of maximum absorption and the average molar absorptivities for the acetophenones which were determined from several scans at different concentrations.

The 1-chloro-1-nitro-1-(*p*-X-phenyl)ethanes were accurately weighed into 50-ml volumetric flasks and diluted to the mark with the appropriate stock solution of aqueous ethanol. Aliquots of these solutions were transferred to 25-ml volumetric flasks and diluted with the appropriate solvent for the kinetic runs. Runs were made in triplicate and the amount of substrate used was that amount calculated to give a final infinity absorption value between 1.00 and 2.00 OD units. For the runs containing sodium perchlorate or sodium chloride, the desired concentrations were obtained by pipetting aliquots of these salt solutions into the reaction flasks. The flasks were vigorously shaken, stoppered, and placed in the oil or water bath at the desired temperature; 1-ml aliquots were removed with a pipet and diluted to 10 ml with 95% ethanol. The optical densities of these solutions were determined at the appropriate wavelength in matched 1.000 cm cells using 95% ethanol as the blank.

The infinity absorption values were obtained by allowing the reaction to proceed through several half-lives until a constant OD reading was obtained. Calculations were made from the integrated first-order rate expression

$$kt = 2.303 \log [(OD_\infty - OD_0)/(OD_\infty - OD_t)]$$

where k = first-order rate constant, t = time in seconds, OD_∞ = optical density at infinity time, OD_0 = optical density at zero time, and OD_t = optical density at time t. A plot of log $(OD_\infty - OD_t)$ *vs.* t gives a straight line with slope equal to $-k/2.303$. The slopes were calculated from a least-squares computer program.

Hydrolysis of 1-Chloro-1-nitro-1-(*p*-X-phenyl)ethanes in 90% Formic Acid.—Kinetics for these runs could not be followed spectrophotometrically because of solvent cut-off in the range of interest due to the high concentration of formic acid. The rates were followed instead by measuring the amount of chloride ion released by the reaction as a function of time. The Volhard titrimetric procedure was employed.[28]

Samples of the 1-chloro-1-nitro-1-(*p*-X-phenyl)ethanes sufficient to give a final concentration of approximately 3.0×10^{-2} mol/l. were accurately weighed into 25-ml volumetric flasks and diluted to the mark with stock 90% formic acid containing 0.065 mol/l. of sodium perchlorate. The flasks were shaken until dissolution of the substrate was complete and were then immersed in an oil or water bath at the desired temperature; 2-ml aliquots were removed at various time intervals and pipetted into 5 ml of water contained in a 50-ml erlenmeyer flask.

A known excess of standard silver nitrate solution was added to the flask, followed by 2 ml of dilute nitric acid, 1 ml of a saturated solution of ferric ammonium sulfate in dilute nitric acid, and 1 ml of nitrobenzene. The mixture was vigorously agitated with a magnetic stirrer and the excess silver nitrate was back titrated to the rusty-red end point with standard potassium thiocyanate.

Calculations were made from the integrated first-order rate expression

$$k = (2.303/t) \log [a/(a - x)]$$

where k = first-order rate constant, t = time in seconds, a = initial quantity of substrate in given volume, x = amount of substrate reacting in time t, and $a - x$ = amount of substrate remaining at time t. A plot of log $[a/(a - x)]$ *vs.* t gives a straight line with slope equal to $k/2.303$.

Activation Parameters.—Activation parameters were calculated by least-squares programs utilizing the Arrhenius and absolute rate equations.

Registry No.—**2a,** 31659-47-9; **2b,** 31657-66-6; **2c,** 31657-67-7; **2d,** 31657-68-8; **2e,** 31657-69-9; **2f,** 31657-70-2.

[28] D. A. Skoog and D. M. West, "Fundamentals of Analytical Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1966, p 262.

Chlorination of Alkenes with Trichloramine[1]

KURT W. FIELD[2] AND PETER KOVACIC*

Department of Chemistry, University of Wisconsin—Milwaukee, Milwaukee, Wisconsin 53201

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Trichloramine in nonpolar solvent gave excellent yields of vicinal dichlorides with certain types of olefins. Nitrogen was generated almost quantitatively, along with the by-products, ammonium chloride and basic material. With 1-hexene, 1-octene, cyclopentene, cyclohexene, 3-chloropropene, and 1,1-dichloroethylene as substrates, yields of the corresponding *vic*-dichlorides ranged from 89 to 97%. The *meso*:*dl* ratios for chlorination of the isomeric 2-butenes were similar to those obtained from molecular chlorine under radical conditions. Additional evidence for a radical mechanism was derived from relative reactivities, catalysis, formation of some *cis*-1,2-dichlorocyclohexane from cyclocyclohexene, and participation of an alkane additive. The high addition:substitution ratios suggest that free chlorine atoms are generated in no more than minor amounts. The detailed aspects of the radical pathway are discussed.

The most pertinent prior reference describes the formation of 1,2-dichlorocyclohexane in 77% yield from cyclohexene and trichloramine.[3] However, there has been no follow-up of this work since it appeared more than 40 years ago.

