(14) P. Beronius, A.-M. Nilsson, and G. Wikander, *Acta Chem. Scand.*, **24**, 2826 (1970), have recently shown that the association constant for LiBr is some 14 times that of Bu_4NBr in acetone at 298.15 K, i.e. $K_a = 4680$ vs. 334. In this study a value of $K_a \simeq 1950$ for LiBr gives a racemization rate constant at 298.15 K of $5.9613 \pm 0.0008 \times 10^{-3}$ l./mol sec for the lowest three concentrations.

(15) A. R. Stein, *Tetrahedron Lett.*, 4145 (1974).
(16) E. Downer and J. Kenyon, *J. Chem. Soc.*, 1156 (1939).
(17) Ford and Pietsek (ref 8d) report $k = 5.8 \times 10^{-4}\ M^{-1}\ sec^{-1}$ at 347.8 K for the *n*-Bu_4NBr-catalyzed elimination with 1-phenylbromopropane in acetone, a reaction that would presumably be more facile than that of the ethane derivative in question.

Bimolecular Homolytic Substitution at Carbon. A Stereochemical Investigation[1]

Charles J. Upton*[2] and Joseph H. Incremona

Department of Chemistry, Duquesne University, Pittsburgh, Pennsylvania 15219

Received August 20, 1975

Photochlorination of 1,1-dichlorocyclopropane (**1**) at 0–5°C in carbon tetrachloride yields 1,1,1,3-tetrachloropropane (**2**) and 1,1,1,3,3-pentachloropropane (**3**) as major products, with lesser amounts of 1,1,1,2,3-pentachloropropane (**4**). Photobromination of **1** yields 1,3-dibromo-1,1-dichloropropane (**5**) as the only product. Both the chlorination and bromination were shown to be radical processes, accelerated by benzoyl peroxide and azobisisobutyronitrile and inhibited by benzoquinone or darkness. The stereochemistry of the ring opening of **1** was determined from a ^1H NMR analysis of the 1,1,1,3-tetrahalopropane-*2,3-d*$_2$ isomers produced upon photochlorination and photobromination of 1,1-dichloro-2,3-*trans*-dideuteriocyclopropane (**7**) and its cis isomer **8**. In each case, **7** yielded >96% erythro isomer, and **8** >96% threo isomer. The results clearly demonstrate that attack of both chlorine and bromine atoms on the cyclopropane ring, occurs with essentially complete inversion of configuration. The proposed mechanism involves ring opening via an SN2-like transition state; attack of the halogen atom is postulated to occur at a minor lobe of the C_1–C_2 hybrid orbital, with concomitant cleavage of the C_1–C_2 bond. Evidence favoring the proposed mechanism over one proceeding via a bridged intermediate or transition state is presented.

Bimolecular homolytic substitution (SH2) reactions represent one of the most common reaction pathways available to free radicals.[3] Examples of SH2 displacements at multivalent atoms are well documented, and have been recently reviewed.[4] Unfortunately, few studies have examined the particular case of an SH2 displacement at saturated carbon, leaving the mechanism and stereochemistry the subject of speculation.

Theoretical and experimental approaches to this problem[5–15] have not predicted a favored stereochemical path. A simple Hückel MO approach predicted that the reaction might have a low degree of stereospecificity.[6] Initial experimental attempts to detect an SH2 displacement on carbon by iodine atoms, by observing racemization of optically active *sec*-butyl iodide in either liquid or vapor phase, were unsuccessful.[7,8] Displacement occurred instead on iodine,[9,10] yielding the *sec*-butyl radical and molecular iodine which on recombination gave racemic products. A similar result has recently been reported for methyl iodide,[11] as well as for bromine exchange in bromotrichloromethane.[12] Several attempts to detect an intramolecular SH2 (SHi) reaction have also been unsuccessful,[13,14] although Kaplan[15] has proposed an SHi reaction to explain the formation of cyclopropane and cyclopentane from decomposition of 1,3-diiodopropane and 1,5-diiodopentane.

