at 25° fall in the order benzene (1), toluene (4.8×10^2), *p*-xylene (2.1×10^3), *m*-xylene (2.0×10^5). The observation that the reaction rate is highly sensitive to changes in the number of ring methyl substituents adds support to the conclusion that acetyl hypobromite is a polar rather than a radical brominating agent in acetic acid. Variations in hydrocarbon reactivity very similar to those encountered in the present study have been observed with certain polar halogenating agents other than acetyl hypobromite. The reactivity ratios benzene (1), toluene (6.1×10^2), *p*-xylene (2.2×10^3), *m*-xylene (2.1×10^5)—and benzene (1), toluene (3.4×10^2), *p*-xylene (2.1×10^3), *m*-xylene (1.9×10^5)—have been reported, respectively, for reaction with bromine in 85% acetic acid and with chlorine in pure acetic acid.[8] That is, the electrophilicities of acetyl hypobromite and chlorine in acetic acid (and also of bromine in 85% acetic acid) are about the same.

Acknowledgment. The authors are indebted to the National Science Foundation for a grant in support of this research.

[8] H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **79**, 1421, 5175 (1957).

Chlorination Studies of Unsaturated Materials in Nonpolar Media. IV. The Ionic Pathway for Alkylated Ethylenes. Products and Relative Reactivities[1]

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The rapid chlorination of neat alkylethylenes at ambient temperatures in the presence of oxygen as a radical inhibitor is considered. 1-Substituted or 1,2-disubstituted olefins (no branching at the double bond) (allyl chloride, 1-butene, cis- and trans-2-butene, and cyclohexene) had been found previously to give predominantly addition products, stereospecifically trans for the 1,2-cases, accompanied by very minor amounts of allylic substitution products. t-Butylethylene gave largely the unrearranged dichloride II, but 10% of 4-chloro-2,3-dimethyl-1-butene (I), a result of methyl migration, was detected. In contrast, it had been found previously that isobutylene gave predominantly the substitution product, 3-chloro-2-methyl-1-propene, with a shifted double bond. This apparently general tendency for branched olefins to react by substitution rather than addition has now been demonstrated for 2-methyl-1-butene, trimethylethylene, and tetramethylethylene. The respective products are: 2-(chloromethyl)-1-butene (III), 1-chloro-2-methyl-cis-2-butene (IV), 1-chloro-2-methyl-trans-2-butene (V), and 1,2-dichloro-2-methylbutane (VI) (58:29:8:5); 3-chloro-2-methyl-1-butene (VII) and 2,3-dichloro-2-methylbutane (IX) (85.5:1.45); and 3-chloro-2,3-dimethyl-1-butene (X) and 2,3-dichloro-2,3-dimethylbutane (XI) (99.7:0.3). Relative reactivities of the olefins toward chlorine were determined by competitive experiments and found to correlate with the sum of Taft's σ^* *constants for the alkyl substituents regardless of their orientation on the double bond. For both the linear cis-2-butene and the branched trimethylethylene, the addition process is favored by the energy of activation; hence the predominant substitution observed in the latter case is the result of an over-compensating entropy effect. The results are discussed in terms of electrophilic attack by chlorine, and possible transition states and intermediates are considered.*

Introduction

Chlorination of simple olefins in nonpolar media can follow either a free-radical or ionic pathway dependent on the structure and concentration of the olefin.[1,2] One can isolate the ionic pathway by use of radical inhibitors such as oxygen. This paper deals with products and relative reactivities of ionic chlorination of a series of ethylenes substituted with successively larger numbers of alkyl groups. Each of these substrates has been chlorinated previously[3-8]; however, because of ambiguities owing to mixed reaction pathways, secondary reactions, and lack of sensitive analytical tools, a systematic reinvestigation was undertaken.

Results

Product Compositions. Product distributions from chlorination of ten representative olefins are given in Table I. Each reaction was carried out by passing a limited amount of chlorine (*ca.* 1%) in an oxygen gas stream into neat olefin at −9 or 25° in the dark; reaction mixtures were analyzed directly by use of a g.l.p.c. instrument equipped with a flame ionization detector; g.l.p.c. areas were converted to molar quantities by means of calibration factors determined from synthetic mixtures of authentic compounds except

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[1] For part III, see M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 2172 (1965).

[2] M. L. Poutsma, *ibid.*, **87**, 2161 (1965).

[3] G. C. Ecke, N. C. Cook, and F. C. Whitmore, *ibid.*, **72**, 1511 (1950).

[4] (a) J. Burgin, W. Engs, H. P. A. Groll, and G. Hearne, *Ind. Eng. Chem.*, **31**, 1413 (1939); (b) I. D'yakonov and D. V. Tishchenko, *J. Gen. Chem. USSR* (Eng. Transl.), **9**, 1258 (1939); *Chem. Abstr.*, **34**, 710 (1940).

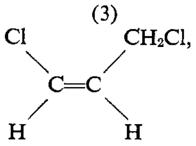
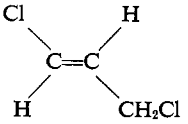
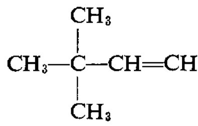
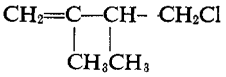
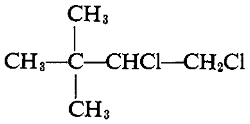
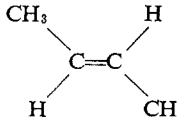
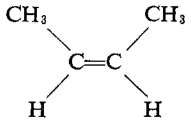
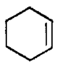
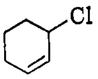
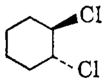
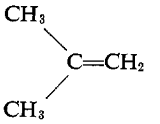
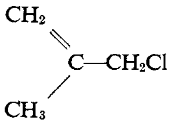
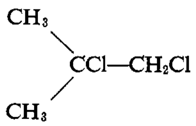
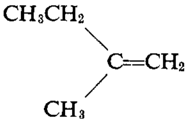
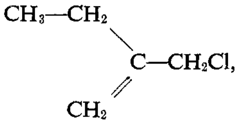
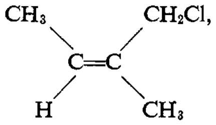
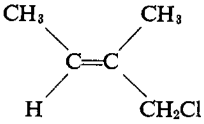
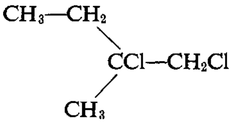
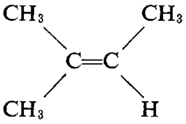
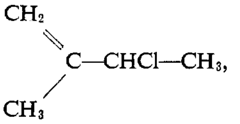
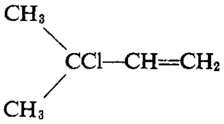
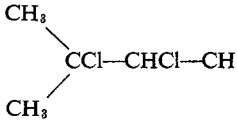
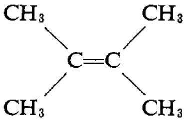
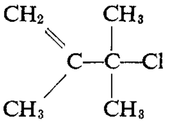
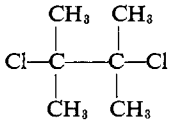
[5] R. A. Gutner and D. V. Tishchenko, *J. Gen. Chem. USSR* (Eng. Transl.), **8**, 1062 (1938); *Chem. Abstr.*, **33**, 3755 (1939).