The bulk of the previous investigations involving the interaction of *N*-chloramines with olefins involves the chloramination reaction. Only a brief summary will be presented since a review of the subject is available elsewhere.[4] Coleman and coworkers revealed that trichloramine underwent addition to various olefins, *e.g.*, ethylene, isobutylene, cyclohexene, and styrene.[5-7] *N*,*N*-Dichloro-*β*-chloroalkylamines were postulated as the initial adducts which were converted to *β*-chloroalkylamines, <20%, after work-up with concentrated hydrochloric acid. Unspecified amounts of dichloride, along with nitrogen and ammonium chloride, were also obtained. Unsymmetrical olefins formed *β*-chloroalkylamines in which chlorine was affixed to the least substituted olefinic carbon atom. Under photolytic or thermal conditions chloramine gave low yields of *vic*-dichlorides with simple olefins.[8,9] *N*-Halo-1,2,4-

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[1] Paper XVI. Chemistry of *N*-Halamines. Preliminary communication: K. W. Field and P. Kovacic, *Syn.*, 135 (1969). Presented at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, ORGN 107.

[2] From the Ph.D. Thesis of K. W. F., Case Western Reserve University, 1970; the research was carried out at the University of Wisconsin—Milwaukee.

[3] N. Stoll, *Bull. Soc. Chim. Belg.*, **38**, 71 (1929).

[4] P. Kovacic, M. K. Lowery, and K. W. Field, *Chem. Rev.*, **70**, 639 (1970).

[5] G. H. Coleman, G. M. Mullins, and E. Pickering, *J. Amer. Chem. Soc.*, **50**, 2739 (1928).

[6] G. H. Coleman and H. P. Howells, *ibid.*, **45**, 3084 (1923).

[7] G. H. Coleman and A. W. Campbell, *ibid.*, **50**, 2754 (1928).

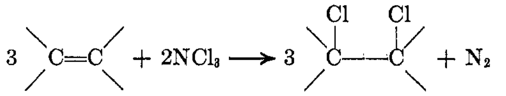
[8] Y. Ogata, Y. Izawa, and H. Tomioka, *Tetrahedron*, **23**, 1509 (1967).

[9] H. Prakash and H. H. Sisler, *J. Org. Chem.*, **35**, 3111 (1970).

triazoles have also been investigated as halogen donors in this type of reaction.[10] This paper describes a detailed investigation of the synthetic merits of the trichloramine–alkene reaction, along with a treatment of the mechanistic aspects.

Results and Discussion

We found that a solution of trichloramine in methylene chloride functions as a halogenating agent for various types of olefins (eq 1). Excellent yields, 81–97%,


(1)

of *vic*-dichlorides were obtained from substrates (Table I) of the type $CH_2{=}CHR$, $RCH{=}CHR$, and $CH_2{=}CX_2$ (R = alkyl; X = halogen). Nitrogen was generated almost quantitatively (~90% yield) with certain olefins, along with the by-products, ammonium chloride and basic material. These substances were also reported by Coleman and coworkers.[5–7] Due to the nature of the by-products and the specificity of addition *vs.* substitution, simple purification methods sufficed to provide pure, >98%, *vic*-dichloride.

TABLE I

CHLORINATION OF OLEFINS WITH TRICHLORAMINE

Olefin[a]	Temp, °C	Product	Yield, %
1-Butene[b]	−15 ± 3	1,2-Dichlorobutane	81
Isobutylene[b]	−15 ± 3	3-Chloro-2-methylpropene	50
		1,2-Dichloro-2-methylpropane	25
1-Hexene[c]	0 ± 2	1,2-Dichlorohexane	97
1-Hexene[c,d]	0 ± 2	1,2-Dichlorohexane	90
1-Hexene[c,e]	0 ± 2	1,2-Dichlorohexane	94
1-Octene[c]	0 ± 2	1,2-Dichlorooctane	93
Cyclopentene[c]	0 ± 2	*trans*-1,2-Dichlorocyclopentane	89
Cyclohexene[b]	0 ± 2	*trans*-1,2-Dichlorocyclohexane	92
Cyclohexene[c]	0 ± 2	*trans*-1,2-Dichlorocyclohexane	91
		cis-1,2-Dichlorocyclohexane	~3
3-Chloropropene[b]	2 ± 2	1,2,3-Trichloropropane	92
cis-1,2-Dichloroethylene[f,g]	25 ± 2	1,1,2,2-Tetrachloroethane	82
cis-1,2-Dichloroethylene[f,h]	25 ± 2	1,1,2,2-Tetrachloroethane	56
1,1-Dichloroethylene[b]	25 ± 1	1,1,1,2-Tetrachloroethane	89
Trichloroethylene[b,i]	23 ± 1	Pentachloroethane	32
Trichloroethylene[b,j]	23 ± 1	Pentachloroethane	41

[a] Molar ratio, NCl_3:olefin = 0.04:0.09. [b] Trichloramine solution was added dropwise to the olefin in methylene chloride. [c] Olefin in methylene chloride was added dropwise to trichloramine solution. [d] Fourfold scale. [e] Molar ratio, NCl_3:olefin = 0.04:0.075. [f] Trichloramine solution and olefin combined in one portion. [g] The mixture of olefin and trichloramine was purged with nitrogen and illuminated for 4 hr with a 275-W sun lamp. [h] Complete reaction after 1 week. [i] 24 hr at 23°; a slightly yellow color still remained. [j] Benzoyl peroxide, 0.1 g, was added to the olefin solution prior to trichloramine addition.

