryl groups. One compound, *N,N'*-bis(trifluoromethylsulfonyl)-*N,N'*-bis(2,4,5-trichlorophenyl)oxamide, provided a chemiluminescent quantum yield of 34%, making it the most efficient nonenzymatic compound known. Molecular sieves were found to be effective catalysts for the preparation of certain trifluoromethylsulfonamides from the amine and trifluoromethylsulfonyl chloride and for the preparation of the oxamides from oxalyl chloride and sulfonamide.

Peroxyoxalate chemiluminescence[2] is illustrated by the reaction sequence outlined in Scheme I.

Chemiluminescence quantum yields of 0.10 to 0.18 einstein mol^{-1} (10–18%) have been reported for the oxalic ester A with fluorescers such as 9,10-bis(phenylethynyl)anthracene (green) and 1-chloro-9,10-bis(phenylethynyl)anthracene (yellow).[3,4] Other oxalic esters such as bis(2,4,6-trichlorophenyl) oxalate,[5,6] bis(2,4-dinitrophenyl) oxa-

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