

Chlorination Studies of Unsaturated Materials in Nonpolar Media. III. Competition between Ionic and Free-Radical Reactions during Chlorination of the Isomeric Butenes and Allyl Chloride¹

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Chlorination of *cis*- and *trans*-2-butene, 1-butene, and allyl chloride, either neat or in nonpolar solvents in the presence of oxygen to ensure ionic reaction has been found to give 97–98% addition products (stereospecifically *trans* in the former two cases) and 2–3% allylic substitution products with shifted double bonds; analogous chlorination of isobutylene gave 87% substitution. Chlorination of the linear butenes under nitrogen in the absence of initiators and inhibitors gave quite different product distributions characterized by loss of stereospecificity in the addition products and by a greater percentage of substitution products; the latter (15–20% of the total products) were mixtures of allylic isomers with shifted and unshifted double bonds in which geometrical integrity was maintained. These results are interpreted in terms of predominantly radical-chain reactions which are spontaneously initiated by interaction between the reagents. Such radical chlorination of 1-butene gave a small amount of allylcarbinyl chloride but no cyclobutyl nor cyclopropylcarbinyl chlorides. In contrast, identical treatment of isobutylene gave no changes from the ionic behavior; a certain fraction of radical chlorination of isobutylene could be induced however by illumination. The dependence of product distributions from dark and illuminated chlorinations under nitrogen on olefin concentration for each of the butenes and allyl chloride is reported. From these quantitative data and qualitative data for several other olefins, the following empirical rule is proposed. Dark chlorination of any neat olefin, free from other functionality, in the absence of added initiators and inhibitors, will lead to a significant fraction of radical reaction except for olefins which bear two alkyl groups on at least one end of the double bond. Possible reasons for this behavior are discussed based on experiments with mixtures of olefins. Previous attempts to correlate chlorination products with olefin structure are shown to be inadequate because of a failure to realize the duality of mechanism involved. From competitive photochlorinations of various olefins with cyclohexane as standard, relative rates of addition of chlorine atom to double bonds and of abstraction of allylic hydrogens by chlorine atom were determined. Allylic hydrogen atoms are only slightly more reactive than their saturated counterparts; the indiscriminate nature of chlorine atom (compared to other radicals) toward organic molecules is displayed in this series.

(1) (a) Presented in part before the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964; (b) for part II, see M. L. Poutsma, *J. Am. Chem. Soc.*, 87, 2161 (1965).

Introduction

In the preceding paper,^{1b} it was reported that dark chlorination of neat cyclohexene at 25° in the absence of inhibitors and initiators is a free-radical process because of spontaneous initiation of radical chains by interaction between chlorine and the olefin. This radical pathway can however be superseded by a different process, presumably proceeding through ionic intermediates, by the use of radical inhibitors such as oxygen or of polar solvents. Finally, even in the absence of inhibitors, the ionic route begins to compete effectively with the radical process if the olefin is progressively diluted with inert, nonpolar solvents. The first result appeared to be at variance with a report² that chlorination of neat isobutylene followed an ionic pathway. To solve this apparent conflict and to determine the generality of the cyclohexene results, we have investigated the liquid phase chlorination of the isomeric butenes in detail.

Chlorination of 1- and 2-butene in a flow reactor at 50–100° with reaction products as the liquid phase has been reported³ to give 55–65% and 75% of addition products, respectively; the extent of substitution was inferred from the amount of hydrogen chloride produced and the structure(s) of the substitution product(s) was not determined.⁴ In the same study,³ isobutylene gave up to 90% of the substitution product, 3-chloro-2-methyl-1-propene. Lucas and Gould⁵ chlorinated the individual isomeric 2-butenes at –20° in diffuse light and found that predominantly *trans* addition occurred; the *trans* olefin gave *meso*-2,3-dichlorobutane while the *cis* isomer gave the *dl* modification.

Results

trans-2-Butene. Treatment of neat *trans*-2-butene under nitrogen in the dark at –9° with a limited quantity of chlorine (<10% conversion) led to rapid⁶ formation of four products detectable by g.l.c. analysis on a polypropylene glycol column in a ratio of 4:14:73:9⁷ (increasing order of retention time). These were

(2) W. Reeve, D. H. Chambers, and C. S. Prickett, *ibid.*, 74, 5369 (1952); see discussion in ref. 1b.

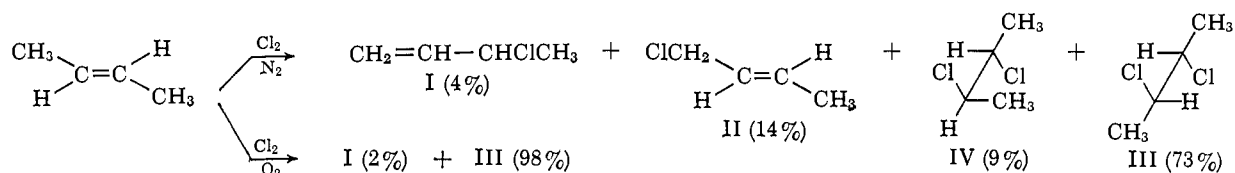
(3) H. P. A. Groll, G. Hearne, F. F. Rust, and W. E. Vaughan, *Ind. Eng. Chem.*, 31, 1239 (1939); J. Burgin, W. Engs, H. P. A. Groll, and G. Hearne, *ibid.*, 31, 1413 (1939).

(4) Since the degree of conversion was large enough that considerable quantities of polychlorides were formed, it is impossible to deduce the initial product distribution.

(5) H. J. Lucas and C. W. Gould, Jr., *J. Am. Chem. Soc.*, 63, 2541 (1941).

(6) The designation "rapid" will be used for all reactions which were fast enough not to allow the reaction mixture to become yellow; see Experimental section for amounts of reagents.

(7) All product ratios determined from g.l.c. have been corrected to molar ratios by calibration with known compounds except where noted in the Experimental section.



shown by isolation and comparison to authentic samples to be 3-chloro-1-butene (I), 1-chloro-*trans*-2-butene (II), *meso*- (III), and *dl*-2,3-dichlorobutane (IV), respectively. Repetition of this chlorination with illumination provided by three 275-w. sun lamps at 6–9 in. led to a small increase in the amount of substitution from 18 to 26% of the total product. In sharp contrast, chlorination under oxygen led to essentially complete elimination of II and IV (II/I < 0.1 and

but infrared analysis of isolated material allowed ready identification. Illumination again caused a small enhancement of substitution. Chlorination in the presence of oxygen led to elimination of products VI and III (VI/I < 0.06 and III/IV < 0.01), with I and IV produced in a ratio of 3:97. The effect of olefin concentration on product composition for dark and illuminated runs under nitrogen is shown in Table II and Figure 2. The same pattern is observed as for *trans*-

Table I. Effect of Olefin Concentration on Product Distribution from Chlorination of *trans*-2-Butene under Nitrogen at -9°

N ^a	Dark						III/IV	N ^a	Illuminated					
	I ^{b,c}	II ^{b,c}	III ^{b,c}	IV ^{b,c}	II/I	I ^{b,c}			II ^{b,c}	III ^{b,c}	IV ^{b,c}	II/I	III/IV	
1.00	4.0	12.4	75.1	8.4	3.1	8.9	1.00	5.8	22.4	56.8	15.0	3.9	3.8	
	4.4	15.4	70.1	10.2	3.5	6.9		5.2	19.1	57.6	18.1	3.7	3.2	
0.92	4.0	12.0	76.0	7.9	3.0	9.6	0.92	6.1	22.6	56.7	14.6	3.7	3.9	
0.70	5.3	15.5	68.8	10.4	3.0	6.6	0.73	7.4	24.5	52.7	15.4	3.3	3.4	
0.56	5.1	17.7	66.5	10.6	3.5	6.3	0.56	6.5	23.3	56.2	14.0	3.6	4.0	
0.39	5.2	18.0	66.0	10.9	3.5	6.1	0.39	6.5	23.6	55.9	14.0	3.7	4.0	
	5.3	15.3	69.6	9.7	2.9	7.2	0.26	7.0	20.4	58.1	14.5	2.9	4.0	
0.15	4.6	13.4	71.7	10.3	3.0	7.0	0.15	5.6	16.9	64.9	12.7	3.0	5.1	
	4.8	12.6	72.5	10.1	2.7	7.2	0.12	6.1	17.2	63.0	13.6	2.8	4.6	
0.085	3.9	9.5	76.5	10.1	2.4	7.6								
0.079	4.0	11.0	75.3	9.7	2.8	7.8	0.079	5.9	18.5	60.0	15.5	3.1	3.9	
0.070	3.8	8.4	78.7	9.0	2.2	8.7	0.075	5.2	15.3	66.3	13.3	2.9	5.0	
0.050	2.9	5.9	83.3	7.9	2.0	10.6	0.045	6.2	15.6	61.9	16.3	2.5	3.8	
0.041	2.7	6.2	83.4	7.7	2.3	10.8	0.041	6.3	18.0	60.1	15.6	2.9	3.9	
0.030	2.1	3.5	89.6	4.7	1.7	18.9								

^a Mole fraction of olefin in 1,1,2-trichlorotrifluoroethane. ^b Molar percentage of total observed products. ^c I = 3-chloro-1-butene, II = 1-chloro-*trans*-2-butene, III = *meso*-2,3-dichlorobutane, and IV = *dl*-2,3-dichlorobutane.