Several studies were undertaken to determine optimum reaction conditions. The molar ratio of trichloramine:olefin was usually 0.04:0.09; however, as shown with 1-hexene only a slight decrease in yield was observed when a molar ratio of 0.04:0.075 was used. It should be noted that 0.04 mol of trichloramine is theoretically capable of producing 0.06 mol of the corresponding dichloride. In the presence of a 25% excess of the olefin, excellent yields can be obtained. With cyclohexene, the mode of addition, olefin to trichloramine or vice versa, did not affect the yield of dichloride or the amount of side products. The effect of temperature on the chlorination of cyclohexene in methylene chloride solvent was investigated. Below −40° nitrogen was not evolved; however, upon warming to −30 ± 5° the reaction proceeded. Best yields were realized in the −30–0° range. At 38° the yield decreased, accompanied by a corresponding increase in side products. The use of other nonpolar organic solvents for chlorination of cyclohexene at 0 ± 2° did not alter the yield of dichloride in most cases. The low yield figure obtained with carbon disulfide is attributed to a slow reaction of trichloramine with solvent, as evidenced by gas evolution from a mixture of the two.

When compared to other chlorinating agents (Table II), the merits of trichloramine become evident. Although not widely recognized, it is well established that the formation of *vic*-dichlorides from molecular chlorine and olefins has limited synthetic utility due to the occurrence of side reactions.[11–14] The situation is improved in the presence of oxygen.[15] Certain olefinic substrates with sulfuryl chloride also give undesirable by-products.[16] Phosphorus pentachloride has been investigated only to a relatively small extent, as is also the case for tetrabutylammonium iodotetrachloride[17] and iodobenzene dichloride.[15] It should be noted that the trichloramine solutions are easy to prepare and safe to handle with simple precautions.[18]

TABLE II

YIELDS OF *vic*-DICHLORIDES FROM VARIOUS METHODS

Halogenating agent	*vic*-Dichloride, %, from			
	1-Hexene	1-Octene	Cyclohexene	3-Chloropropene
NCl_3	97	93	91	92
SO_2Cl_2	79[a]	63[a]	89[b]	80–90[b]
PCl_5[c]		83	87	
Cl_2[d]			70	

[a] Reference 16. [b] M. S. Kharasch and H. C. Brown, *J. Amer. Chem. Soc.*, **61**, 3432 (1939). [c] D. P. Wyman, J. Y. C. Wang and W. R. Freeman, *J. Org. Chem.*, **28**, 3173 (1963). [d] H. Böhme and R. Schmitz, *Chem. Ber.*, **88**, 357 (1955).

Recent studies involving the reaction between chlorine and certain types of olefins, *e.g.*, $CH_2{=}CHR$ and $RCH{=}CHR$, in the absence of initiators and inhibitors revealed that the mechanism was predominantly radi-

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(10) H. G. O. Becker, *et al.*, *Z. Chem.*, **9**, 325 (1969).

(11) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, New York, N. Y., 1966, p 105.

(12) M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 2161 (1965).

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(14) M. L. Poutsma, *ibid.*, **87**, 4285 (1965).

(15) M. L. Poutsma, "Methods in Free-Radical Chemistry," E. S. Huyser, Ed., Vol. 1, Marcel Dekker, New York, N. Y., 1969, Chapter 3, section VI.

(16) M. S. Kharasch and A. F. Zavist, *J. Amer. Chem. Soc.*, **73**, 964 (1951).

(17) R. E. Buckles and D. F. Knaack, *J. Org. Chem.*, **25**, 20 (1960).

(18) P. Kovacic and S. S. Chaudhary, *Org. Syn.*, **48**, 4 (1968).

cal.[12,13] In the presence of oxygen as inhibitor, the pathway was diverted almost completely in the polar direction. These significant reports by Poutsma clarified conflicting mechanistic interpretations in previous investigations.

Polar addition of chlorine to the 2-butene isomers gave 97–98% addition products, stereospecifically trans. Under radical conditions there was a loss of stereospecificity, accompanied by a greater percentage of substitution products (15–20%).[13] Chlorination of the isomeric 2-butenes with trichloramine under nitrogen in the dark gave *meso*:*dl* ratios corresponding closely to those obtained for chlorine under radical conditions (Table III). The substitution products normally observed with chlorine were essentially absent in our case (less than 2% of unidentified material). A small amount of polar reaction may accompany the radical category with both halogenating agents.[13]

TABLE III

meso:*dl* RATIOS FOR CHLORINATION OF 2-BUTENES

2-Butene	Chlorinating agent	1,2-Dichlorobutane, %[a] Meso	*dl*
Cis	Cl_2 (polar)[b]	0	100
	Cl_2 (radical)[b]	33	67
	NCl_3	28	72
Trans	Cl_2 (polar)[b]	100	0
	Cl_2 (radical)[b]	88	12
	NCl_3	86	14

[a] Per cent of the isomeric mixture. [b] Reference 13.

Fundamental similarities in the two chlorination systems are also apparent from a comparison of the *meso*:*dl* ratios for various mole fractions, N, of *cis*-2-butene in nonpolar solvent. Analysis of a trichloramine reaction in methylene chloride, $N = \sim 1$ to $N = 0.30$, gave a constant ratio of *ca.* 0.4. The ratios obtained for chlorine in 1,1,2-trichlorotrifluoroethane ranged from 0.49 for $N = 1$ to 0.43 for $N = 0.40$.[13] Trichloramine must be used in solution, whereas chlorine can be passed directly into the neat olefin.