[6] D. V. Tishchenko, *J. Gen. Chem. USSR* (Eng. Transl.), **6**, 1116 (1936); *Chem. Abstr.*, **31**, 1003 (1937).

[7] A. Lauchenauer and H. Schinz, *Helv. Chim. Acta.*, **34**, 1514 (1951).

[8] D. V. Tishchenko, *J. Gen. Chem. USSR* (Eng. Transl.), **8**, 1232 (1938); *Chem. Abstr.*, **33**, 4190 (1939).

Table I. Product Distributions from Chlorination of Neat Olefins under Oxygen

Olefin	Temp., °C.	Substn. products (% of total)	Addn. products (% of total)	Ref.
$CH_3CH_2CH=CH_2$	−9	$CH_3—CH=CH—CH_2Cl$ (3)	$CH_3—CH_2—CHCl—CH_2Cl$ (97)	a
$ClCH_2CH=CH_2$	−9	 (1.4)  (0.1)	$ClCH_2—CHCl—CH_2Cl$ (98.5)	a
 $CH_3—\overset{CH_3}{\underset{CH_3}{C}}—CH=CH_2$	25	 $CH_2=\underset{CH_3}{C}—\underset{CH_3}{CH}\text{-}CH_2Cl$ I (10)	 $CH_3—\overset{CH_3}{\underset{CH_3}{C}}—CHCl—CH_2Cl$ II (90)	b,c
	−9	$CH_3—CHCl—CH=CH_2$ (2)	*meso*-$CH_3—CHCl—CHCl—CH_3$ (98)	a
	−9	$CH_3—CHCl—CH=CH_2$ (3)	*dl*-$CH_3—CHCl—CHCl—CH_3$ (97)	a
	25	 (20)	 (80)	d
	−9	 (87)	 (13)	a,e
	25	 III (58)  IV (29)  V (8)	 VI (5)	b,f
	25	 VII (85.5)  VIII (<0.05)	 IX (14.5)	b,g
	25	 X (99.7)	 $Cl—\overset{CH_3}{\underset{CH_3}{C}}—\overset{CH_3}{\underset{CH_3}{C}}—Cl$ XI (0.3)	b,h

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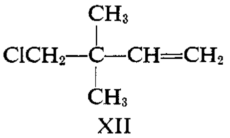
[a] Reference 1. [b] Present study. [c] Only product II detected in ref. 3 under conditions which may have been largely radical. [d] Reference 2. [e] Similar results observed in ref. 4 for reactions run to much higher conversion. [f] Products III and VI observed previously from chlorination in the presence of sodium bicarbonate; ref. 5. [g] References 6 and 7. [h] Product X observed in ref. 8.

where noted. Identification of products is described in the Experimental Section.

For each of the six linear or simple cyclic (monosubstituted or 1,2-disubstituted) olefins considered, chlorination under oxygen gave predominantly addition products (*trans* for the 1,2-disubstituted cases). However, dark chlorination in the absence of oxygen was predominantly a radical reaction because of spontaneous initiation of radical chains.[1,2] The radical products have already been described[1] for all but *t*-butylethylene; for this olefin the radical products are dichloride II and 4-chloro-3,3-dimethyl-1-butene (XII) in a ratio of *ca.* 7:1. In contrast, chlorination under


$ClCH_2—\overset{CH_3}{\underset{CH_3}{C}}—CH=CH_2$

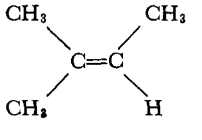
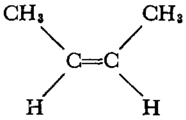
XII

Table II. Product Distribution from Ionic Chlorination of 2-Methyl-1-butene at 25°

Olefin concn.[a]	III[b]	IV[b]	V[b]	VI[b]
100	59.5	28.3	7.8	4.4
50	57.7	29.2	8.2	4.9
10	57.0	30.2	8.1	4.7

[a] Volume per cent in 1,1,2-trichlorotrifluoroethane. [b] Percentage of total observed products; g.l.p.c. areas not corrected.

Table III. Effect of Temperature on Addition/Substitution Ratios for Chlorination under Oxygen

Olefin	Concn.[a]	Temp., °C.	Addn./substn.[b,c]
	100	25.0 ± 0.1[d]	0.181
	10	25.0 ± 0.1[d]	0.160
	22	39.5 ± 0.1[d]	0.140
	22	25.0 ± 0.1[d]	0.156
	22	−8.5 ± 0.2[d]	0.195
	22	−40 ± 1.[e]	0.220
	22	−79 ± 1.[f]	0.325
	100	0 ± 1.[g]	29
	100	−79 ± 1.[f]	61

[a] Volume per cent in 1,1,2-trichlorotrifluoroethane. [b] Corrected molar ratio. [c] IX/VII for 2-methyl-2-butene; *dl*-2,3-dichlorobutane/3-chloro-1-butene for *cis*-2-butene. [d] Thermostated bath. [e] Acetonitrile slush bath. [f] Acetone–Dry Ice bath. [g] Ice bath.

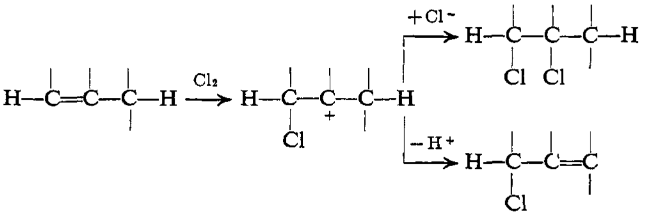
oxygen of olefins with branching at the double bond gave predominantly substitution products. For this class of olefins, dark chlorination in the absence of oxygen remains ionic rather than becoming radical; dark runs under nitrogen gave results essentially identical with those under oxygen. For 1,1-disubstituted olefins (isobutylene and 2-methyl-1-butene), the addition product could be forced to become the major product if chlorination was carried out under nitrogen with illumination provided by three 275-w. sunlamps; under these conditions, added cyclohexane was attacked[1] and obviously considerable radical reaction had been induced. However, for trimethyl- and tetramethylethylene, such a light source was not intense enough to induce detectable radical reaction in competition with the now much more rapid ionic reaction (*vide infra*).

No significant effect of olefin concentration could be detected for chlorination of 2-methyl-1-butene under oxygen when the olefin was progressively diluted with 1,1,2-trichlorotrifluoroethane; results are given in Table II. The effects of temperature on the addition/substitution ratio are shown in Table III for neat *cis*-2-butene and trimethylethylene diluted with 1,1,2-trichlorotrifluoroethane.