IV/III < 0.003) whereas I and III were produced in a still rapid⁶ reaction in a ratio of 2:98. G.l.c. analysis showed that, if either of the stereoisomers of 2-chloro-2-butene (V) were present, they were below the limits of detection (<5% of the amount of I). Results of a quantitative study of the effects of olefin concentration (in 1,1,2-trichlorotrifluoroethane as diluent) on product ratios from dark and illuminated reactions at low conversion under nitrogen are listed in Table I. The ratio of addition to substitution is shown graphically in Figure 1. The most striking effect of dilution is the sharp increase in the amount of addition at low olefin concentrations for the dark runs; illumination with an essentially constant light source led to somewhat lower addition:substitution ratios at all concentrations and eliminated much of the sharp increase at low concentrations. Note also that the dark runs gave a consistently higher *meso:dl* ratio than the corresponding illuminated ones.

cis-2-Butene. Analogous chlorination of *cis*-2-butene in the dark under nitrogen at -9° gave a reaction mixture the g.l.c. spectrum of which showed four peaks with retention times identical with those from *trans*-2-butene in a ratio of 6:10:28:56 (increasing order of retention time). However, isolation showed that, whereas I, III, and IV were indeed formed, the second peak was due to 1-chloro-*cis*-2-butene (VI). We have been unable to separate isomers II and VI by g.l.c.,

2-butene although illumination is less effective in counteracting the increase in addition at low olefin

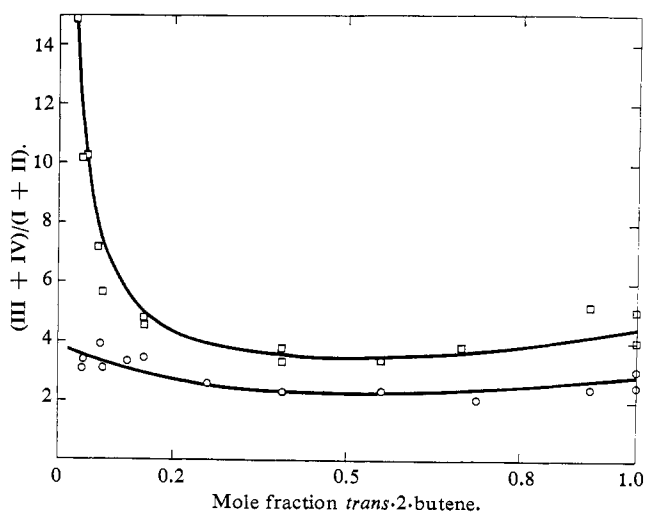
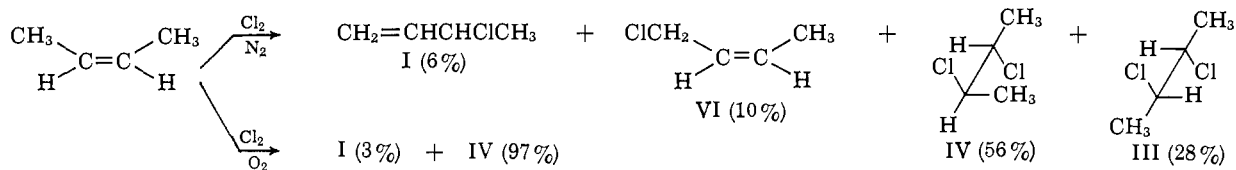


Figure 1. Dependence of addition:substitution ratio on olefin concentration for chlorination of *trans*-2-butene under nitrogen at -9° : \square , darkness; \circ , illumination.

concentration. Note that for this butene isomer the *meso:dl* ratio is consistently lower in dark runs than in corresponding illuminated ones.



1-Butene. Dark chlorination of neat 1-butene under nitrogen at -9° gave in a rapid⁶ reaction a mixture which showed four peaks in the g.l.c. analysis in a ratio of 2.5:4.5:7.5:85.5 (increasing order of retention time). By isolation and comparison to authentic materials, the first peak proved to be due to 3-chloro-1-butene (I), the second to 4-chloro-1-butene (VII), the third to a mixture of the isomers of 1-chloro-2-butene (II + VI), and the last to 1,2-dichlorobutane (VIII). Neither in dark nor illuminated chlorinations

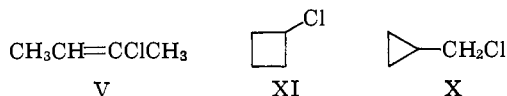
dichloro-2-methylpropane (XII) in a ratio of 87:13 along with traces of 1-chloro-2-methylpropene (XIII) (XIII/XI ~ 0.015); varying amounts of *t*-butyl chloride were also detected. Repetition with the same source of illumination used throughout this study changed the ratio of XI:XII from 6.7 to values of unity or less; repetition under oxygen on the other hand gave a ratio of XI:XII of 88:12, indistinguishable from that under nitrogen. Thus, in contrast to 1- and 2-butene, a significant change in chlorination behavior for iso-

Table II. Effect of Olefin Concentration on Product Distribution from Chlorination of *cis*-2-Butene under Nitrogen at -9°

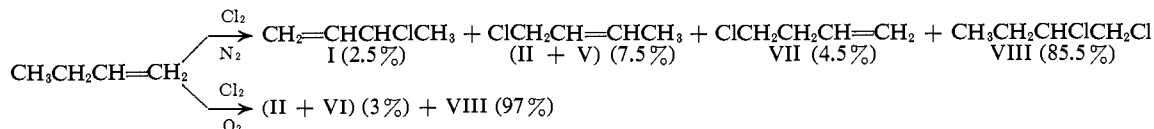
N ^a	Dark					III/IV	N ^a	Illuminated					III/IV
	I ^{b,c}	VI ^{b,c}	III ^{b,c}	IV ^{b,c}	VI/I			I ^{b,c}	VI ^{b,c}	III ^{b,c}	IV ^{b,c}	VI/I	
1.00	6.2	11.2	31.3	51.3	1.8	0.61	1.00	7.9	17.3	47.3	27.5	2.2	1.7
	5.9	8.9	25.1	60.0	1.5	0.42							
0.92	6.7	13.5	36.5	43.2	2.0	0.84	0.92	8.3	17.7	45.6	28.3	2.1	1.6
0.57	7.2	13.7	33.6	45.5	1.9	0.74	0.57	8.7	18.8	45.3	27.2	2.2	1.7
0.40	7.2	14.0	33.7	45.1	1.9	0.75	0.40	8.3	17.2	43.3	31.1	2.1	1.4
0.15	5.8	8.9	27.3	57.9	1.6	0.47	0.15	7.7	14.6	42.8	34.9	1.9	1.2
0.081	5.0	6.9	25.0	63.0	1.4	0.40	0.081	6.3	11.0	38.0	44.7	1.8	0.85
0.042	4.3	4.5	18.3	72.9	1.1	0.25	0.042	5.3	8.1	33.5	53.1	1.5	0.63

^a Mole fraction of olefin in 1,1,2-trichlorotrifluoroethane. ^b Molar percentage of total observed products. ^c I = 3-chloro-1-butene, VI = 1-chloro-*cis*-2-butene, III = *meso*-2,3-dichlorobutane, and IV = *dl*-2,3-dichlorobutane.

of 1-butene could any cyclobutyl chloride (IX) or cyclopropylcarbinyl chloride (X) be detected. Repetition of the chlorination in the presence of oxygen led to elimination of I and VII as products (I/(II + VI) < 0.03) and to a ratio of (II + VI):VIII of 3:97; in



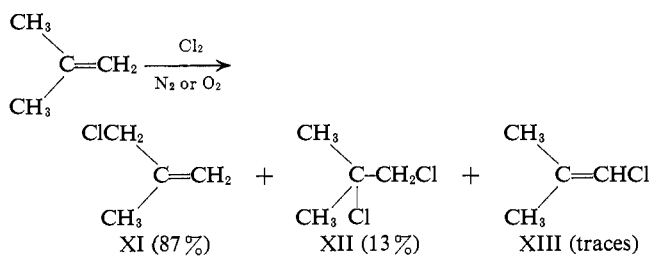
this case, reaction under oxygen had become slow enough just to allow a pale yellow color to appear in solution during the chlorine addition. Concentration studies are shown in Table III and Figure 3. Two facts are noteworthy: (1) once again addition is favored by dilution especially in the dark runs, and (2) the ratio of VII:I is quite insensitive to changes in experimental conditions. The values for VII may be



up to 10% high since this peak overlapped slightly with that of 3-chloro-2-methylpropene (XI) which was formed in small amounts (especially under ionic conditions, *vide infra*) from an isobutylene impurity in the 1-butene; traces of *cis*-2-butene in the starting olefin mean that the values for I and (II + VI) are somewhat less reliable than those in Tables I and II.

Isobutylene. Chlorination of isobutylene in the dark under nitrogen at -9° gave two major products identified as 3-chloro-2-methylpropene (XI) and 1,2-

butylene occurs when the dark runs under nitrogen are illuminated rather than when nitrogen is replaced by oxygen.