Chlorination in the presence of several different solvents did not affect the *meso*:*dl* ratios from the 2-butene isomers (Table IV). In each case the isomeric 2,3-dichlorobutanes composed 98% of the reaction mixture. With *o*-dichlorobenzene and carbon disulfide as diluents, only traces of ammonium chloride were formed. It seems that the salt arises from the action on trichloramine of hydrogen chloride[19] which is most likely generated during hydrogen abstraction. The paucity of ammonium chloride suggests that these side reactions are essentially eliminated in certain solvents. A possible rationale is the formation of a complex from solvent and the abstracting entity,[12,15,20–22] thereby increasing the selectivity of the radical moiety.

TABLE IV

EFFECT OF SOLVENT ON STEREOCHEMISTRY OF CHLORINATION

2-Butene	Solvent	1,2-Dichlorobutane, %[a] Meso	*dl*
Cis	CH_2Cl_2	28	72
	CCl_4	31	69
	o-$Cl_2C_6H_4$	30	70
	CS_2	28	72
Trans	CH_2Cl_2	86	14
	CCl_4	89	11

[a] Per cent of the isomeric mixture.

Several other findings are in accord with a radical pathway. In the presence of cyclohexane, halogenation of *cis*-2-butene with trichloramine gave cyclohexyl chloride, 2–3%, in addition to the isomeric 2,3-dichlorobutanes. A similar finding was observed for the chlorine–cyclohexene–cyclohexane system.[12] According to the literature, the relative reactivity per hydrogen for abstraction by a chlorine atom is 0.6 for a primary allylic hydrogen in *cis*-2-butene *vs.* a secondary hydrogen in cyclohexane.[13] A radical mechanism is consistent with attack on the alkane.[12,15] Identification of the major side product, *cis*-1,2-dichlorocyclohexane, ~2–3%, from the chlorination of cyclohexene proved mechanistically informative. Ionic reaction of chlorine gave 99% of the adduct as *trans*-1,2,-dichlorocyclohexane; however, under radical conditions up to 4% cis addition was obtained.[12] Our observed order of reactivity, $CH_2{=}CCl_2 > cis\text{-}ClCH{=}CHCl$, is in accord with prior studies entailing addition of chlorine[22] and polymerization.[23] The difference in reactivity[15] appears to be substantially greater for trichloramine in comparison with chlorine. Factors affecting the relative rates in radical additions have been discussed.[22]

In an attempt to intercept the chain-propagating radicals, several inhibitors were added to the trichloramine–cyclohexene mixture. No inhibition was observed (Table V). In the presence of cumene, there was no formation of dicumyl. The decrease in yield with oxygen may be due to loss of trichloramine during oxygen sweep. With *cis*-2-butene, identical *meso*:*dl* ratios were obtained in the presence of oxygen or nitrogen.

TABLE V

EFFECT OF INHIBITORS ON CHLORINATION

Olefin	Inhibitor	*vic*-Dichloride Yield, %[a]	
Cyclohexene	2,6-Di-*tert*-butylphenol[b]	86	
	Cumene[c]	87	
	Oxygen	81	
	d	87	
		meso	*dl*
cis-2-Butene	Oxygen	29	71
	d	28	72

[a] The *meso*:*dl* ratio is given for 2,3-dichlorobutane. [b] Molar ratio, $NCl_3:C_6H_{10}:2,6\text{-}[(CH_3)_3C]_2C_6H_3OH = 0.04:0.09:0.15$. [c] Molar ratio, $NCl_3:C_6H_{10}:(CH_3)_2CHC_6H_5 = 0.04:0.09:0.045$; no dicumyl was detected by glpc analysis. [d] Under nitrogen.

A brief investigation was made of the effect of photolytic conditions. The product distribution was essentially unchanged with cyclohexene (very fast reaction in both cases). In the case of *cis*-1,2-dichloroethylene, the reaction rate was markedly increased, accompanied by a substantial increase in the yield of tetrachloroethane. We are uncertain whether photolysis favors the reaction which takes place under stan-

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(19) W. A. Noyes, *J. Amer. Chem. Soc.*, **42**, 2173 (1920).

(20) G. A. Russell, *ibid.*, **80**, 4987 (1958).

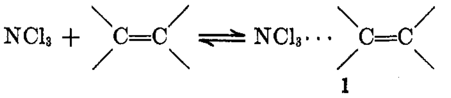
(21) C. Walling and M. F. Mayahi, *ibid.*, **81**, 1485 (1959).

(22) M. L. Poutsma and R. L. Hinman, *ibid.*, **86**, 3807 (1964).

(23) F. W. Billmeyer, Jr., "Textbook of Polymer Science," Interscience, New York, N. Y., 1965, p 263.

dard conditions or dissociates the reagent to chlorine[24] which then participates.

The indicated mechanistic schemes seem relevant in view of the experimental data and literature analogy. Initiation could be of the molecule-induced type[12,25] (eq 2 and 3). Equation 2 appears plausible since this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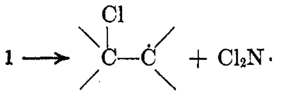
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type of complex is postulated for many "even" molecule reactions. Although trichloramine is not an "even" type, it has been classified as the most covalent molecule in the unsymmetrical category because the electronegativities of chlorine and nitrogen are essentially the same.[26] Initiation under certain conditions might also occur *via* initial homolysis of the N-Cl bond (47.7 kcal/mol)[27] (eq 4). A third possibility involves

$$NCl_3 \rightleftharpoons Cl\cdot + \mathbf{3} \qquad (4)$$

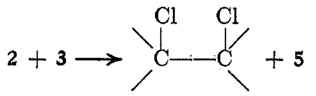
a molecule-induced reaction by traces of molecular chlorine.[18] Finally, **2** might arise by interaction of the olefin with a species generated subsequently, *e.g.*, **3**, **4**, or **6**.