Relative Reactivities. Mixtures of successive pairs of olefins were treated in turn with a small amount of chlorine under oxygen. Quantitative g.l.p.c. product analysis was used to determine relative reactivities of each pair of olefins as shown in detail in Table IV. In most cases, relative reactivities were determined at two to four different ratios of starting olefins; no variations were apparent. The relative reactivities of 11 olefins toward ionic chlorination in nonpolar solvents are summarized in Table V. Since this list involves a number of successive comparisons each of which has limited accuracy, comparisons between widely separated entries in Table V probably represent little more than orders of magnitudes; for this reason all values are included in a single list although some were determined at 25° and others at −9° (see Table IV). Several sets of literature data[9–15] for relative reactivities of olefins toward various reagents under conditions shown in the table are included for comparison.

Discussion

It is well known that liquid-phase chlorination of linear olefins gives predominantly addition products while chlorination of olefins with branching at the double bond gives predominantly allylic substitution products.[4,16] Taft[17] suggested that the results were best explained in terms of formation of a carbonium ion intermediate which was partitioned between collapse with chloride ion and loss of an α-proton. Although it has been shown[1] that many of the data used for this correlation were in fact derived from radical reactions, the results described in this paper support the over-all generalization (addition from linear, and substitution from branched olefins) even more firmly when only chlorinations free from radical contributions are considered.



The relative reactivities for chlorination of the various olefins under oxygen (Table V) support an electrophilic attack by the chlorine molecule. These relative reactivities derived from competitive studies parallel the relative rates of bromination in methanol determined by DuBois and Mouvier[9] by direct rate measurements; note particularly the rate enhancement (10^1 to 10^2) which accompanies each successive attachment of an electron-releasing alkyl group to the basic eth-

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(9) J. E. Dubois and G. Mouvier, *Tetrahedron Letters*, 1325 (1963).

(10) S. V. Anantakrishnan and C. K. Ingold, *J. Chem. Soc.*, 1396 (1935).

(11) D. Swern, *J. Am. Chem. Soc.*, **69**, 1692 (1947).

(12) (a) List compiled in J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964, p. 44, from data in H. J. Lucas and W. F. Eberz, *J. Am. Chem. Soc.*, **56**, 460 (1934), and H. J. Lucas and Y. Liu, *ibid.*, **56**, 2138 (1934); see also R. W. Taft, Jr., E. L. Purlee, P. Riesz, and C. A. DeFazio, *ibid.*, **77**, 1584 (1955), and R. W. Taft, Jr., *ibid.*, **74**, 5372 (1952). The value <0.001 is based on the stated lack of reactivity of 2-butene compared to measured rate constants for the other olefins; (b) *cf.* P. D. Bartlett and G. D. Sargent, *ibid.*, **87**, 1297 (1965).

(13) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

(14) M. Szwarc and J. H. Binks, "Theoretical Organic Chemistry," Buterworths and Co. (Publishers) Ltd., 1959, p. 262, and R. P. Buckley and M. Szwarc, *Proc. Roy. Soc.* (London), **A240**, 396 (1957).

(15) M. L. Poutsma and R. L. Hinman, *J. Am. Chem. Soc.*, **86**, 3807 (1964).

(16) H. P. A. Groll, G. Hearne, F. F. Rust, and W. E. Vaughan, *Ind. Eng. Chem.*, **31**, 1239 (1939).

(17) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **70**, 3364 (1948).

Table IV. Relative Reactivities of Olefins toward Chlorine under Oxygen

Reactant A	Reactant B	Temp., °C.[a]	$(A)_0/(B)_0$	Rel. react. B/ Rel. react. A
Trimethylethylene	Tetramethylethylene	−9	1.12[b]	38
			3.35	35
			7.9	40
				38[c]
2-Methyl-1-butene	Trimethylethylene	25	2.28[b]	67[d]
			3.9	74
			8.7	65
				69[c,d]
Isobutylene	Trimethylethylene	−9	2.79[e]	176
			5.6	213
				195[c]
Cyclohexene	2-Methyl-1-butene	25	0.118[b]	3.41[d]
			4.24	3.22
			9.6	3.41
				3.3[c,d]
Isobutylene	*trans*-2-Butene	−9	0.28[f]	0.92
			0.71	0.84
			1.31	0.89
			4.00	0.79
				0.86[c]
Isobutylene	*cis*-2-Butene	−9	0.27[f]	1.10
			0.82	1.07
			2.70	1.10
				1.09[c]
1-Butene	*trans*-2-Butene	−9	1.35[f]	>38
			2.30	>34
			8.3	52[g]
				50[c,g]
Allyl chloride	1-Butene	−9	9.3[e]	430
			9.3	200
				3×10^2[c,h]
cis-Dichloroethylene	Allyl chloride	−9	9[b]	>6000[i]

[a] 25.0 ± 0.1°, −9.0 ± 0.2°. [b] Method 3. [c] Mean value. [d] Calibration factors for products from 2-methyl-1-butene were assumed; this could affect the relative reactivity factor in Table III for this olefin but not for trimethylethylene or cyclohexene since such factors cancel in the over-all comparison. [e] Method 2. [f] Method 1. [g] Only this run had sufficient product from 1-butene to measure accurately. [h] These two olefins are too far apart in reactivity to measure accurately by the present method so no attempt was made to determine if the large difference between identical runs was real or due to experimental error in determining the trace of trichloropropane formed. [i] No tetrachloroethane detected.

Table V. Relative Reactivities of Olefins in Addition Reactions

Olefin	Chlorination[a]	Bromination[b]	Bromination[c]	Epoxidation[d]	Hydration[e]	Dibromocarbene[f]	Methyl radical[g]	Chlorine atom[h]
cis-Dichloroethylene	$<5 \times 10^{-7}$							0.34
Allyl chloride	3×10^{-3}							0.60
Ethylene		1.0×10^{-2}	0.49	4.2×10^{-2}			1.26	
1-Butene	1.00[i]	1.00[i]	1.00[i,j]	0.92–1.10[i,k]		1.00[i,l]	1.00[i]	1.00[i]
t-Butylethylene	1.15							
cis-2-Butene	6.3×10	4.3×10[m]		$2.1–2.8 \times 10$[n]	<0.001		0.13	1.03
trans-2-Butene	5.0×10						0.26	0.97
Cyclohexene	5.0×10			2.8×10		5.7		0.80
Isobutylene	5.8×10		2.72	2.0×10	1.00[i]	1.4×10	1.34	0.94
2-Methyl-1-butene	1.6×10^2							
Trimethylethylene	1.1×10^4	1.2×10^3[o]	5.1	2.8×10^2	0.58	4.6×10	0.21	
Tetramethylethylene	4.3×10^5	9.6×10^3	6.9			5.0×10		

[a] Competitive chlorination in mixed olefins as solvent in presence of oxygen at 25 or −9°; present study. [b] Direct rate measurements in methanol–0.2 *N* NaBr at 25°; ref. 9. [c] Competitive bromination in methylene chloride in the presence of excess HBr at −78°; ref. 10. [d] Direct rate measurements of epoxidation with peracetic acid in acetic acid at 25°; ref. 11. [e] Direct rate measurements in 1.0 *N* HNO_3 at 25°; ref. 12. [f] Competitive reaction with dibromocarbene generated from bromoform–potassium *t*-butoxide in *t*-butyl alcohol–pentane at 0°; ref. 13. [g] Competitive reaction with methyl radicals generated from diacetyl peroxide in isooctane at 65°; ref. 14. [h] Competitive reaction with chlorine atoms in olefin–cyclohexane mixtures at 25 and −9°; ref. 1 and 15. [i] Relative value assigned for each column. [j] Propylene. [k] Range of four cases of RCH=CH_2. [l] 1-Hexene. [m] *cis*-2-Pentene. [n] Range of six cases of RCH=CHR′. [o] 3-Methyl-2-pentene.