Allyl Chloride. Chlorination of neat allyl chloride under nitrogen in the dark at -9° was noticeably slower than that of 1-butene, this being the only substrate of the series considered in this paper for which chlorine color developed in a dark uninhibited

reaction. The major product (98-99%) was identified as 1,2,3-trichloropropane (XIV); two minor products were not isolated but had g.l.c. retention times appropriate for *cis*- (XV) and *trans*-1,3-dichloropropane (XVI) and different from that of 2,3-dichloropropane (XVII). Repetition with illumination led, in a considerably more rapid reaction, to the same products but with a greater XVI/XV ratio. In several runs under nitrogen a trace of a peak with the correct retention time for 3,3-dichloropropane (XVIII) ap-

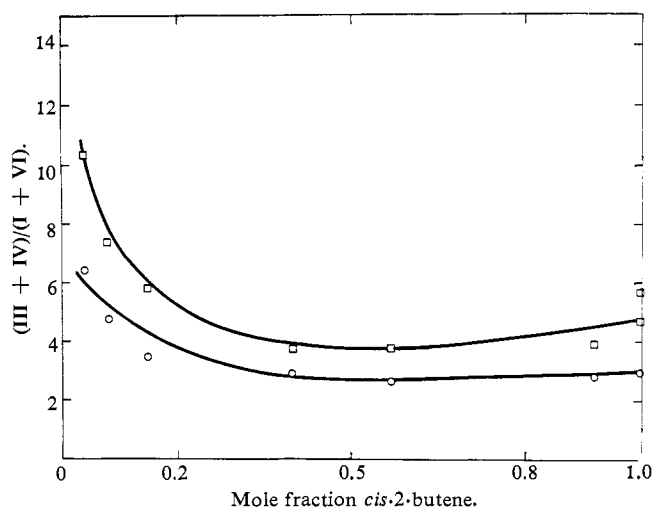


Figure 2. Dependence of addition:substitution ratio on olefin concentration for chlorination of *cis*-2-butene under nitrogen at -9° : \square , darkness; \circ , illumination.

peared in the g.l.c. analysis but it was always $<5\%$ of either XV or XVI. Chlorination under oxygen gave 98–99% of XIV; the only other product of

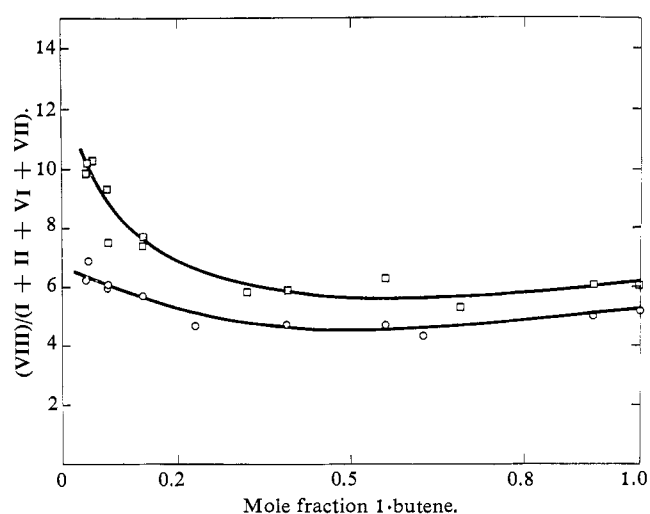


Figure 3. Dependence of addition:substitution ratio on olefin concentration for chlorination of 1-butene under nitrogen at -9° : \square , darkness; \circ , illumination.

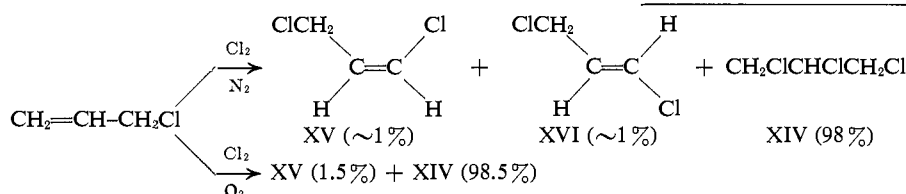
decreased, the time required for complete reaction in the dark runs under nitrogen increased to at least 30 min.

Table III. Effect of Olefin Concentration on Product Distribution from Chlorination of 1-Butene under Nitrogen at -9°

N ^a	Dark						N ^a	Illuminated					
	I ^{b,c}	VII ^{b,c,d}	(II + VI) ^{b,c}	VIII ^{b,c}	(II + VI)/I	VII/I		I ^{b,c}	VII ^{b,c,d}	(II + VI) ^{b,c}	VIII ^{b,c}	(II + VI)/I	VII/I
1.00	2.3	4.4	7.5	85.8	3.3	1.95	1.00	2.9	5.1	8.4	83.7	2.9	1.77
0.92	2.3	4.4	7.5	85.7	3.3	1.91	0.92	3.0	5.2	8.5	83.4	2.9	1.74
0.69	2.6	5.3	8.1	84.0	3.1	2.02	0.63	3.5	6.1	9.1	81.3	2.6	1.77
0.56	2.3	4.2	7.3	86.2	3.2	1.86	0.56	3.1	5.6	8.9	82.4	2.9	1.80
0.39	2.5	4.6	7.5	85.3	3.0	1.84	0.39	3.2	5.6	8.8	82.4	2.7	1.75
0.32	2.4	4.9	7.4	85.2	3.1	2.01	0.23	3.3	6.0	8.4	82.3	2.5	1.81
0.14	2.0	3.6	6.0	83.4	3.0	1.82	0.14	2.8	5.0	7.1	85.0	2.5	1.76
0.078	1.9	4.0	5.9	88.1	3.1	2.08	0.078	2.7	4.9	6.6	85.8	2.4	1.81
	1.9	4.2	5.6	88.3	2.9	2.17		2.8	5.3	6.3	85.7	2.3	1.92
0.055	1.4	3.2	4.2	91.1	3.1	2.33							
0.043	1.4	3.3	4.2	91.0	3.0	2.37	0.045	2.4	5.0	5.3	87.3	2.2	2.06
0.041	1.5	2.9	4.9	90.8	3.3	1.91	0.041	2.6	5.1	6.1	86.2	2.3	1.94

^a Mole fraction of olefin in 1,1,2-trichlorotrifluoroethane. ^b Molar percentage of total observed product. ^c I = 3-chloro-1-butene, II = 1-chloro-*trans*-2-butene, VI = 1-chloro-*cis*-2-butene, VII = 4-chloro-1-butene, and VIII = 1,2-dichlorobutane. ^d Maximum; see text.

significance was now the *cis*-substitution product XV (XV/XVI > 10); at least 45 min. was required for complete reaction at a mole fraction of allyl chloride of



0.39. Results of a concentration study are shown in Table IV; because of the small amounts of XV and



XVI formed, their ratio is probably more accurate than their absolute values. As the olefin concentration

Olefin-Cyclohexane Mixtures. Dark chlorination of each of the butenes and allyl chloride in cyclohexane as solvent under nitrogen led to production of chloro-

cyclohexane (XIX) in significant amounts except for isobutylene; however, chlorination of isobutylene-cyclohexane mixtures with illumination did lead to production of XIX. Under oxygen, on the other hand, each of these olefins could be chlorinated in cyclohexane without attack on the latter. A series of experiments was conducted in which each olefin, in turn, was chlorinated to low conversion under nitrogen with illumination at -9° in the presence of varying

Table IV. Effect of Olefin Concentration on Product Distribution from Chlorination of Allyl Chloride at -9°

N^a	XV ^{b,c}	XVI ^{b,c}	XIV ^{b,c}	XVI/ XV
0.39 ^d	1.3	0.1	98.5	0.07
0.39 ^e	0.8	1.2	98.0	1.5
1.00 ^f	1.2	0.9	97.9	0.8
	0.8	0.7	98.5	0.9
0.69 ^f	0.6	0.7	98.6	1.1
0.39 ^f	0.7	1.0	98.3	1.5
0.27 ^f	0.5	0.7	98.8	1.5
0.14 ^f	0.6	0.4	99.0	0.65
0.071 ^f	0.9	0.4	98.7	0.4

^a Mole fraction of olefin in 1,1,2-trichlorotrifluoroethane. ^b Molar percentage of total observed products. ^c XIV = 1,2,3-trichloropropane, XV = *cis*-1,3-dichloropropene, and XVI = *trans*-1,3-dichloropropene. ^d Under oxygen. ^e Under nitrogen with illumination. ^f Under nitrogen in the dark.

described above as products. The peaks for 3-chloro-1-butene (I) and 4-chloro-1-butene (VII) could be observed but could not be measured accurately because of interference from the cyclohexane peak; the band for 3-chloro-2-methyl-1-propene (XI) occurred on the tail of this solvent peak and hence its estimation is less accurate than that of the other products. Results are shown in Tables V-IX along with appropriate product ratios which will be considered in more detail in the Discussion section.

Butene Mixtures. The relative reactivities of the isomeric butenes towards liquid phase chlorination under oxygen were determined and will be presented in detail in a future paper. We need note here only that: (1) the reactivities of isobutylene and the 2-butenes were within 20% of each other but were ~50

Table V. Chlorination of *trans*-2-Butene under Nitrogen with Illumination at -9° in the Presence of Cyclohexane

N^a	II ^{b,c}	III ^{b,c}	IV ^{b,c}	XIX ^{b,c}	(III + IV)/ II	III/IV	12(III + IV)· (F)/ (XIX) ^d	2(II)· (F)/ (XIX) ^d
0.80	1.00	2.58	0.67	0.81	3.26	3.85	11.8	0.61
0.77	1.00	2.68	0.68	0.96	3.37	3.95	12.5	0.62
0.67	1.00	2.92	0.72	2.21	3.64	4.07	9.7	0.44
0.67	1.00	2.77	0.72	1.88	3.49	3.82	10.9	0.52
0.58	1.00	2.93	0.73	2.83	3.65	4.04	11.4	0.52
0.50	1.00	2.90	0.73	3.17	3.63	3.99	12.1	0.55

^a Mole fraction of olefin in cyclohexane. ^b Molar amount relative to II. ^c II = 1-chloro-*trans*-2-butene, III = *meso*-2,3-dichlorobutane, IV = *dl*-2,3-dichlorobutane, and XIX = chlorocyclohexane. ^d $F = (\text{cyclohexane})_0/(\text{trans-2-butene})_0$.