Once formed, reactive **3** could subsequently participate in a number of processes (eq 5–8). Possible pathways for generation of *vic*-dichloride are illustrated (eq 8–11). Nitrogen might also be produced as described in eq 12. In relation to energetics, a favorable driving force is associated with the ultimate formation of nitrogen.

$$2\,\mathbf{3} \rightleftharpoons \underset{\mathbf{4}}{Cl_2NNCl_2} \qquad (5)$$

$$2\,\mathbf{3} \rightleftharpoons NCl_3 + \underset{\mathbf{5}}{NCl} \qquad (6)$$

$$2\,\mathbf{5} \longrightarrow \underset{\mathbf{6}}{ClNNCl} \qquad (7)$$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$$\mathbf{2} + NCl_3 \longrightarrow \mathbf{7} + \mathbf{3} \qquad (9)$$

$$2\,\mathbf{2} + \mathbf{4} \longrightarrow 2\,\mathbf{7} + \mathbf{6} \qquad (10)$$

$$2\,\mathbf{2} + \mathbf{6} \longrightarrow 2\,\mathbf{7} + N_2 \qquad (11)$$

$$\mathbf{5} + \mathbf{6} \longrightarrow NCl_3 + N_2 \qquad (12)$$

Although tetrachlorohydrazine and dichlorodiazine have not been isolated, their fluorine analogs are well documented.[28–30] Based on analogy between trifluoramine, $\Delta H_f = -26 \pm 2$ kcal/mol, and trichloramine, $\Delta H_f = 55.4$ kcal/mol, **4** and **6** would most likely be very unstable.[31] In fact, failure was met in an attempt to prepare tetrachlorohydrazine from hydrazine dihydrochloride by a procedure similar to that for trichloramine.[18] Even at temperatures as low as −50°, nitrogen was generated quantitatively. Several other investigators have also postulated Cl_2N, ClN, and Cl_2N_2 as reaction intermediates.[24,32] In a related study,[33] chlorodifluoramine was found to react under photolytic conditions with ethylene to give 1,2-dichloroethane and tetrafluorohydrazine.

The trichloramine–cyclohexene reaction also produced ~4% yield of 7-azabicyclo[4.1.0]heptane. Since chloramination is known to proceed to a limited extent in this type of system,[5] the aziridine product is probably generated *via* 2-chloro-*N*,*N*-dichlorocyclohexylamine. Addition of chloronitrene (**5**) is deemed unlikely since several attempts to prepare the *N*-fluoro derivative of the aziridine from cyclohexene and fluoronitrene were unsuccessful.[34] Similarly, no adduct of **5** with cyclohexene resulted from the use of dichloramine–triethylamine.[35] The paucity of nitrogen adducts presumably reflects the relatively high activation energy needed for addition of nitrogen radicals to the double bond.[9] The figure for the addition of $F_2N\cdot$ to simple olefins is about 12–14 kcal/mol,[36] in contrast with a value ≤1.4 kcal/mol for chlorine atoms.[37] Since the activation energy for reaction of the 2-chloroethyl radical with chlorine is 0–1 kcal/mol,[38] the analogous interactions with **4** and **6** should also be near zero.

Unlike the chlorinations involving chlorine or sulfuryl chloride, the trichloramine procedure produces *vic*-dichlorides accompanied by very minor amounts of other organic materials. The greater selectivity with trichloramine for addition *vs.* substitution is taken as evidence for no more than quite minor involvement of free chlorine atoms.[12,15,22] One can account for the similar *meso*:*dl* ratios for the products from the 2-butenes and either chlorine or trichloramine on the basis of formation of the same crucial intermediate, **2**, in both cases. Lack of inhibition in chlorination with trichloramine suggests that carbon radical **2** reacts more readily with intermediates containing the N-Cl bond than with the inhibitors. The rapidity of reaction even at low temperatures reflects the very favorable energetics. In contrast, inhibition occurs with the chlorine–olefin system[12,18] (compare the bond dissociation energies for Cl-Cl, 58 kcal/mol,[27] and N-Cl, 47.7 kcal/mol; a number of the components containing the N-Cl bond in our reaction system should be considerably more labile).

With several substrates appreciable participation of ionic reactions seems likely.[13,14] Isobutylene gave 3-chloro-2-methylpropene (**10**), 50% yield, and 1,2-dichloro-2-methylpropane (**11**), 25% yield (Table I). A substantial amount of ammonium chloride, 66% yield, was also obtained. Photolytic conditions pro-

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[25] J. C. Martin and E. H. Drew, *J. Amer. Chem. Soc.*, **83**, 1232 (1961).

[26] L. Pauling, *ibid.*, **54**, 3570 (1932).

[27] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 85.

[28] J. K. Ruff, *Chem. Rev.*, **67**, 665 (1967).

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[35] W. LeNoble, cited in ref 34.

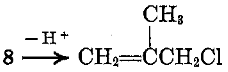
[36] A. J. Dijkstra, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc. A*, 582 (1966).

[37] E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. II, Reinhold, New York, N. Y., 1954, p 673.