ylene skeleton.[18] DuBois and Mouvier[9] achieved a linear correlation of rates for 13 olefins with a two-parameter equation which employed Taft's inductive σ^* constant and steric substituent constant (E_S).[19]

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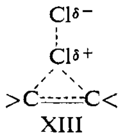
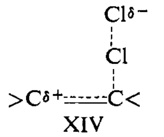
(18) The results of Anantakrishnan and Ingold[10] derived from competitive bromination studies in a less polar medium at a much lower temperature surprisingly show much less sensitivity to structure. The lack of agreement between these two sets of data[9,10] and the possible difficulties inherent in competitive rate measurements with bromine have been discussed by P. S. Skell, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 30S.

(19) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

Since our data are less extensive and involve only one compound, *t*-butylethylene, with a large substituent, we have attempted a correlation with $\Sigma\sigma^*$ alone. A good correlation exists for the seven olefins having only methyl or ethyl substituents, but *t*-butylethylene reacts "too slowly" as might have been anticipated. In Figure 1 the data are plotted along with the least-squares line defined by $\log k_{\text{rel}} = 5.816 - 4.15\Sigma\sigma^*$, for which $r = 0.997$ and $s = 0.157$.[20] This line was calculated excluding the point for *t*-butylethylene. A two-parameter treatment for all eight points gave $\log K_{\text{rel}} = 5.851 - 6.67\Sigma\sigma^* + 0.95\Sigma E_s$ with $r = 0.998$.[20] However, the significance of this equation is probably limited since only a single *t*-butyl compound is included. Attempts to include allyl chloride gave much less satisfactory correlation.[21] An interesting aspect of these correlations is that no account need be taken of the *position* of the substituents but only of their relative inductive electron-donating powers. Thus isobutylene and 2-butene (each having two methyl groups and two hydrogens) show almost identical rates even though one could form a tertiary carbonium ion by addition of an electrophile and the other a less-stable secondary ion. On the other hand, trimethylethylene and isobutylene (or 2-methyl-1-butene), which can form similar tertiary carbonium ions, differ in rate by a factor of almost 200 (or 70).[22] This behavior is more compatible with a transition state which involves partial bonding of the chlorine molecule with both termini of the olefinic system with little development of positive charge on carbon as in structure XIII (π-complexing) than with one which involves attack at a single terminus with development of carbonium ion character as in structure XIV (σ-complexing).[23] Note that a similar reactivity pattern has been observed for epoxidation and addition of dibromocarbene (Table V), reactions generally formulated as proceeding through three-center bridged transition states. In contrast, a quite different reactivity pattern is observed for hydration of olefins, a reaction generally believed to involve formation of an open carbonium ion in the slow step[24]; isobutylene has a reactivity comparable to that of trimethylethylene but $>10^3$ greater than that of *trans*-2-butene.[12]



XIII



XIV

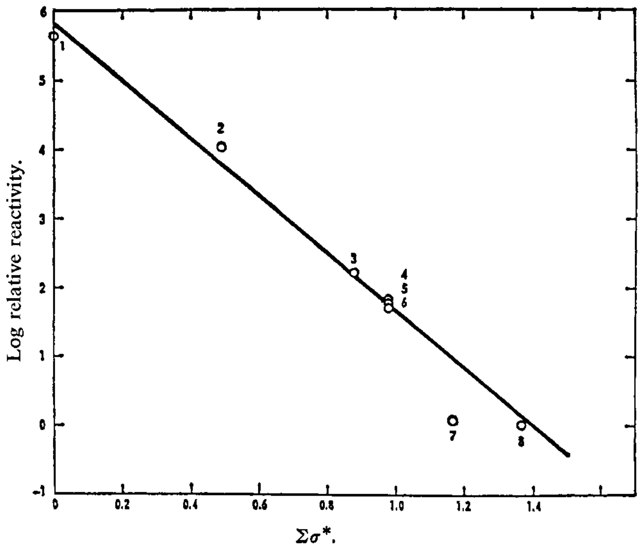


Figure 1. Correlation of relative reactivities of olefins toward polar chlorination with the summation of inductive σ constants: 1, tetramethylethylene; 2, trimethylethylene; 3, 2-methyl-1-butene; 4, *cis*-2-butene; 5, isobutylene; 6, *trans*-2-butene; 7, *t*-butylethylene (not included in least-squares line); and 8, 1-butene.

The reactivity pattern of olefins toward electrophilic reagents is quite different from that toward radicals as shown in Table V for methyl radical and chlorine atom, two extremes of radical behavior. The relative rate spread between *cis*-dichloroethylene and *cis*-dimethylethylene (2-butene) is $>10^8$ for chlorine molecule attack and *ca.* 3 for chlorine atom attack. The dramatic difference in response to polar substituents between the two reaction courses is obvious.

The correlation with a common substituent parameter of relative rates for three olefins which give predominant addition and four olefins which give predominant substitution suggests a similar type of *transition state* (XIII rather than XIV) throughout the series. The Taft hypothesis[17] also assumed a single type of *intermediate* from which both addition and substitution occurred; however, recent advances in knowledge concerning carbonium ions suggest that more complex situations must be considered. First of all, since the reaction takes place readily in a nonpolar medium which would not promote ion dissociation, it is reasonable to assume that the intermediate is an ion pair and that the chloride ion formed in the initial, rate-limiting step is the nucleophile for the addition step and the base for the proton loss. However, the exact nature of the carbonium ion poses a more difficult question. Stereospecific *trans* addition to *cis*- and *trans*-2-butene[25] suggests a cyclic chloronium ion intermediate for these olefins for which an open ion

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(20) See H. H. Jaffé, *Chem. Rev.*, **53**, 253 (1953), and W. A. Pavelich and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **79**, 4940 (1957), for calculations and definitions of terms.

(21) It should be noted that as the members of each pair of olefins being chlorinated became less and less reactive, the average chlorine concentration during a competitive run became greater. For example, at a constant chlorine input rate, a transient yellow color developed during the 1-butene *vs.* allyl chloride runs while no color could be detected visually in the other cases. The possibility exists that these chlorinations involve not only first-order but also second-order terms in chlorine so that the observed relative rates are a composite of two reaction modes; such second-order terms would be more important at higher chlorine concentrations. Second-order dependence on halogen, common in bromination, has *not* been observed in chlorinations in polar solvents, but no absolute kinetics have been determined in nonpolar solvents. See P. B. D. De la Mare, *Quart. Rev.* (London), **3**, 126 (1949), for a review.