Table VI. Chlorination of *cis*-2-Butene under Nitrogen with Illumination at -9° in the Presence of Cyclohexane

N^a	VI ^{b,c}	III ^{b,c}	IV ^{b,c}	XIX ^{b,c}	(III + IV)/ VI	III/IV	12(III + IV)· (F)/ (XIX) ^d	2(VI)· (F)/ (XIX) ^d
0.81	1.00	2.60	1.95	1.05	4.55	1.34	12.4	0.45
0.78	1.00	2.64	2.20	1.34	4.84	1.20	12.5	0.43
0.68	1.00	2.76	2.17	2.40	4.92	1.27	11.8	0.40
0.68	1.00	2.76	2.20	2.36	4.96	1.26	12.0	0.40
0.58	1.00	2.84	2.03	3.55	4.87	1.40	11.8	0.40
0.51	1.00	2.81	2.27	5.21	5.07	1.24	11.2	0.37

^a Mole fraction of olefin in cyclohexane. ^b Molar amount relative to VI. ^c VI = 1-chloro-*cis*-2-butene, III = *meso*-2,3-dichlorobutane, IV = *dl*-2,3-dichlorobutane, and XIX = chlorocyclohexane. ^d $F = (\text{cyclohexane})_0/(\text{cis-2-butene})_0$.

Table VII. Chlorination of 1-Butene under Nitrogen with Illumination at -9° in the Presence of Cyclohexane

N^a	(II + VI) ^{b,c}	VIII ^{b,c}	XIX ^{b,c}	VIII/ (II + VI)	12 (VIII)· (F)/ (XIX) ^d	6(II + VI)· (F)/ (XIX) ^d
0.80	1.00	9.61	2.52	9.6	12.0	0.59
0.77	1.00	10.15	3.25	10.2	11.2	0.55
0.67	1.00	10.66	5.54	10.7	11.5	0.54
0.67	1.00	10.18	5.23	10.2	11.6	0.57
0.57	1.00	10.74	8.53	10.7	11.3	0.53
0.50	1.00	10.65	10.26	10.7	12.4	0.58

^a Mole fraction of olefin in cyclohexane. ^b Molar amount relative to (II + VI). ^c II = 1-chloro-*trans*-2-butene, VI = 1-chloro-*cis*-2-butene, VIII = 1,2-dichlorobutane, and XIX = chlorocyclohexane. ^d $F = (\text{cyclohexane})_0/(\text{1-butene})_0$.

Table VIII. Chlorination of Isobutylene under Nitrogen with Illumination at -9° in the Presence of Cyclohexane

N^a	XI ^{b,c}	XII ^{b,c}	XIX ^{b,c}	XII/ XI	12 (XII)· (F)/ (XIX) ^d	2(XI)· (F)/ (XIX) ^d
0.80	1.00	1.72	0.42	1.72	12.4	1.20
0.67	1.00	1.71	0.91	1.71	11.3	1.10
0.67	1.00	1.37	0.74	1.37	11.1	1.36
0.57	1.00	1.30	0.96	1.30	12.1	1.55
0.50	1.00	1.55	1.41	1.55	13.2	1.42

^a Mole fraction of olefin in cyclohexane. ^b Molar amount relative to XI. ^c XI = 3-chloro-2-methyl-1-propene, XII = 1,2-dichloro-2-methylpropane, and XIX = chlorocyclohexane. ^d $F = (\text{cyclohexane})_0/(\text{isobutylene})_0$.

amounts of cyclohexane. G.l.c. analysis allowed quantitative determination of all the monochlorides except those listed below and all of the dichlorides

times greater than the reactivity of 1-butene⁸ which was, in turn, at least 50 times greater than that of allyl

(8) Successive rate enhancements of 50-100-fold were again observed in going to trimethyl- and then to tetramethylethylene; in other words, each addition of an alkyl group to the ethylenic linkage gives a dramatic

Table IX. Chlorination of Allyl Chloride under Nitrogen with Illumination at -9° in the Presence of Cyclohexane

N^a	XV ^{b,c}	XVI ^{b,c}	XIV ^{b,c}	XIX ^{b,c}	XVI/ XV	12 (XIV). (F)/ (XIX) ^d	6(XV + XVI). (F)/ (XIX) ^d
0.84	0.0078	0.0115	1.00	0.32	1.47	7.0	0.067
0.57	0.0072	0.0115	1.00	1.25	1.61	7.3	0.068
0.25	<i>e</i>	<i>e</i>	1.00	5.38	<i>e</i>	6.7	<i>e</i>

^a Mole fraction of olefin in cyclohexane. ^b Molar amount relative to XIV. ^c XV = *cis*-1,3-dichloropropene, XVI = *trans*-1,3-dichloropropene, XIV = 1,2,3-trichloropropane, and XIX = chlorocyclohexane. ^d F = (cyclohexane)₀/(allyl chloride)₀. ^e Too small to measure accurately.

chloride; and (2) the ratio of addition to substitution observed for each olefin was the same whether determined from chlorination of that olefin alone under oxygen or in mixture with another. An interesting set of observations was made for chlorination of a 1:1 mixture of isobutylene and *trans*-2-butene. Under oxygen, each substrate consumed approximately one-half of the available chlorine to give product ratios of III/I \sim 50 and XII/XI = 0.15, the same values as from individual runs under oxygen. Under nitrogen in the dark, each olefin again consumed approximately one-half of the chlorine, but, whereas the product distribution from *trans*-2-butene (I, II, III, and IV) was essentially the same as from dark chlorination of this olefin alone under nitrogen, the ratio XII/XI from isobutylene was \sim 1 rather than 0.15 as observed from dark chlorination of this olefin alone under nitrogen. Dark chlorination of isobutylene under nitrogen has been affected in similar fashion by the presence of 2-butene as by external illumination.

Other Olefins. A variety of olefins has been treated with chlorine in the dark under nitrogen in the presence of an equal volume of cyclohexane. A significant quantity of chlorocyclohexane (corresponding to 20–60% of the total chlorine introduced) was detected by g.l.c. analysis for runs with allyl chloride, 1-butene, *cis*- and *trans*-2-butene, 1-pentene, 2-pentene, cyclopentene, 1-hexene, cyclohexene,^{1b} 3-heptene, and norbornene.⁹ Very little or no chlorocyclohexane was produced from identical treatment of isobutylene, trimethylethylene,⁹ 2-methyl-1-butene,⁹ tetramethylethylene,⁹ 2,4,4-trimethyl-1- and -2-pentene, and styrene.

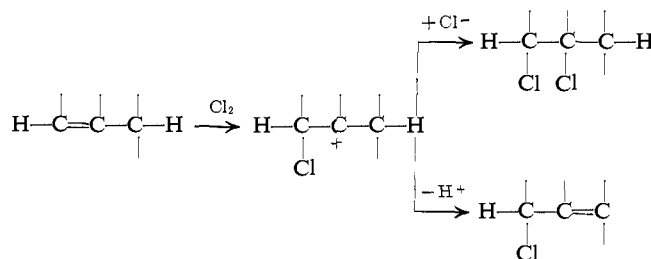
Discussion

Competitive Reaction Pathways. Dependence on Experimental Conditions. It appears that dark chlorination of each of the olefins in the presence of the radical inhibitor oxygen is proceeding through ionic intermediates. This mechanism had been suggested by Taft¹⁰ to explain the chlorination data then available. However, it is now apparent that many of the results considered by Taft¹⁰ were actually from radical reactions. The ionic pathway does indeed exist but, for many olefins (*vide infra*), can be observed only in

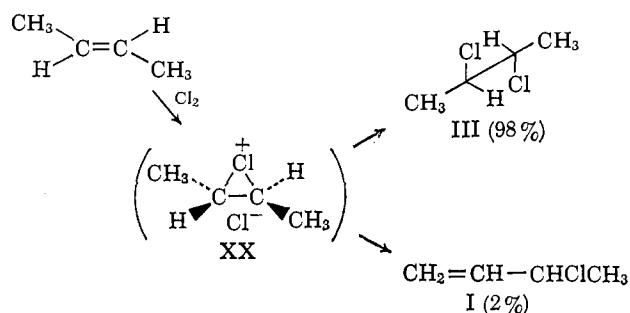
rate increase. This pattern has been generally observed in addition reactions involving electrophilic attack such as bromination (J. E. DuBois and G. Mouvier, *Tetrahedron Letters*, 1325 (1963)) and epoxidation (D. Swern, *J. Am. Chem. Soc.*, 69, 1692 (1947)). The similarity in rates between the symmetrically and unsymmetrically substituted dimethylethylenes is suggestive of a bridged intermediate with little charge localization on carbon in the transition state.

(9) These substrates have been studied in more detail and we hope to report concerning them in future papers.

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



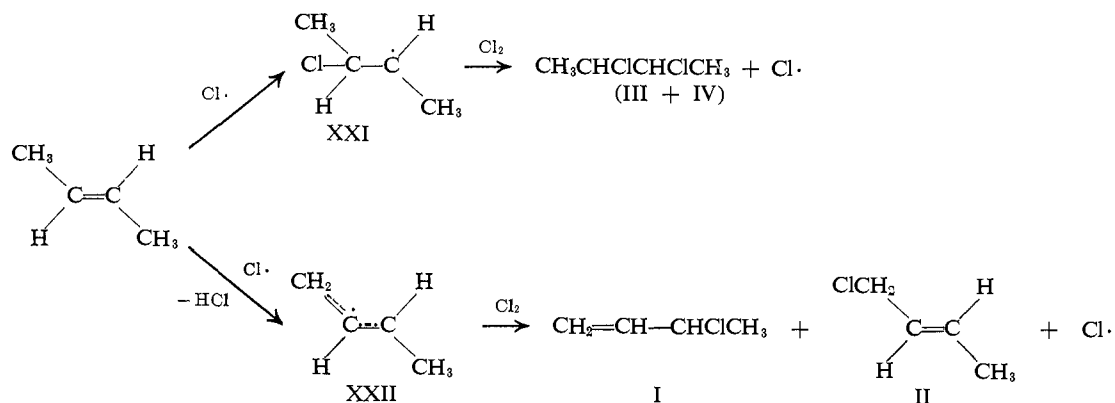
the presence of radical inhibitors. Especially significant is the fact that under inhibited conditions the only substitution products observed bear chlorine on a carbon atom which was originally olefinic; that is, 1-butene gives the internal olefins II and VI but not the terminal olefin I whereas the 2-butenes give only I but not II or VI. The intermediate in these nonionizing media would be expected to be a rather tight ion pair; the stereospecific *trans* addition from the *cis*- and *trans*-2-butene pair suggests a bridged intermediate for these two at least. The ionic pathway can be illustrated for *trans*-2-butene as shown below, with



similar intermediates for the other olefins.