[38] P. B. Ayscough, A. J. Cocker, F. S. Dainton, and S. Hirst, *Trans. Faraday Soc.*, **58**, 318 (1962).

duced no significant change in distribution of the organic products. Ionic reaction (eq 13–17) most likely

$$(CH_3)_2C{=}CH_2 + NCl_3 \longrightarrow \underset{\mathbf{8}}{(CH_3)_2\overset{+}{C}CH_2Cl} + \underset{\mathbf{9}}{NCl_2^-} \quad (13)$$



$$\mathbf{8} \xrightarrow{-H^+} \underset{\mathbf{10}}{CH_2{=}C(CH_3)CH_2Cl} \quad (14)$$

$$\mathbf{8} + \mathbf{9} \longrightarrow \underset{\mathbf{11}}{(CH_3)_2CClCH_2Cl} + \mathbf{5} \quad (15)$$

$$\mathbf{9} \longrightarrow \mathbf{5} + Cl^- \quad (16)$$

$$\mathbf{8} + Cl^- \longrightarrow \mathbf{11} \quad (17)$$

involves positive chlorine in the initial step.[5] Precedence exists for the decomposition indicated in eq 16.[39]

Poutsma[13] found that molecular chlorine and isobutylene gave **10** and **11** in the ratio of 87:13. Evidence was presented to support the contention that a polar process was involved. For example, under photolytic conditions the ratio was unity or less. Comparison of these data with our own suggests that a combination of radical and ionic mechanisms may pertain in the trichloramine system. If **6** is generated according to eq 7, this intermediate might be responsible for radical addition. Alternatively, a purely ionic process may pertain; the difference in product distribution from chlorine and trichloramine may reflect a change in the gegenanion.

Styrene, 1-methylcyclohexene, and norbornene gave complex product mixtures with trichloramine. The major component in the case of norbornene was nortricyclyl chloride, the same product as obtained from use of chlorine in a process designated as ionic.[40] The reaction of chlorine with styrene is known to be in the ionic category when no external initiation is supplied.[13]

Experimental Section

Materials.—Oxygen (Airco USP) was passed through a sulfuric acid scrubber before use. Nitrogen (Linde, H. P. Dry) was passed through consecutive scrubbers containing Fieser's solution, lead acetate solution, sodium hydroxide pellets, and sulfuric acid.[41] Cyclohexene (Matheson Coleman and Bell) was distilled from sodium and methylene chloride (Fisher Chemical Co.) from calcium hydride. Carbon tetrachloride (Fisher Chemical Co.), *o*-dichlorobenzene (Eastman Organic Chemicals), and carbon disulfide (Matheson Coleman and Bell) were distilled from Drierite. The butene isomers, CP grade (99%), and chlorine CP grade (99.5%), were obtained from J. T. Baker Chemical Co. *trans*-2-Chlorocyclohexanol was obtained from K & K Laboratories, Inc. Most reagents were used as received after their purity had been checked by glpc analysis.

Analytical Procedures.—Infrared spectra were obtained with a Beckman IR-8 spectrophotometer on neat samples or as ~10% solutions in carbon disulfide. Nmr spectra were determined with a Varian HA-100 instrument on ~20% deuteriochloroform solutions with tetramethylsilane as an internal standard. Refractive indexes were recorded from a Bausch and Lomb refractometer. All spectra were taken on samples purified by glpc. Gas chromatography was carried out with an Aerograph Hi-Fi 1200 (column A, 200 ft by 0.01 in., stainless steel, SE-30, Perkin-Elmer wall-coated open tube) or with an Aerograph 1800 [column B, 15 ft by 0.25 in., Carbowax 20M (20%) on Chromosorb P (60–80 mesh), and column C, 4 ft by 0.25 in., molecular sieve (5A)]. Melting points, Thomas-Hoover capillary apparatus, and boiling points are uncorrected. Analysis for positive chlorine is described elsewhere.[18]

Preparation of Trichloramine Solution.—Trichloramine was prepared[18] in purified methylene chloride, carbon tetrachloride, *o*-dichlorobenzene, or carbon disulfide. Unless otherwise specified, chlorinations were performed with trichloramine in methylene chloride.

General Procedure. A. Chlorination of Olefins.—In a 250-ml three-necked flask fitted with a mechanical stirrer, condenser, and addition funnel was placed a solution (*ca.* 60 ml) of trichloramine (0.04 mol) in methylene chloride. A solution of the olefin (0.09 mol) in 32 ml (0.5 mol) of methylene chloride was added over a period of 1–1.5 hr at the desired temperature, after which a sample was removed for glpc analysis. The olefin need not be dissolved in methylene chloride; however, use of a dilute solution permits easier temperature regulation. The mixture was stirred for an additional 20–30 min at the same temperature and then poured into a solution of 10 ml of concentrated hydrochloric acid and 40 ml of water. After the resulting two-phase system was stirred magnetically for 30 min, the aqueous layer was separated. The organic phase was washed with two 50-ml portions of distilled water and dried over anhydrous sodium sulfate. Removal of solvent under reduced pressure, followed by distillation of the residue through a short Vigreux column, afforded the *vic*-dichloride (Table I). Glpc analysis of the water-washed and unwashed organic portion gave similar product compositions.

The acidic water wash contained, in each case, a small amount of ammonium chloride, identified by the reaction with solutions of sodium hydroxide and silver nitrate and by the infrared spectrum. Nitrogen, which was evolved almost quantitatively during the addition of trichloramine, was characterized by glpc peak enhancement (column C at 25°, helium flow 12 ml/min).