(22) It might be suggested that the isobutylene–*trans*-2-butene comparison is improper since isobutylene is 1.37 kcal./mole more stable in the ground state and hence reacts more slowly than predicted from consideration of carbonium ion stabilities alone. However, this cannot apply to the 2-methyl-1-butene–trimethylethylene pair for the latter is 70-fold more reactive even though it is 1.49 kcal./mole more stable. Heat of formation data are taken from F. D. Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

(23) See ref. 12b for a similar discussion.

(24) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, N. Y., 1959, p. 374; J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 223.

(25) Largely *trans* addition was observed previously although no quantitative limits were set: H. J. Lucas and C. W. Gould, Jr., *J. Am. Chem. Soc.*, **63**, 2541 (1941).

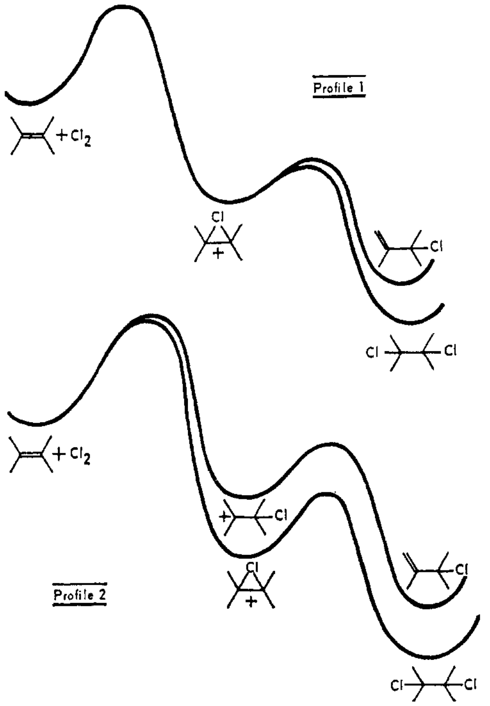


Figure 2. Possible extreme reaction profiles for polar reaction of chlorine with an olefin.

would be secondary (and apparently of higher energy since the chloronium ion occurs).[26] However, Fahey[27] has recently found that ionic chlorination of *cis*- and *trans*-1-phenylpropene is nonstereospecific with a tendency toward *cis* addition in carbon tetrachloride or pentane solution. This result suggests that, if the open carbonium ion can be not only secondary but also benzylic, it becomes the intermediate rather than (or along with) a cyclic chloronium ion.[27,28] Hence any extrapolation from linear to branched olefins, for which an open ion would be tertiary (and hence possibly more stable than its corresponding cyclic analog), appears dangerous. In fact, the competition between over-all addition and substitution may be the result not of a single intermediate whose favored mode of decomposition depends on the degree of alkyl substitution, but rather the result of two intermediates: a chloronium ion formed from linear olefins which undergoes preferentially *trans* nucleophilic ring opening by chloride ion and an open, tertiary α-chlorocarbonium ion formed from branched olefins which undergoes preferentially proton loss. In schematic terms, we cannot distinguish between reaction profiles 1 and 2 of Figure 2[29] on the basis of present experimental data.

Chlorination of *t*-butylethylene was undertaken as a probe for Wagner–Meerwein rearrangement. The majority of product is formed without skeletal change; however, minor product I is the result of a methyl migration followed by expulsion of a proton. Again, the ambiguity in structure of the initially formed ion or ions does not allow more detailed interpretation of this result.

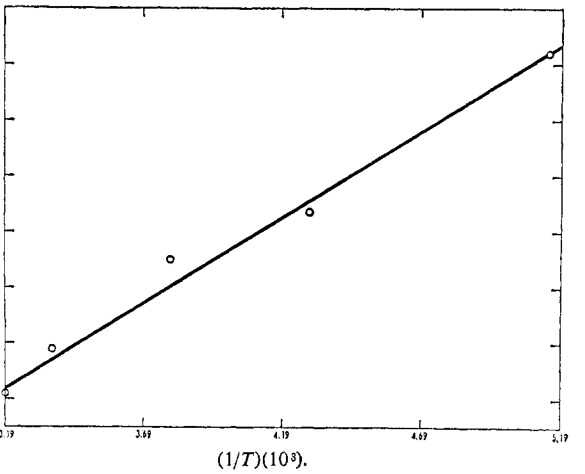
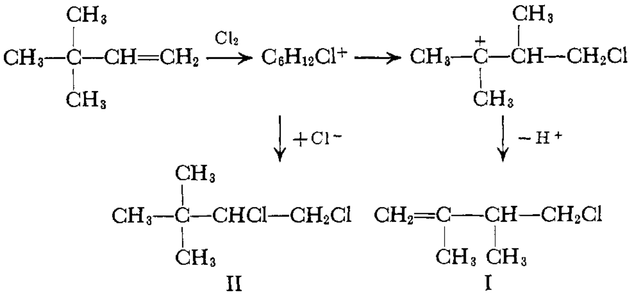


Figure 3. Arrhenius plot of ratio of addition to substitution (IX/VII) from polar chlorination of trimethylethylene.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH{=}CH_2 \xrightarrow{Cl_2} C_6H_{12}Cl^+ \longrightarrow CH_3-\overset{+}{\underset{CH_3}{C}}-\overset{CH_3}{CH}-CH_2Cl$$

$$\downarrow{+Cl^-} \qquad \downarrow{-H^+}$$

$$\underset{\text{II}}{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CHCl-CH_2Cl} \qquad \underset{\text{I}}{CH_2{=}\underset{CH_3}{C}-\underset{CH_3}{CH}-CH_2Cl}$$

The present study has added further information concerning the substitution pathway with respect to direction of elimination. Proton loss was known to occur almost exclusively from the α-carbon atom not bearing the incoming chlorine atom so that the products are allylic rather than vinylic chlorides.[17] We chose to re-examine the case of 2-methyl-1-butene to determine whether Saytzeff- or Hoffman-type elimination predominated[30]; previously only Hoffman elimination to give the least-substituted olefin III had been detected.[5] The actual product ratio, III:(IV + V) = 3.1:20, suggests equally facile loss of primary and secondary hydrogen atoms on a statistical basis, but the more than threefold dominance of IV over V shows a preferential loss of one of the methylene protons (which are not equivalent in the majority of conformations of either a cyclic or open ion). Hence correction of the III:(IV + V) ratio by a statistical factor of 2:3 may not be entirely valid; even so, if the elimination reaction shows any preference for Saytzeff orientation as usually observed in E1 reactions,[30] it is a small one.

Data for *cis*-2-butene and trimethylethylene show that addition is favored by lower temperatures in *both* cases even though substitution is the predominant reaction course for trimethylethylene at ordinary temperatures; hence there must be an overriding entropy effect in the latter case. An Arhennius plot of the trimethylethylene data (Figure 3) gives a reasonably good

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(26) *trans* addition also rules out a cyclic, four-center, concerted addition mechanism since this should give exclusively *cis* addition.

(27) R. C. Fahey and C. Schubert, *J. Am. Chem. Soc.*, in press.

(28) For a general discussion of the competition between bridged and open ions in additions of electrophiles to olefins based on observed stereochemistry, see M. J. S. Dewar and R. C. Fahey, *ibid.*, **85**, 2245, 2248, 3645 (1963).