Next let us consider the results from dark runs under nitrogen, limiting attention first to those with neat olefins. The fact that removal of the inhibitor oxygen leads to no change in product composition from isobutylene shows that the ionic process is still predominant for this branched olefin during dark chlorination under nitrogen; this conclusion is supported by the absence of attack on added cyclohexane. However, the nature of the products and the attack on cyclohexane show that the ionic pathway has been largely replaced by a radical one (without any attempt at initiation) for the other three butenes and allyl chloride. The butenes were the best grade materials available and were transferred to the reaction vessel by vaporization and condensation under nitrogen; no peroxides could be detected by the usual tests. For example with *trans*-2-butene, at least three changes from the inhibited runs occur: (1) the substitution product is a mixture of

not only terminal olefin I but also internal olefin II (free from its geometrical isomer VI), a compound bearing chlorine on a carbon atom which was saturated in the starting material; (2) the addition product is a mixture of diastereomers III and IV; and (3) the addition:substitution ratio has decreased from 50 to 4.5. The chain-propagating steps for such a radical pathway can be illustrated for *trans*-2-butene as shown.



The nature of the products gives structural information concerning radicals XXI and XXII. The minimum *meso:dl* ratio obtained from *trans*-2-butene was 3.2 in an illuminated run while the maximum ratio from the *cis* isomer was 1.7 in a similar run. First of all, the radical chlorine addition is obviously considerably less stereoselective than the ionic addition. Secondly, the failure to observe identical *meso:dl* ratios from the two olefins could be the result of (1) a certain fraction of residual stereospecific ionic reaction in all runs imposed on a completely nonstereospecific radical process,¹¹ or (2) a certain amount of stereoselectivity in the radical reaction. Only 15% of residual ionic reaction could explain the values cited above; therefore, although even this value seems high (*vide infra*), assignment of any stereoselectivity to this radical chlorine addition is rather tenuous. Even if one were tempted to postulate involvement of a bridged radical¹² such as XXIIc, it should be pointed out that chain transfer of radicals with chlorine molecule may be close to diffusion controlled¹³ and that significant product formation may occur before radicals XXIa and XXIb are completely equilibrated by rotation (this view would require that each radical prefer to attack chlorine molecule on the side *trans* to the added chlorine atom). Free-radical additions to the *cis*- and *trans*-2-butenes have been observed to be stereospecific for hydrogen bromide^{14a} but completely nonstereospecific for methyl mercaptan,^{14b} benzene-sulfonyl iodide,^{14c} and bromotrichloromethane.^{14d}

(11) The *meso:dl* ratio for the 2,3-dichlorobutane derived from photochlorination of 2-chlorobutane in the gas phase was 2.5 at 35°: P. S. Fredricks and J. M. Tedder, *Proc. Chem. Soc.*, 9 (1959); this value is probably a close approximation to the *meso:dl* ratio to be expected from a radical XXI which had lost all "memory" of its source of production.

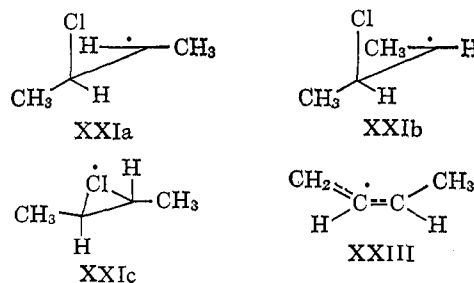
(12) See P. S. Skell, D. L. Tuleen, and P. D. Read, *J. Am. Chem. Soc.*, 85, 2849 (1963), and W. Thaler, *ibid.*, 85, 2607 (1963), for discussions of bridging in β -halo radicals.

(13) E_a for reaction of 2-chloroethyl radical with chlorine has been estimated at 0–1 kcal./mole: P. B. Ayscough, A. J. Cocker, F. S. Dainton, and S. Hirst, *Trans. Faraday Soc.*, 58, 318 (1962).

(14) (a) P. S. Skell and R. G. Allen, *J. Am. Chem. Soc.*, 81, 5383 (1959); (b) P. S. Skell and R. G. Allen, *ibid.*, 82, 1511 (1960); (c) P. S. Skell and J. H. McNamara, *ibid.*, 79, 85 (1957); (d) P. S. Skell and R. C. Woodworth, *ibid.*, 77, 4638 (1955).

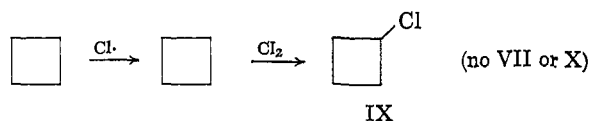
Since the substitution products from *trans*-2-butene are solely I and II (but not VI), radical XXII, derived by hydrogen abstraction, has retained its *trans* stereochemistry. In harmony with this result, *cis*-2-butene gave I and VI but not II as expected for radical XXIII. From 1-butene, both II and VI are formed since both radicals XXII and XXIII can be generated by hydrogen abstraction from the mixture of conformations of the

starting olefin. The ratio (II + VI)/I from 1-butene lies between the ratio II/I from *trans*-2-butene and VI/I from *cis*-2-butene as expected. The ability of allylic radicals to maintain geometrical integrity under



mild conditions has been demonstrated by Walling and Thaler¹⁵ for analogous radical chlorination of the butenes with *t*-butyl hypochlorite.

The production of 4-chloro-1-butene (VII) from radical chlorination of 1-butene deserves comment since its precursor must be the allylcarbonyl radical (XXIV) or some modification thereof. The facile interconversion of allylcarbonyl, cyclopropylcarbonyl, and cyclobutyl derivatives in carbonium ion processes is well known, but this type of rearrangement is much less facile in radical reactions.¹⁶ Photochlorination of cyclobutane has been reported^{16a} (and confirmed in the present study) to produce only cyclobutyl chloride (IX); however, photochlorination of methylcyclopropane produces a mixture of cyclopropylcarbonyl

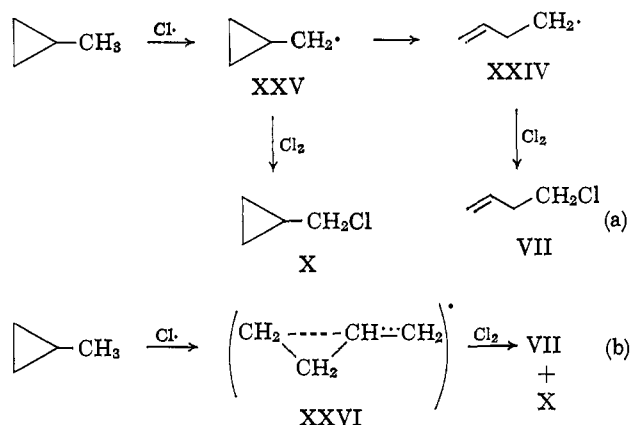


(X) and allylcarbonyl chlorides (VII) (as well as ring-substituted and ring-opened products).^{16a} Labeling

(15) C. Walling and W. Thaler, *ibid.*, 83, 3877 (1961).

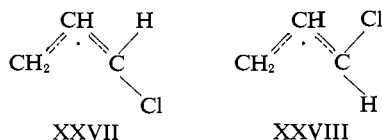
(16) (a) J. D. Roberts and R. H. Mazur, *ibid.*, 73, 2509 (1951); (b) E. Renk, P. R. Shafer, W. H. Graham, R. H. Mazur, and J. D. Roberts, *ibid.*, 83, 1987 (1961).

experiments^{16b} were consistent with either of two paths (a and b). Our recognition of 1-butene chlorination as



a source of the allylcarbinyl radical allows the third and final entry into this triad of intermediates generated in the presence of chlorine. The production of unrearranged VII free from X shows that photochlorination of 1-butene and methylcyclopropane do not involve the same set of intermediates; this fact, coupled with the failure to observe a rate enhancement^{17a} for abstraction of the "homoallylic" hydrogen atom of 1-butene (*vide infra*), shows no positive evidence for the existence of a nonclassical radical such as XXVI. The presently available evidence is explained by the postulate that ring opening of the cyclopropylcarbinyl radical XXV to the allylcarbinyl radical XXIV is rapid enough to compete with attack of XXV on chlorine molecule whereas the reverse ring closure reaction is orders of magnitude less rapid.

Radical chlorination of allyl chloride proceeds predominantly by addition to give XIV; the small amount of substitution must proceed through radicals XXVII and XXVIII. Chain transfer of each of these occurs



predominantly at the end away from the chloro substituent already present to produce products XV and XVI, respectively; dichloride XVIII is, at best, a very minor product.