Yields (distilled product) are based on trichloramine, three available chlorines. Product yields in several cyclohexene studies (temperature, solvent, and Table V) were determined by glpc analysis (column B) with bromobenzene as internal standard. Nitrogen evolution during chlorination was monitored with a Precision Scientific Co. wet test meter.

The indicated data were obtained in a temperature study with cyclohexene, °C (% yield of *trans*-1,2-dichlorocyclohexane): 38 ± 1 (80); 0 ± 2 (>91); −30 ± 5 (89).

B. Chlorination of *cis*- and *trans*-2-Butene.—The oven-dried apparatus consisted of a 250-ml, three-necked flask equipped with a Telfon stirring bar, constant pressure addition funnel, thermometer, and a Dry Ice reflux condenser. The butene isomers were introduced as gases and condensed; the amount was determined by volumetric calibration marks on the reaction vessel. The apparatus was flushed with nitrogen for 30 min prior to addition. The requisite amount of trichloramine solution (molar ratio, olefin:NCl_3 = 10) was placed in the addition funnel by means of a syringe. The trichloramine solution was added dropwise at −15 ± 3° (carbon tetrachloride–Dry Ice bath) over *ca.* 30 min in the dark with a slow nitrogen purge. After the mixture was swept with nitrogen for an additional 10 min at −15°, a sample was removed for anslysis. The remainder of the reaction mixture was washed with water, and the organic portion was dried over anhydrous sodium sulfate. Glpc analysis (column B) of the water-washed and unwashed organic phase gave identical *meso*:*dl* ratios (Table III). Less than 2% of unidentified side products was detected.

Chlorination Products. 1,2-Dichlorobutane, bp 123–124°, n^{25}_{D} 1.4432 (lit.[42a] bp 124°, n^{15}_{D} 1.4474), possessed an infrared spectrum identical with that published.[43a]

***meso*-2,3-Dichlorobutane.**—The major product from *trans*-2-butene, collected by glpc, possessed an infrared spectrum identical with that of authentic *meso*-2,3-dichlorobutane.

***dl*-2,3-Dichlorobutane.**—The principal product from *cis*-2-butene, isolated by preparative glpc, was shown to be *dl*-2,3-dichlorobutane on the basis of the infrared spectrum.

3-Chloro-2-methylpropene and 1,2-Dichloro-2-methylpropane.—Isobutylene afforded a mixture which was separated by distillation through a 24-in. spinning-band column: 3-chloro-2-methylpropene, bp 70–71° (lit.[13] bp 71°), infrared spectrum identical with the published spectrum;[43b] 1,2-dichloro-2-methyl-

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(39) F. A. Johnson, *Inorg. Chem.*, **5**, 149 (1966).

(40) M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 4293 (1965).

(41) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 393.

(42) R. C. Weast, Ed., "Handbook of Chemistry and Physics," 48th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967–1968, (a) p C-218; (b) p C-490; (c) p C-308.

(43) "Sadtler Standard Spectra," The Sadtler Research Laboratories, Philadelphia, Pa., 1965, (a) Vol. 23, No. 23668; (b) Vol. 4, No. 4689; (c) Vol. 4, No. 4653; (d) Vol. 1A, No. 182.

propane, bp 102–104°, infrared spectrum identical with that of authentic material. Evaporation of the water wash gave ammonium chloride, 66% yield based on trichloramine. Illumination of an identical chlorination with a 275-W sun lamp did not change the ratio of 3-chloro-2-methylpropene to 1,2-dichloro-2-methylpropane.

1,2-Dichlorohexane: bp 66° (22 mm); n^{24}_{D} 1.4483.

1,2-Dichlorooctane: bp 87–88° (13 mm); n^{25}_{D} 1.4516.

***trans*-1,2-Dichlorocyclopentane:** bp 53–55° (27 mm); n^{25}_{D} 1.4781 [lit.[44] bp 53–53.5° (25 mm); n^{25}_{D} 1.4781]; nmr δ 1.22 (4 H), 1.47 (2 H), and 2.40 (2 H).

***trans*-1,2-Dichlorocyclohexane:** bp 32° (0.7 mm); $n^{24.5}_{\mathrm{D}}$ 1.4889 [lit.[12] bp 66–67° (11 mm); n^{24}_{D} 1.4891]. A sample, collected by glpc, was identical with authentic material (Aldrich Chemical Co.).

1,2,3-Trichloropropane: bp 156–158°; n^{25}_{D} 1.4823 (lit.[42b] bp 156°; n^{20}_{D} 1.4858). The infrared spectrum was in agreement with the published data.[43c]

1,1,2,2-Tetrachloroethane.—Modified general procedure A was used. A 500-ml flask equipped with a condenser topped with a drying tube was charged with trichloroamine, *cis*-1,2-dichloroethylene, and solvent. After 1 week under nitrogen, the yellow color had disappeared. Ammonium chloride was removed by filtration and the tetrachloride isolated by distillation, bp 144–145°, n^{26}_{D} 1.4913 (lit.[42c] bp 146°, n^{20}_{D} 1.4944). The infrared spectrum was in agreement with the published spectrum.[43d] A similar experiment went to completion in 4 hr (disappearance of yellow color) under illumination with a 275-W sun lamp (Table I).

1,1,1,2-Tetrachloroethane: bp 128–129°, n^{25}_{D} 1.4805 (lit.[42c] bp 129–130°; n^{20}_{D} 1.4821); ir (neat) 3050, 2975, 1420, 1280, 1197, 1052, 955, 810, 745, 714 cm^{-1}; nmr δ 4.28 (singlet).