(29) Of course, these are extreme pictures; it is not unreasonable that each type of intermediate ion could give both addition and substitution in different proportions.

(30) D. Banthorpe, "Elimination Reactions," Elsevier Publishing Co., Amsterdam, 1963, Chapter 3.

line ($r = 0.994$)[22] from which E_a (addition) $-$ E_a (substitution) = -0.82 kcal./mole. Although, as extensive data could not be obtained for *cis*-2-butene,[31] the two data points separated by 74° give E_a (addition) $-E_a$ (substitution) = *ca.* -1 kcal./mole. Our inability to distinguish between reaction profiles 1 and 2 (Figure 2) does not allow us to attach physical significance to these activation parameters.

Experimental Section

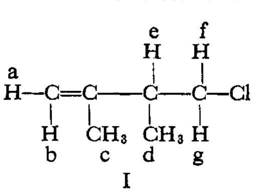
Infrared spectra were determined as 10% carbon disulfide solutions on a Beckman IR5A instrument; n.m.r. spectra were determined as 20% carbon tetrachloride solutions on a Varian A-60 instrument and results are expressed in p.p.m. downfield from internal TMS; boiling points are uncorrected.

Materials. Treatment of most of the starting materials has been described previously.[1,2] *2-Methyl-1-butene* (K & K Laboratories), *trimethylethylene* (Matheson Coleman and Bell), and *t-butylethylene* (Columbia Organic Chemicals) were each distilled from Drierite through a 3-ft. glass-helix-packed column and center cuts (b.p. 32, 39.5, and 41.5°, respectively) were retained. A mixture of 100 g. of pinacolyl alcohol (Columbia Organic Chemicals) and 75 ml. of 85% phosphoric acid was slowly heated from 80 to 135° while volatile material formed was allowed to distil. The distillate was washed with water, dried, and distilled from Drierite through the same column; after rejection of a considerable forerun, 30 g. of *tetramethylethylene*, b.p. 73.5°, was collected (>99.5% pure by g.l.p.c.).

Product Identification. The products from allyl chloride, the three isomeric butenes, and cyclohexene have been described previously.[1,2] Chlorination of *t*-butylethylene under oxygen in the dark (3:1 ratio of olefin:chlorine) (quantitative runs were carried to much lower conversion) gave a reaction mixture which showed two major bands in the g.l.p.c. spectrum (conditions given below), A and B (order of increasing retention time), plus a third minor component (less than 20% of A) which was not identified. Distillation allowed isolation of B in 60% yield, b.p. 91–92° (70 mm.), $n^{24}\text{D}$ 1.4548, identified as *1,2-dichloro-3,3-dimethylbutane* (*II*) (lit.[3] b.p. 52° (11 mm.), $n^{20}\text{D}$ 1.4553); the n.m.r. spectrum of B showed a complex multiplet at 3.4–4.0 and a sharp singlet at 1.07 p.p.m. with relative areas of 3.1:8.9. Product A was isolated by preparative g.l.p.c. from a low-boiling fraction (52–64° at 70 mm.) and assigned the structure *4-chloro-2,3-dimethyl-1-butene* (*I*).

Anal. Calcd. for $C_6H_{11}Cl$: C, 60.76; H, 9.35; Cl, 29.89. Found: C, 60.86; H, 9.44; Cl, 29.87.

The infrared spectrum of A showed bands at 1650 (m) (C=C stretch) and 895 cm.$^{-1}$ (vs) ($R_2C{=}CH_2$). The n.m.r. spectrum is consistent with structure I if



$$\overset{a}{H}-\underset{\underset{b}{H}}{C}=\underset{\underset{c}{CH_3}}{C}-\overset{\overset{e}{H}}{\underset{\underset{d}{CH_3}}{C}}-\overset{\overset{f}{H}}{\underset{\underset{g}{H}}{C}}-Cl$$

I

J_{ef}, J_{eg}, and J_{fg} are each *ca.* 7 c.p.s. Protons a and b occur as a narrow multiplet at 4.75 p.p.m. weakly coupled to methyl group c which occurs as a narrow multiplet at 1.70 p.p.m. Methyl group d appears at 1.13 p.p.m. as a doublet ($J = 7$ c.p.s.) split by proton *e*. Proton e should be split into a quartet by methyl group d with each member further split by protons f and g. If all coupling constants were identical a six-line pattern (1:5:10:10:5:1 intensities) would be predicted; a sextet (J = *ca.* 7 c.p.s.), with each line somewhat broadened, is observed at 2.45 p.p.m. Finally, nonequivalent protons[32] f and g should appear as an AB pattern with further splitting by proton e; in fact, centered at 3.42 p.p.m. is a set of four lines of similar intensity flanked by two weak lines on either side, the set of which can be separated into two AB patterns with J = *ca.* 7 c.p.s. The relative areas observed were (a + b):c:d:e:(f + g) = 1.90:2.95:3.20:1.00:1.95.

From a photochlorination of *t*-butylethylene under nitrogen, *4-chloro-3,3-dimethyl-1-butene* (*XII*), $n^{24}\text{D}$ 1.4302, was isolated by preparative g.l.p.c.

Anal. Calcd. for $C_6H_{11}Cl$: C, 60.76; H, 9.35; Cl, 29.89. Found: C, 60.22; H, 9.93; Cl, 29.62.

The infrared spectrum showed bands at 1645 (m) (C=C stretch) and 995 and 915 cm.$^{-1}$ (s) ($RCH{=}CH_2$). The n.m.r. spectrum showed a multiplet at 4.8–6.0, a singlet at 3.30, and a singlet at 1.10 p.p.m. with relative areas of 3.05:1.95:6.0.

Chlorination of 2-methyl-1-butene gave a reaction mixture which showed four bands in the g.l.p.c. spectrum, C–F (order of increasing retention time), in addition to a variable-intensity band with a retention time identical with that of *t*-amyl chloride (*vide infra*). Correlation of relative retention times of the six possible allylic chloromethylbutenes with structure has been worked out with reasonable certainty by Walling and Thaler[33] on the basis of products expected from photochlorination of 2-methyl-1-butene, 3-methyl-1-butene, and 2-methyl-2-butene with *t*-butyl hypochlorite. Repetition of this procedure allowed tentative identification of C as *2-(chloromethyl)-1-butene* (*III*) and D and E as geometrical isomers of *1-chloro-2-methyl-2-butene* (*IV and V*). Reduction of tiglic acid with lithium aluminum hydride to the corresponding alcohol, b.p. 136–137.5°, $n^{23.5}\text{D}$ 1.4408 (lit.[34] b.p. 137–138°, $n^{25}\text{D}$ 1.4402), and conversion of the latter to its chloride with phosphorus trichloride by the procedure of Hatch and Noyes[34] gave, after flash distillation, a reaction mixture which showed a major band in the g.l.p.c. spectrum corresponding to E (as well as smaller bands assigned to pyridine and to VII, an allylic rearrangement product). Hence we assign E as V and D as IV. Product F was assumed to be *1,2-dichloro-2-methylbutane* (*VI*). In more recent work[35] products C–F have each been isolated and shown to possess the assigned structures on the basis of analytical and spectrzl data.