Finally, the third set of experimental conditions to be considered are the runs under nitrogen with illumination (external initiation). For 1- and 2-butene, the changes from dark runs are rather minor as shown in Figures 1, 2, and 3; in each case a lower ratio of addition to substitution corresponds to a greater percentage of radical reaction. However, for isobutylene the change is more dramatic; it is possible to force addition to become the major reaction course. Our conclusion is that, for 1- and 2-butenes, illumination has increased by a small increment the percentage of radical reaction in a chlorination which was already largely

(17) (a) It should be noted that hydrogen abstraction by chlorine atom is an unfavorable probe for nonclassical rate enhancements since the major factor determining reactivity towards chlorine atom appears to be the electronic nature of the ground state rather than the stability of the resultant radical: G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4997 (1958); *Tetrahedron*, **8**, 101 (1960). (b) For a compilation of reactivities, see G. A. Russell, A. Ito, and D. G. Hendry, *J. Am. Chem. Soc.*, **85**, 2976 (1963).

radical in the dark whereas, for isobutylene, illumination has induced a considerable percentage of radical reaction into a chlorination which was ionic in the dark.

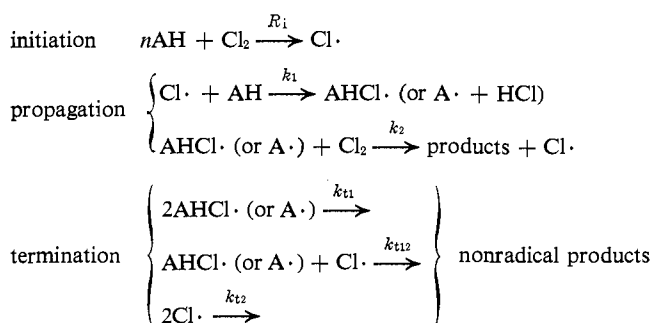
For chlorination of cyclohexene,^{1b} it was possible to determine the percentage of radical reaction at any olefin concentration, since there was a high-concentration region in which dark and illuminated reactions gave identical product distributions and hence we could be sure the solely radical reaction had been isolated. For the butenes this cannot be done with as great certainty because, at all concentrations, illumination gave minor changes in product composition characteristic of the reaction's being more nearly completely radical. However, we feel that the minima in the addition:substitution curves for illuminated runs (lower curves of Figures 1-3) represent very nearly the purely radical reaction. These values were no longer sensitive to small changes in light intensity caused by variations in the placement of lamps and reaction vessel and runs could be easily reproduced; however, the isobutylene results were quite sensitive to such changes and were not easily reproduced (see Table VIII), and the purely radical reaction has not been achieved for this olefin. On this basis, the percentages of radical reaction in the dark runs (upper curves of Figures 1-3) at a mole fraction of olefin of 0.5-0.6 can be estimated as 1-butene, ~85; *trans*-2-butene, ~70; and *cis*-2-butene, ~80%. For these dark runs the same rapid increase in ionic reaction at low olefin concentration occurs as observed previously for cyclohexene.^{1b} Note that as ionic reactions become progressively more important, addition:substitution increases and, for 2-butene, II/I and VI/I decrease as expected. For allyl chloride, the decrease in XVI/XV is diagnostic of increasing ionic reaction. The slight increases in addition:substitution ratios at very high mole fractions of olefin appear to be real but remain unexplained at the moment.

General Behavior of Olefins toward Chlorine. Results from chlorination studies of the 18 olefins considered so far (in more or less detail) are consistent with the following generalization. *Dark chlorination of any neat olefin, free from other functionality, in the absence of inhibitors, will lead to a significant fraction of radical reaction except for those olefins which bear two alkyl groups (or apparently one phenyl group)¹⁸ on at least one end of the double bond.*

In attempting to understand the reasons for this empirical generalization, we point out two comparisons. First, a comparison can be made among the linear olefins, 2-butene, 1-butene, and allyl chloride. From competitive studies under oxygen, the rate of ionic chlorination has been found to decrease at least 50-fold for each successive member of this series. Yet all three olefins show quite similar radical:ionic ratio vs. olefin concentration behavior; for example, at mole fraction of 0.50, chlorination of each olefin is largely radical but with a small ionic contribution. Evidently the over-all rates of the radical reaction must also lie in the order 2-butene > 1-butene > allyl chloride; hence, there seems to be a parallel response of both processes to structure within this series of olefins as the

(18) This is based on the chlorination of styrene which we find to be ionic under all conditions where no external initiation is supplied.

groups on the double bond become more and more electron withdrawing. In this connection, olefins with very electron-poor double bonds such as the polychloroethylenes are stable to chlorine in the dark¹⁹ and hence *both* the ionic and the radical-initiating reactions must have become very slow. Secondly, a comparison of *trans*-2-butene and isobutylene can be made. Under very similar conditions of absence of both external initiation and inhibition, chlorination of the former is largely radical and of the latter, ionic. Two alternatives are possible: (1) the ionic reaction is more rapid for the branched olefin which can give a tertiary carbonium ion by addition of an electrophile, or (2) the radical reaction is more rapid for the linear olefin. The first hypothesis can be shown to be false by the experimental observation that these two olefins have very similar ionic rates. Apparently then, the radical reaction must be more rapid for 2-butene than for isobutylene. Changes in rates of initiation, propagation, and/or termination could be responsible (AH represents the olefin).



In the extreme of entirely alkyl radical coupling, the rate law is of the form

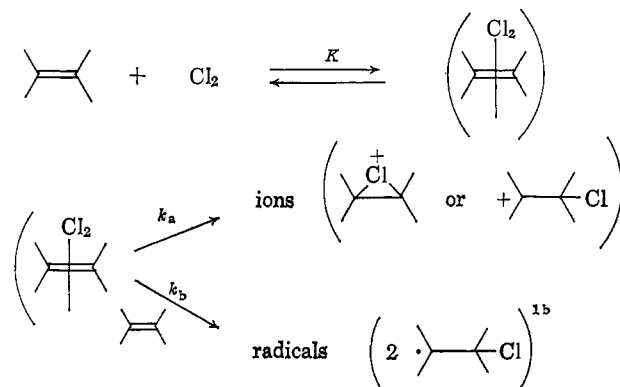
$$\text{rate} = \left(\frac{R_i}{2k_{t1}} \right)^{1/2} k_2(\text{Cl}_2)$$

where R_i is the rate of initiation. Since very similar radicals are involved from both olefins, large effects on k_2 and k_{t1} seem unlikely. In the other extreme of chlorine atom coupling, the rate law is of the form

$$\text{rate} = \left(\frac{R_i}{2k_{t2}} \right)^{1/2} k_1(\text{AH})$$

Here k_{t2} is invariant and differences in k_1 are small as shown in Table X. In either case then, the likely source of difference between the two olefins is in the initiation process which must be more rapid for 2-butene. This conclusion received experimental support from the observation that, in the absence of inhibitors, mixtures of isobutylene and 2-butene follow a largely radical course; 2-butene acts as an initiator for concurrently present isobutylene. Incidentally, this result eliminates the possibility that the lack of radical reaction for isobutylene alone is due to a small k_2 ; in that case, radicals derived from isobutylene would build up in the mixed olefin run and lead to overall inhibition. These two comparisons show that the ionic and radical pathways react to structure in a rather subtle fashion and seem to be interrelated. An attractive mechanistic possibility is the following.

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



Chlorine could form a complex with the olefin, similar in nature to that of halogens with aromatics,²⁰ which is an energy minimum; the complex could then either rearrange to ionic intermediates or react with more olefin to produce radicals. Such a scheme has certain merits: (1) it provides a two-step path for the radical initiation reaction which apparently must be at least a three-body reaction,^{1b} and (2) it involves a connection between the two pathways, both of which seem to be favored by electron-rich double bonds. However, any such scheme must be considered as tentative; confirmation will require a much better knowledge of the kinetic behavior. Unfortunately such information cannot be obtained by the experimental techniques used in the present study since the reactions appear too rapid to allow control of the chlorine concentration except by rapid-reaction techniques.

Relative Rates of Chlorine Atom Attack on Olefins.

A considerable amount of information is available concerning the relative rates of attack of chlorine atom on various types of hydrogen atoms in saturated and alkylaromatic hydrocarbons.^{17b} However, because of the complexities of mechanism revealed by the present study, similar values are not known for relative rates of abstraction of allylic hydrogen atoms and addition to double bonds. On the reasonable assumption that our illuminated chlorinations are almost entirely radical, such values can now be obtained for the butenes; the runs in cyclohexane (Tables V-IX) were carried out so that the relative rates could be related to a common standard, the abstraction of a cyclohexyl hydrogen atom. For *trans*-2-butene, the radical addition:abstraction product ratio ((III + IV)/(I + II)) was taken from Figure 1 as 2.3 and (II/I) from Table I as 3.6; these values give (III + IV)/(II) as 2.9 compared to a lowest value of 3.26 from the cyclohexane series. This may indicate that a small fraction of ionic reaction has occurred even in the illuminated cyclohexane runs or that there is a small medium effect. We will adopt the convention that k_a is the rate constant for addition of chlorine atom to an olefin as a whole and k_t is the rate constant for abstraction of a single hydrogen atom, each relative to $k_t = 1.00$ for cyclohexane. Then k_a for *trans*-2-butene can be determined from the expression $12(\text{III} + \text{IV})(\text{cyclohexane})_0/(\text{XIX})(\text{trans-2-butene})_0$ ²¹ as shown in Table V. Similarly, k_t for *trans*-2-butene is de-

(20) See, for example, N. Ogimachi, L. J. Andrews, and R. M. Keefer, *ibid.*, **77**, 4202 (1955).