Pentachloroethane: bp 160–164°; n^{24}_{D} 1.5040 (lit.[42c] bp 162°; n^{15}_{D} 1.5054). The infrared spectrum was identical with that of commercial material (Aldrich Chemical Co.).

Nortricyclyl Chloride.—This was the major product from norbornene by comparison of the infrared spectrum (glpc collection) with the published spectrum.[45]

Authentic Materials. *meso*-2,3-Dichlorobutane.[13]—The compound was prepared by passing chlorine gas through liquefied *trans*-2-butene under oxygen until a yellow color appeared. Distillation of the crude dichloride provided a major fraction, bp 112–113.5° (lit.[13] bp 112.5°); glpc analysis revealed that the product was 97% meso and 3% *dl*. Preparative glpc gave material of >99% purity, n^{25}_{D} 1.4396 (lit.[13] n^{24}_{D} 1.4392).

***dl*-2,3-Dichlorobutane.**[13]—The procedure was identical with that described for the meso isomer except that *cis*-2-butene was used. Distillation of the crude dichloride gave a major fraction, bp 116–117.5° (lit.[13] bp 116.5°); glpc analysis provided the ratio, 96% *dl* and 4% meso. Pure *dl*, >90%, was isolated by preparative glpc, n^{25}_{D} 1.4416 (lit.[13] n^{24}_{D} 1.4413).

1,2-Dichloro-2-methylpropane.[13]—The material was prepared by photochlorination of *tert*-butyl chloride. A 100-ml flask was charged with 50 ml of *tert*-butyl chloride and exposed to a 275-W sun lamp for 45 min. During illumination, steady streams of chlorine and nitrogen were passed through the liquid *via* two dispersion tubes. After excess *tert*-butyl chloride was removed, distillation gave 10.7 g of the desired product: bp 102–104° (lit.[13] bp 103–104°); n^{25}_{D} 1.4353; nmr δ 1.62 (6 H) and 3.64 (2 H).

1,2-Dichlorohexane.—A literature method was used.[16] To a solution of benzoyl peroxide (0.1 g) in 1-hexene (8.5 g, 0.1 mol) was added dropwise a solution of sulfuryl chloride (17.5 g, 0.13 mol) in 1-hexene (36 g, 0.43 mol) at 63–65°. After the solution had been stirred for an additional 2 hr at the same temperature, work-up afforded 1,2-dichlorohexane (83%): bp 66° (22 mm); n^{26}_{D} 1.4471 [lit.[16] bp 59–65° (14 mm); n^{20}_{D} 1.4500].

1,2-Dichlorooctane.—The procedure for 1,2-dichlorohexane was employed with 1-octene. 1,2-Dichlorooctane was isolated in 60% yield: bp 87° (9 mm); n^{27}_{D} 1.4503 [lit.[16] bp 67–71° (4 mm); n^{20}_{D} 1.4531].

***cis*-1,2-Dichlorocyclohexane.**—Adherence to a published procedure[46] gave the desired product, bp 93.5° (29.5 mm) [lit.[12] bp 99–100° (30 mm)]. According to preparative glpc analysis the material was predominantly the cis isomer, n^{25}_{D} 1.4934 (lit.[46] n^{25}_{D} 1.4945).

Mechanistic Studies. A. Yield Effect of Solvent.—A constant molar ratio (NCl_3:C_6H_{10}:solvent = 0.04:0.09:0.5) was employed, solvent (% yield of *trans*-1,2-dichlorocyclohexane): CH_2Cl_2 (89); CCl_4 (84); *o*-$C_6H_4Cl_2$ (86); CS_2 (70).

B. Chlorination of *cis*-2-Butene in the Presence of Cyclohexane.—The method used is described in part B of the general procedure. A mixture of cyclohexane and *cis*-2-butene (molar ratio, C_6H_{12}:C_4H_8:NCl_3 = 0.23:0.23:0.023) was chlorinated at $-15 \pm 3°$. Glpc analysis (column B) revealed the presence of chlorocyclohexane, 2–3%, and a *meso*:*dl* ratio of 72:28 for the dichloride. The yield of chlorocyclohexane was not determined quantitatively but based on area ratios obtained from glpc.

C. Solvent Effect on Stereochemistry of Addition.—The 2-butene isomers were chlorinated as described for 2-butene in general prodedure B (Table IV). In a similar study, *cis*-2-butene was chlorinated; however, samples were removed periodically to determine the *meso*:*dl* ratio (glpc, column A) at various mole fractions, *N*, of olefin in methylene chloride.

D. Inhibitor Study.—Cyclohexene was chlorinated by a modified general procedure. A common inhibitor of radical reactions was added to the reaction mixture prior to trichloramine addition (Table V). Oxygen was introduced through a gas dispersion tube.

Registry No.—Trichloramine, 10025-85-1; 1-butene, 106-98-9; isobutylene, 115-11-7; 1-hexene, 592-41-6, 1-octene, 111-66-0; cyclopentene, 142-29-0; cyclohexene, 110-83-8; 3-chloropropene, 107-05-1; *cis*-1,2-dichloroethylene, 156-59-2; 1,1-dichloroethylene, 75-35-4; trichloroethylene, 79-01-6; 1,2-dichlorohexane, 2162-92-7; 1,2-dichlorooctane, 21948-46-9.

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