Chlorination of trimethylethylene under oxygen in the dark (4:1 ratio of olefin:chlorine) gave a reaction mix-

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[31] Any slight occurrence of uninhibited radical reactions adds significantly to the observed yield of substitution product since it is such a minor product from the polar reaction.

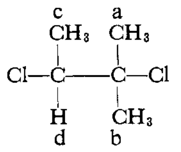
[32] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 379.

[33] C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).

[34] L. F. Hatch and P. R. Noyes, *ibid.*, **79**, 345 (1957).

[35] M. L. Poutsma and J. L. Kartch, unpublished results.

ture which showed three bands in the g.l.p.c. spectrum; G, H, and J (order of increasing retention time); careful distillation gave >95% pure samples of each although most of the material came off in intermediate mixed fractions and considerable decomposition and hydrogen chloride evolution occurred. Infrared spectroscopy showed G, b.p. 85–86°, to be *t*-amyl chloride (authentic sample from Matheson Coleman and Bell). Fraction H, b.p. 91.5–93.0°, n^{23}D 1.4285, was assigned as *3-chloro-2-methyl-1-butene* (*VII*) (lit.[4a] b.p. 93.8°, n^{20}D 1.4304). The infrared spectrum showed bands at 1645 (m) (C=C stretch) and 900 cm.$^{-1}$ (vs) ($R_2C{=}CH_2$). The n.m.r. spectrum showed a multiplet at 5.00, a multiplet at 4.82, a quartet at 4.50 (J = 7 c.p.s.), a narrow multiplet at 1.82, and a doublet at 1.57 p.p.m. (J = 7 c.p.s.) with relative areas of 0.95:1.0:0.95: 2.85:3.25; these bands can be assigned to the two nonequivalent olefinic protons, the methine proton α to a methyl group, the allylic methyl group with long-range coupling to the olefinic protons, and the terminal methyl group, respectively. Fraction J, b.p. 126–128°, n^{23}D 1.4404, was assigned as *2,3-dichloro-2-methylbutane* (*IX*) (lit.[36] b.p. 129°, n^{25}D 1.4410). The n.m.r. spectrum showed a quartet at 4.13 (J = 7 c.p.s.), a rather sharp singlet at 1.70, and a sharp band at 1.62 p.p.m. with a partially resolved shoulder at *ca.* 1.59 p.p.m. with relative areas of 1.0:4.8:4.2; apparently methyl groups a and b, nonequivalent even with rapid rotation[32] since they are adjacent to an asymmetric center, occur at 1.70 and 1.62 p.p.m. while methyl group c, split by proton d, occurs as a doublet at 1.70 and 1.59 p.p.m. (J = (0.11 p.p.m.) (60 Mc.) = *ca.* 7 c.p.s.). Since the retention time of *3-chloro-3-methyl-1-butene* (*VIII*) could be derived from the *t*-butyl hypochlorite study,[33] an upper limit for its presence could be set at 10^{-3} the amount of VII.



$$Cl{-}\underset{H}{\overset{CH_3}{C}}{-}\underset{CH_3}{\overset{CH_3}{C}}{-}Cl$$

IX

Chlorination of tetramethylethylene under the same conditions gave a reaction mixture which showed only one significant band in the g.l.p.c. spectrum; this mixture is extremely sensitive to decomposition during g.l.p.c. analysis if the inlet and/or column are "dirty." Distillation led to serious decomposition but a product, b.p. 41.5° (68 mm.), n^{23}D 1.4350, *ca.* 90% pure by g.l.p.c., was isolated and assigned as *3-chloro-2,3-dimethyl-1-butene* (*X*) (lit.[37] b.p. 32° (45 mm.), n^{25}D 1.4352). The infrared spectrum showed bands at 1640 (m) (C=C stretch) and 900 cm.$^{-1}$ (vs) ($R_2C{=}CH_2$). The n.m.r. spectrum showed a multiplet at 5.03, a multiplet at 4.80, a narrow multiplet at 1.92, and a singlet at 1.70 p.p.m. with relative areas of 1.05: 1.0:3.0:5.95 along with a few small extraneous bands; assignments are analogous to those of compound VII.

Treatment of pinacol with concentrated hydrochloric acid[38] saturated with calcium chloride gave *2,3-dichloro-2,3-dimethylbutane* (*XI*), m.p. 158–160° after sublimation (lit.[38] m.p. 160°), n.m.r. showing only a singlet at 1.77 p.p.m. This material was shown to be stable under chlorination conditions.

Quantitative Chlorination Procedure. A 25-ml., three-necked flask immersed in a constant temperature bath (−9 or 25°) was equipped with a Teflon magnetic stirring bar, a capillary gas inlet tube, and a Dry Ice condenser (or ordinary reflux condenser for olefins boiling above room temperature) fitted with a drying tube. The butenes were introduced as gases and condensed into the reaction flask by the condenser containing Dry Ice; others were introduced by pipet. In each case for the product ratios reported, 10 ml. (*ca.* 100 mmoles) of olefin was treated with 0.5–1.0 mmole of chlorine which was first condensed in a small calibrated trap and then swept into the reaction mixture with an oxygen stream in the dark in a period of 4–6 min.; stirring was provided by an immersible magnetic stirring motor. G.l.p.c. analyses of these reaction mixtures on a 2-m. Perkin-Elmer column "R" (polypropylene glycol) were performed with the same equipment described previously[1,2] and molar ratios determined in the same fashion.[1,2] Occasional comparisons of total product area and the amount of chlorine added with the area of a known amount of internal standard added after reaction showed that the observed products accounted for 100 ± 10% of the chlorine introduced. Retention times of the products from the butenes at 52°, from allyl chloride at 92°, and from cyclohexene under temperature-programmed conditions have been reported previously.[1,2] At 60° and a helium flow of *ca.* 200 ml./min., observed retention times in minutes for products described in this paper were: VIII, 4.5; VII, 7; III, 10; X, 11; IV, 12; V, 14; IX, 21.5; VI, 28; and XI, 35. At 85° and a helium flow of *ca.* 200 ml./min., observed retention times were: XII, 5; I, 7; and II, 27. Calibration factors for conversion of g.l.p.c. areas to molar quantities were determined for all cases except 2-methyl-1-butene for which pure products (III–VI) were not isolated; however, these never varied by >10% from unity as long as compounds of equal carbon content were compared.

Relative Reactivity Measurements. For each run, a mixture (*ca.* 10 ml.) of two olefins, A and B, was placed in the apparatus described above and treated with 0.5–1.0 mmole of chlorine under oxygen in the dark. The initial ratio of olefin concentrations, $(A)_0/(B)_0$, was determined by one of three methods: if both A and B were gaseous at room temperature, approximate quantities of each were condensed into the reaction vessel and the actual concentration ratio was determined from g.l.p.c. analysis of a 1-μl. aliquot before chlorination on an instrument equipped with column "R" and a thermal conductivity detector (method 1); if only A was gaseous, it was condensed into the flask up to the desired calibration mark on the flask and B was then added by pipet (method 2); if both were liquids, both were added by pipet (method 3). Methods 1 and 2 did not appear to be accurate to

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(36) F. M. Beringer and H. S. Schultz, *J. Am. Chem. Soc.*, **77**, 5533 (1955).