(21) This is a legitimate approximation to an exact logarithmic expression since conversions were low enough that (cyclohexane)₀ and (trans-2-butene)₀ were essentially constant throughout a run.

terminated from $2(I + II)(\text{cyclohexane})_0/(\text{XIX})(\text{trans-2-butene})_0^{21}$; however, since I could not be measured directly, $2(II)(\text{cyclohexane})_0/(\text{XIX})(\text{trans-2-butene})_0$ was calculated and corrected by $(II)/(I) = 3.6$ to give k_t . Since no trends were apparent over a 4-fold change in $(\text{cyclohexane})_0/(\text{trans-2-butene})_0$, average values were used. In this fashion, we have calculated k_a for *trans*-2-butene as 11.4 and k_t as 0.69. These values predict $(III + IV)/(I + II)$ to be 2.7 compared with 2.3 observed in Figure 1; hence the values for k_a may be a little high as mentioned above. For *cis*-2-butene, we have taken $(VI)/(I) = 2.15$ from Table II; then $k_a = 12.0$ and $k_t = 0.60$ from Table VI; the calculated $(III + IV)/(I + VI)$ is 3.3 compared with 2.7 observed in Figure 2. For 1-butene, we have taken $(II + VI)/(I)$ as 2.85 and $(VII)/(I)$ as 1.80 from Table III; then $k_a = 11.7$, $k_t = 0.76$ for the 3-hydrogen, and $k_t = 0.23$ for the 4-hydrogen from Table VII; the calculated $(VIII)/(I + II + VI + VII)$ is 5.3 compared with 4.5 observed in Figure 3. Values are summarized in Table X.

Table X. Relative Reactivities of Hydrocarbons toward Chlorine Atom in the Liquid Phase

Substrate	Hydrogen abstraction		Relative reactivity ^b
	Temp., °C.	Position ^a	
Cyclohexane	40	2° cyclic	1.00 ^{c,d}
2,3-Dimethylbutane	40	1°	0.37 ^d
		3°	1.45 ^d
Toluene	40	1° benzylic	0.52 ^{d,e}
Ethylbenzene	40	2° benzylic	1.30 ^{d,e}
		1°	0.67 ^{d,e}
Cyclohexane	-9	2° cyclic	1.00 ^c
<i>trans</i> -2-Butene	-9	1° allylic	0.69
<i>cis</i> -2-Butene	-9	1° allylic	0.60
1-Butene	-9	2° allylic	0.76
		1° "homoallylic"	0.23
Isobutylene	-9	1° allylic	<1.1
Allyl chloride	-9	1° allylic, α to Cl	0.07
Cyclohexane	25	2° cyclic	1.00 ^c
Cyclohexene	25	2° cyclic allylic	1.20 ^f
		2° cyclic "homoallylic"	0.72 ^f
Substrate	Addition		Relative reactivity ^g
	Temp., °C.		
<i>trans</i> -2-Butene	-9		11.4
<i>cis</i> -2-Butene	-9		12.0
1-Butene	-9		11.7
Isobutylene	-9		<11.
Allyl chloride	-9		7.0
Cyclohexene	25		9.4 ^f
<i>trans</i> -1,2-Dichloroethylene	25		3.2 ^h
<i>cis</i> -1,2-Dichloroethylene	25		3.95 ^h
1,1-Dichloroethylene	25		3.7 ^h
Trichloroethylene	25		2.3 ^h
Tetrachloroethylene	25		~1.0 ^h

^a 1° = primary, 2° = secondary, 3° = tertiary. ^b Per hydrogen relative to abstraction of a single cyclohexyl hydrogen at the stated temperature. ^c Assigned at each temperature as 1.00. ^d From ref. 17b. ^e Extrapolated to dilute aromatic hydrocarbon. ^f From ref. 1b. ^g Per molecule (double bond) relative to abstraction of a single cyclohexyl hydrogen at the stated temperature. ^h From ref. 19.

It was noted²² some years ago that the presence of an α -phenyl group rather than an α -methylene group led to

(22) G. A. Russell and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 4578 (1955).

an enhanced rate of hydrogen abstraction for most radicals but not for chlorine atom; for example, whereas toluene is some 250 times as reactive as cyclohexane (per hydrogen atom) toward bromine atom at 80°,²² some 20 times as reactive toward polystyryl radical at 60°,²³ and some 2.5 times as reactive toward methyl radical at 182°,²⁴ it was only one-third as reactive toward chlorine atom at 80°. Two factors which influence the reactivity of a C-H bond toward an attacking radical are: (1) stabilization of the resulting radical, e.g., by benzylic resonance in toluene, and (2) electron density in the bond being attacked, most radicals being electrophilic with respect to carbon.¹⁷ The lower the activation energy for radical attack, the lesser will be the degree of bond breaking in the transition state and hence the lesser the contribution of factor 1 compared to factor 2. Chlorine atom reactions proceed with very low activation energies and thus relative reactivities are determined largely by factor 2. In a transition state closely resembling starting materials, a phenyl group will behave inductively in an electron-withdrawing capacity and thus decrease reactivity towards chlorine atom. Examination of Table X shows that an α -vinyl group (similar to an α -phenyl group) gives little rate enhancement towards hydrogen abstraction by chlorine atom. The primary allylic hydrogens in 2-butene are only slightly more reactive than normal primary hydrogens and less reactive than normal secondary hydrogens. The only really pronounced effect is the deactivating influence of an α -chloro substituent in allyl chloride; this effect is well known from photochlorination of alkyl halides.²⁵ The major impression one receives from the relative abstraction reactivities is the very small spread between the quite different types of hydrogen considered, a result which illustrates the very indiscriminate nature of the chlorine atom. For example, towards the *t*-butoxy radical, generally considered to be a rather indiscriminate radical itself, the relative rates of abstraction at 40° of primary paraffinic, primary benzylic, primary allylic (p,s), tertiary paraffinic, secondary allylic (s,p), and cyclic allylic (cyclohexene) hydrogen atoms are 1:10:20:44:61:375¹⁵; the same sequence for chlorine atom at -9-25° is 1.0:1.4:1.75:3.9:2.0:3.2.

Considering the relative addition rates, one again notes a very small spread among the various alkylated ethylenes. Earlier¹⁹ we found that the relative rates of chlorine atom addition to a series of polychloroethylenes seemed more subject to retardation by added chloro substituents at the end of the double bond where the majority of the addition was occurring than to acceleration by added radical-stabilizing chloro substituents at the end of the double bond where the radical would ultimately reside; it was not clear if this retardation was chiefly steric or polar in origin. Unfortunately, a similar complete series for the alkyl-ethylenes (a series which would shed light on this problem) cannot be studied because the radical reaction cannot be isolated from the ionic reaction for

(23) R. A. Gregg and F. R. Mayo, *Discussions Faraday Soc.*, **2**, 328 (1947).

(24) E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1954, p. 500.

(25) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 361.

isobutylene, trimethylethylene,⁹ and tetramethylethylene.⁹ We can see, however, that the upper limit for k_a for isobutylene is already less than k_a for 1-butene; this implies that a significant portion of addition is occurring at the nonterminal end of 1-butene and that the effect of the added alkyl group in isobutylene has been more to decrease the nonterminal component of the addition rather than to increase the terminal component. There is a definite enhancement in k_a for the set of alkylethylenes compared to the set of chloroethylenes with k_a for allyl chloride intermediate in value. Such behavior appears reasonable for attack of the electron-seeking chlorine atom on a double bond.

Experimental

Infrared spectra were determined as 10% carbon disulfide solutions on a Beckman IR-5A instrument; n.m.r. spectra were determined as 20% carbon tetrachloride solutions (internal tetramethylsilane) on a Varian A-60 instrument; boiling points are uncorrected.

Materials. Cyclohexane, 1,1,2-trichlorotrifluoroethane, nitrogen, oxygen, and chlorine were treated as described previously.^{1b} All butenes used for quantitative studies were Phillips research grade: isobutylene (99.84%), *trans*-2-butene (99.81%), *cis*-2-butene (99.89%), and 1-butene (99.82%); C.P. grade olefins (99.0–99.5%) were used for preparative runs. Allyl chloride was distilled through a 3-ft. spinning-band column and a center cut was used. All other olefins used in the qualitative survey were commercial materials distilled before use. Cyclobutane was prepared by alcoholysis of the Grignard reagent derived from cyclobutyl bromide, obtained by brominative decarboxylation of the silver salt of cyclobutane carboxylic acid.²⁶ Methylcyclopropane was prepared by treatment of 1,3-dibromobutane with zinc dust in ethanol and purified by exact analogy to the preparation of cyclopropane by Weston.²⁷

Product Identification. Each butene and allyl chloride was chlorinated, in turn, under oxygen in the dark and under nitrogen with illumination. Each significant product (I–IV, VI–VIII, and XI–XIV) was isolated by distillation and/or preparative g.l.c., except for XV and XVI, and was shown to have the assigned structure by comparison to authentic samples and/or to literature properties as shown below. *3-Chloro-1-butene* (I) was collected by preparative g.l.c. (>96% pure by g.l.c.) from a fraction, b.p. 57–67°, from chlorination of *cis*-2-butene under nitrogen with illumination and had n^{24D} 1.4134 (lit.²⁸ n^{20D} 1.4151). The infrared spectrum was essentially identical with that of a sample prepared from *trans*-2-butene in analogous fashion; the g.l.c. retention time was identical with that of commercial material (Columbia Organic Chemicals), although the latter was contaminated with 1-chloro-2-butene as shown by g.l.c. and infrared. *1-Chloro-trans-2-butene* (II) was collected by preparative g.l.c. (96% pure by g.l.c.) from a fraction, b.p. 64–92°, from chlorination of *trans*-2-butene under nitrogen with illumination and had n^{24D} 1.4325 (lit.²⁹ n^{25D} 1.4327).

(26) J. Cason and R. L. Way, *J. Org. Chem.*, **14**, 33 (1949).

(27) R. E. Weston, Jr., *J. Chem. Phys.*, **26**, 975 (1957).

(28) W. G. Young and L. J. Andrews, *J. Am. Chem. Soc.*, **66**, 421 p. (1944).