(37) L. F. Hatch and G. E. Journeay, *ibid.*, **75**, 3712 (1953).

(38) K. Sisido and H. Nozaki, *ibid.*, **69**, 961 (1947).

better than 5%. After chlorination, the products were determined by g.l.p.c. as described above. Since the extent of conversion of either A or B was always <10%, the relative reactivities were determined from the equation

$$\frac{\text{relative reactivity of B}}{\text{relative reactivity of A}} = \frac{(\text{products from B})(A_0)}{(\text{products from A})(B_0)}$$

Individual runs are given in Table IV; mean values were used to construct column 1 of Table V.

Chlorination Studies of Unsaturated Materials in Nonpolar Media. V. Norbornene and Nortricyclene[1]

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Chlorination of norbornene in carbon tetrachloride solution at 25° in the presence of oxygen to inhibit radical reactions and isolate the ionic pathway gave nortricyclyl chloride (I), exo-2-syn-7-dichloronorbornane (II), trans-2,3- (V), and exo-cis-2,3-dichloronorbornane (III) in a ratio of 65:25.5:6:3.5. In the absence of inhibitors and added initiators, dark chlorination led to spontaneous radical reaction (superimposed on the ionic reaction), the fraction of which increased with increasing norbornene concentration. From several runs under dark and illuminated conditions, the purely radical product distribution has been calculated as: I (18%), III (34%), V (38%), exo-5-chloronorbornene (VI, 7%), and endo-5-chloronorbornene (VII, 3%). The ratio of I:VI from photochlorination of norbornene with t-butyl hypochlorite increases with decreasing hypochlorite concentration. The nature of the intermediates in these ionic and radical chlorinations is considered. Treatment of norbornene with iodobenzene dichloride gave III in moderate yield along with V. Photochlorination of nortricyclene gave approximately equal amounts of a monochloride fraction, which was largely I but also contained VI, and a dichloride fraction, which was largely exo,exo-2,6-dichloronorbornane (XIX). This latter product is formulated as the result of chlorine atom attack on a cyclopropyl carbon atom with inversion.

Introduction

Chlorination of norbornene in pentane solution at −78° has been reported[2] to give 43% nortricyclyl chloride (I) and 37% *exo*-2-*syn*-7-dichloronorbornane (II); ionic intermediates were postulated to explain these results. Olefin chlorinations in nonpolar solvents have recently been shown[3] to involve a duality of mechanism; whereas chlorination of several branched olefins does indeed involve solely ionic intermediates, chlorination of several linear and cyclic olefins proceeds largely through free-radical intermediates because of initiation of radical-chain reactions by interaction of the olefin and chlorine; as an added complication, the percentage of radical reaction for a given olefin decreases as the concentration of olefin decreases. In light of these results and in light of current interest in addition reactions of norbornene and its analogs,[4-6] it appeared interesting to reinvestigate the chlorination of norbornene with the help of more recent analytical techniques.

Results

Treatment of norbornene in carbon tetrachloride solution at 25° with a limited amount of chlorine (<10 mole %) in the presence of oxygen (to inhibit radical reactions) gave a reaction mixture which showed four peaks in the g.l.p.c. spectrum on a poly(propylene glycol) column in a ratio of 65:6:3.5:25.5[7] (in order of increasing retention time). Isolation of the first and last showed them to be I and II, respectively, identical with the products isolated by Roberts and

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[1] (a) Presented in part before the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965; for part IV, see M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 4285 (1965); (b) norbornene = bicyclo[2.2.1]heptene; nortricyclene = tricyclo[2.2.1.$0^{2,6}$]heptane.

[2] J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Am. Chem. Soc.*, **76**, 5692 (1954).

[3] M. L. Poutsma, *ibid.*, **87**, 2161, 2172 (1965).

[4] For representative ionic addition reactions see (a) bromine: J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *ibid.*, **72**, 3116 (1950), and H. Kwart and L. Kaplan, *ibid.*, **76**, 4072 (1954); (b) peracids: H. Kwart and W. G. Vosburgh, *ibid.*, **76**, 5400 (1954); (c) aromatic sulfenyl halides: H. Kwart and R. K. Miller, *ibid.*, **78**, 5678 (1956); S. J. Cristol, R. P. Arganbright, G. D. Brindell, and R. M. Heitz, *ibid.*, **79**, 6035 (1957); H. Kwart, R. K. Miller, and J. L. Nyce, *ibid.*, **80**, 887 (1958); (d) alcohols: S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *ibid.*, **84**, 3918 (1962); (e) mercuric salts: T. G. Traylor and A. W. Baker, *ibid.*, **85**, 2746 (1963); (f) hydrogen bromide: H. Kwart and J. L. Nyce, *ibid.*, **86**, 2601 (1964).

[5] For representative radical addition reactions, see (a) bromine: J. A. Berson and R. Swidler, *ibid.*, **76**, 4060 (1954); (b) thiophenols: S. J. Cristol and G. D. Brindell, *ibid.*, **76**, 5699 (1954); S. J. Cristol and R. P. Arganbright, *ibid.*, **79**, 6039 (1957); (c) aromatic sulfonyl halides: S. J. Cristol and J. A. Reeder, *J. Org. Chem.*, **26**, 2182 (1961); (d) ethyl bromoacetate: J. Weinstock, Abstracts, 128th National Meeting of the American Chemical Society, Minneapolis, Minn., Sept. 1955, p. 19-O; (e) polyhalomethanes: E. Tobler and D. J. Foster, *J. Org. Chem.*, **29**, 2839 (1964); (f) perfluoroalkyl iodides: N. O. Brace, *ibid.*, **27**, 3027 (1962); (g) acetone: W. Reusch, *ibid.*, **27**, 1882 (1962); (h) hydrogen bromide: ref. 4f, and N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 623 (1960); (i) *t*-butyl hypochlorite: E. Tobler, D. E. Battin, and D. J. Foster, *J. Org. Chem.*, **29**, 2834 (1964); (j) formamide: D. Elad and J. Rokach, *J. Chem. Soc.*, 800 (1965).

[6] For miscellaneous addition reactions see (a) phthaloyl peroxide: F. D. Greene and W. W. Rees, *J. Am. Chem. Soc.*, **82**, 890 (1960); (b) nitrosyl halides: J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *ibid.*, **86**, 4074 (1964); (c) benzophenones photochemically: D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1425 (1964); (d) 1,3-dipolar additions: R. Huisgen, *Angew. Chem.*, **75**, 604 (1963); (e) benzenesulfonyl azide: J. E. Franz, C. Osuch, and M. W. Dietrich, *J. Org. Chem.*, **29**, 2922 (1964).

[7] All g.l.p.c. areas have been converted to molar quantities by use of appropriate calibration factors determined from mixtures of known compounds.