(29) L. F. Hatch and S. S. Nesbitt, *ibid.*, **72**, 727 (1950).

The infrared spectrum was consistent with that reported²⁹; the absence of absorption at 13.3 μ could be used to set an upper limit on the amount of *cis* material present as 1%. The g.l.c. retention time was identical with that of commercial material (Columbia Organic Chemicals), although the latter contained some *cis* isomer by infrared; II and VI were not separated by the g.l.c. column used. *meso*-2,3-Dichlorobutane (III) (>99% pure by g.l.c.) was prepared by chlorination of *trans*-2-butene under oxygen and distillation through an 18-in. spinning-band column, b.p. 112.5°, n^{24D} 1.4392 (lit.⁵ b.p. 113.1°, n^{25D} 1.4386). *dl*-2,3-Dichlorobutane (IV) (>96% pure by g.l.c.) was prepared in analogous fashion from *cis*-2-butene, b.p. 116.5°, n^{24D} 1.4413 (lit.⁵ b.p. 117.1°, n^{25D} 1.4409). Commercial 2,3-dichlorobutane (Columbia Organic Chemicals) gave two peaks in the g.l.c. spectrum of the same retention times as those of the *meso* and *dl* forms prepared above; the infrared spectrum of the commercial material contained all the bands expected for a mixture of *meso* and *dl* forms based on spectra of the individual isomers. *2-Chloro-2-butene* (V) (Columbia Organic Chemicals) showed mainly two peaks in the g.l.c. spectrum neither of which was present in any chlorination run of the 2-butenes. *1-Chloro-cis-2-butene* (VI) was collected by preparative g.l.c. (>98% pure by g.l.c.) from a fraction, b.p. 77–83°, from chlorination of *cis*-2-butene under nitrogen with illumination and had n^{24D} 1.4365 (lit.²⁹ n^{20D} 1.4390). The infrared spectrum was consistent with that reported²⁹; the lack of significant absorption at 10.4 μ could be used to set an upper limit on the amount of *trans* material present as 4%. *4-Chloro-1-butene* (VII) (>99% pure by g.l.c.) was prepared by the method of Roberts and Mazur^{16a} and had b.p. 75–75.5°, n^{23D} 1.4205 (lit.^{16a} b.p. 73–74°, n^{25D} 1.4191); the infrared spectrum was consistent with that reported.^{16a} *1,2-Dichlorobutane* (VIII), prepared from chlorination of 1-butene under oxygen, had the same g.l.c. retention time and infrared spectrum as commercial material (Columbia Organic Chemicals). A mixture of 8.4 g. of cyclopropylcarbinol (Columbia Organic Chemicals) and 5 drops of pyridine was treated at 0° with 13.9 g. of thionyl chloride dropwise; after addition, the mixture was heated under reflux for 15 min. Direct distillation gave 6.9 ml. of product, b.p. 82–85.5°, the g.l.c. spectrum of which showed three peaks. Collection of the first peak showed it to be identical with VII by infrared. Collection of the second gave material with n^{24D} 1.4338 (lit.^{16a} n^{25D} 1.4332) and an infrared spectrum consistent with that reported^{16a} for *cyclobutyl chloride* (IX). Collection of the third gave material with n^{24D} 1.4335 (lit.^{16a} n^{25D} 1.4328) and an infrared spectrum consistent with that reported^{16a} for *cyclopropylcarbinyl chloride* (X). The major product from chlorination of isobutylene under oxygen was collected by distillation; a center cut had b.p. 71°, n^{24D} 1.4252 (lit.³⁰ b.p. 71–72°, n^{20D} 1.4274), and an infrared spectrum consistent with that of commercial *3-chloro-2-methylpropene* (XI) (Matheson Coleman and Bell); the minor product was collected by preparative g.l.c. from the high-boiling residue and had n^{23D} 1.4343 (lit.³¹ n^{20D} 1.4370) and an infrared spectrum

(30) W. T. Smith, Jr., and J. T. Sellas, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963–1964, p. 702.

consistent with that of authentic *1,2-dichloro-2-methylpropane* (XII) b.p. 103–104°, n^{23}_D 1.4344, prepared by photochlorination of *t*-butyl chloride. *1-Chloro-2-methylpropene* (XIII) was prepared by isomerization of XI by the method of Burgin, Hearne, and Rust³² and had b.p. 68°, $n^{23.5}_D$ 1.4199 (lit.³² b.p. 68.1°, n^{20}_D 1.4221); its g.l.c. retention time was slightly shorter than that of XI and identical with that of a trace product of chlorination of isobutylene although the latter was never isolated. *1,2,3-Trichloropropane* (XIV), obtained from chlorination of allyl chloride followed by distillation, was identical with commercial material (Matheson Coleman and Bell). A commercial sample labeled “1,3-dichloropropene, high boiling” (Columbia Organic Chemicals) showed two major bands in the g.l.c. spectrum, each of which was collected by preparative g.l.c. and shown to be >99% pure by g.l.c. The first had $n^{23.5}_D$ 1.4676 (lit.³³ n^{25}_D 1.4652 for XV) and both the infrared and n.m.r. spectra were consistent with those reported^{34,35} for *cis*-1,3-dichloropropene (XV). The second had $n^{23.5}_D$ 1.4735 (lit.³³ n^{25}_D 1.4712 for XVI) and both the infrared and n.m.r. spectra were consistent with those reported^{34,35} for *trans*-1,3-dichloropropene (XVI). *3,3-Dichloropropene* (XVIII) was prepared by treatment of acrolein with phosphorus pentachloride³⁶ and had n^{23}_D 1.4478 and b.p. 83–84° (lit.³⁶ n^{20}_D 1.4510 and b.p. 83°). Commercial *2,3-dichloropropene* (XVII) (Matheson Coleman and Bell) had a retention time different

(31) J. M. Hersh and R. E. Nelson, *J. Am. Chem. Soc.*, **58**, 1631 (1936).

(32) J. Burgin, G. Hearne, and F. Rust, *Ind. Eng. Chem.*, **33**, 385 (1941).

(33) L. F. Hatch and R. H. Perry, Jr., *J. Am. Chem. Soc.*, **71**, 3262 (1949).

(34) W. C. Wolfe, H. M. Doukas, and J. S. Ard, *ibid.*, **76**, 627 (1954).

(35) F. S. Mortimer, *J. Mol. Spectry.*, **3**, 335 (1959).

(36) L. J. Andrews and R. E. Kepner, *J. Am. Chem. Soc.*, **70**, 3456 (1948).

from any of the chlorination products of allyl chloride.

Quantitative Chlorinations. The procedure was the same as described previously^{1b} except that the constant temperature bath was maintained at $-9 \pm 0.2^\circ$ and the reaction flask was fitted with a Dry Ice reflux condenser filled with Dry Ice. The butenes were introduced as gases and the amount used determined from volumetric calibration marks on the reaction flask; solvents were introduced by pipet. The g.l.c. analyses were performed with a Micro-Tek 2500R instrument equipped with 2-m. Perkin-Elmer “R” columns (polypropylene glycol) and a flame ionization detector. Injections were performed with a pressure-tight sampler (Micro-Tek Snap Sampler) for samples boiling below room temperature. Except for runs with allyl chloride, analyses were performed at 52°; the retention times in minutes at a helium flow rate of ca. 200 ml./min. were: I, 4; XIII, 5; XI, 6; VII, 6.25; IX, 8; II and VI, 8.5; X, 9.5; XII, 18; III, 21; IV, 24; and VIII, 28. For allyl chloride, analyses were performed at 92°; the retention times in minutes were: XVIII, 3.3; XVII, 5; XV, 5.7; XVI, 7.7; and XIV, 25. All areas were determined from the product of peak height and retention times. These areas were corrected to molar quantities by calibration factors determined from analysis of known mixtures; such factors were not determined for the minor substitution products from allyl chloride (XV and XVI); since the *cis-trans* pair II and VI could not be separated, the same calibration factor was assumed for each. The calibration factors were close to unity except for cases where compounds with different numbers of carbon atoms were compared. Results shown in Tables I–IX were obtained by this general procedure.

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The Stereochemistry of the Bicyclo[3.2.1]octane System. III.^{1,2} The Addition of Dihalocarbene to Bicyclic Olefins

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Reaction of dihalocarbene with norbornene, 1-methylnorbornene, 2-methylnorbornene, and bicyclo[2.2.2]octene-2 furnished derivatives of bicyclo[3.2.1]octene-2 and bicyclo[3.2.2]nonene-2, respectively. Their structures were substantiated by nuclear magnetic resonance (n.m.r.) spectroscopy.

(1) For part II see B. Waegell and C. W. Jefford, *Bull. soc. chim. France*, 844 (1964).

(2) Part of this work was presented at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964, p. 33C.

(3) Visiting Lecturer for the Summer Session, 1964, on leave from the Institute de Chimie, Strasbourg, France.

Introduction

We had reported earlier⁴ that the reaction of dihalocarbenes with norbornene afforded direct entry to the bicyclo[3.2.1]octene-2 system.^{5,6} Furthermore, we ex-

(4) C. W. Jefford, *Proc. Chem. Soc.*, 64 (1963).

(5) This fact has been subsequently corroborated by others: (a) L. Ghosez and P. Laroche, *ibid.*, 90 (1963); (b) W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963); (c) R. C. De Selms and C. M. Combs, *ibid.*, **28**, 2206 (1963); (d) E. Bergmann, *ibid.*, **28**, 2210 (1963).

(6) The course of addition of dihalocarbene to bicyclo[2.2.1]heptadiene is similar to the norbornene case: V. Franzen, *Rev. Chim. (Bucharest)*, **7**, 859 (1962). See also ref. 5b.