It has become increasingly apparent that the only unambiguous examples of SH2 displacements on carbon are radical induced cleavages of the strained carbon–carbon bonds of cyclopropanes. Examples of cyclopropane ring openings under free-radical chlorination,[16] bromination,[17] and iodination[18] are well known. Ring opening of perfluorocyclobutane by fluorine atoms has recently been reported.[19]

The stereochemistry of the radical induced cyclopropane ring opening would be of interest since both nucleophilic[20] and electrophilic[21] ring openings have been studied in some detail. Only a few studies, however, have examined the stereochemistry of the radical induced ring opening, and all have been subject to varying degrees of steric and electronic bias. Applequist and Searle demonstrated that radical attack with inversion is possible. Bromination of 9,10-dehydrodianthracene occurs with inversion at both centers.[22] Attack with retention, however, is sterically restricted. Chlorination of nortricyclene gives *exo,exo*-2,6-dichloronorborane,[23] presumed to arise by initial attack with inversion followed by exo chain transfer. Reaction of bromotrichloromethane with dibenzotricyclo[3.3.0.0^{2,8}]-3,6-octadiene occurs with inversion of configuration by the trichloromethyl radical.[24] More recently, Shea and Skell[25] have shown that photobromination of 2,4-dehydroadamantane occurs with inversion at one center and randomly at the other, yielding a mixture of (a,e)- and (e,e)-2,4-dibromoadamantane. In all of the above examples the cyclopropane ring is part of a structurally more complex polycyclic system, and thus may not be stereochemically indicative of a monocyclic system.

We have previously reported[1] the first example where the stereochemistry of the ring opening of a monocyclic cyclopropane was determined; reaction of chlorine atoms with 1,1-dichlorocyclopropane (**1**) proceeds with >96% inversion of configuration. Our complete results on the photochlorination and photobromination of **1** are presented herein. As our work in this area was being completed, Maynes and Applequist[26] described the ring opening of *cis*- and *trans*-1,2,3-trimethylcyclopropane upon photobromination, the only other monocyclic systems examined to date. Photobromination of the cis isomer gave equal amounts of (*S*)-*meso*- and *dl*-3-methyl-2,4-dibromopentane, while the trans isomer gave the (*R*)-meso, (*S*)-meso, and *dl* products. The results demonstrate that attack at one carbon occurs with inversion of configuration, while bromination at the second carbon occurs nonstereospecifically.

Somewhat more recently, several examples of SH2 displacements by inorganic radicals have been described.[27] Results in these studies appear to indicate that in alicyclic systems, attack with inversion may also be favored.

Results and Discussion

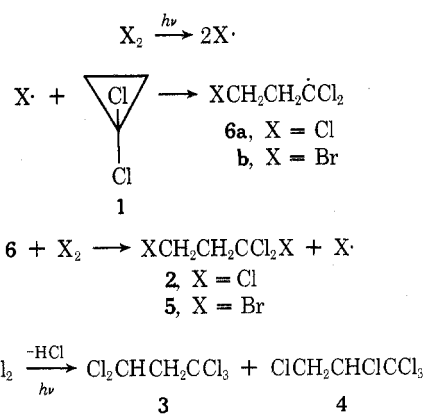
When a carbon tetrachloride solution, 3.14 *M* in 1 and 0.5 *M* in molecular chlorine, is irradiated at 0–5°, the chlorine color fades within 0.5 hr. Analysis by GLC indicated four products: 1,1,1,3-tetrachloropropane (**2**), 1,1,1,3,3-pentachloropropane (**3**), and 1,1,1,2,3-pentachloropropane (**4**), in addition to unreacted **1**, and a trace of what was believed to be 1,1,2-trichlorocyclopropane. The identities of **2–4** are based upon a comparison of their physical[16c,28] and spectral[29] properties with those reported, as well as by comparison to authentic samples. Both **2** and **3** were previously reported for the chlorination of **1** with sulfuryl chloride.[16c]

Yields of **2** and **3** determined by analytical GLC and ^{1}H NMR were 32–36 and 41–45%, respectively, based on chlorine consumed. That **3** and **4** arise from subsequent chlorination of initially formed **2** and not via ring opening of 1,1,2-trichlorocyclopropane is based on the report[16c] that chlorination of the latter yields 1,1,2,2-tetrachlorocyclopropane. Analogously chlorination of cyclopropyl chloride[16b] gives mostly **1**. In addition, photochlorination of **2** has been reported[30] to yield **3** and **4** in mole ratios of ca 7:1; and we have confirmed this report.

Photobromination of **1** also occurs smoothly. Irradiation of a 1.1 *M* solution of bromine in neat **1** at 35 ± 2° results in a total loss of bromine color within 1–2 hr. Analysis by GLC indicated three unidentified minor products (<5% total GLC peak areas) and one major product shown to be 1,3-dibromo-1,1-dichloropropane (**5**) by its physical and spectral properties and elemental analysis. The yield of **5** was as high as 94% as determined by analytical GLC, with no evidence (GLC or ^{1}H NMR) of more highly brominated products.

A radical chain mechanism that accounts for the observed products in each case is shown in Scheme I, and is analogous to those proposed previously for other cyclopropane halogenations.[16-18]

Scheme I

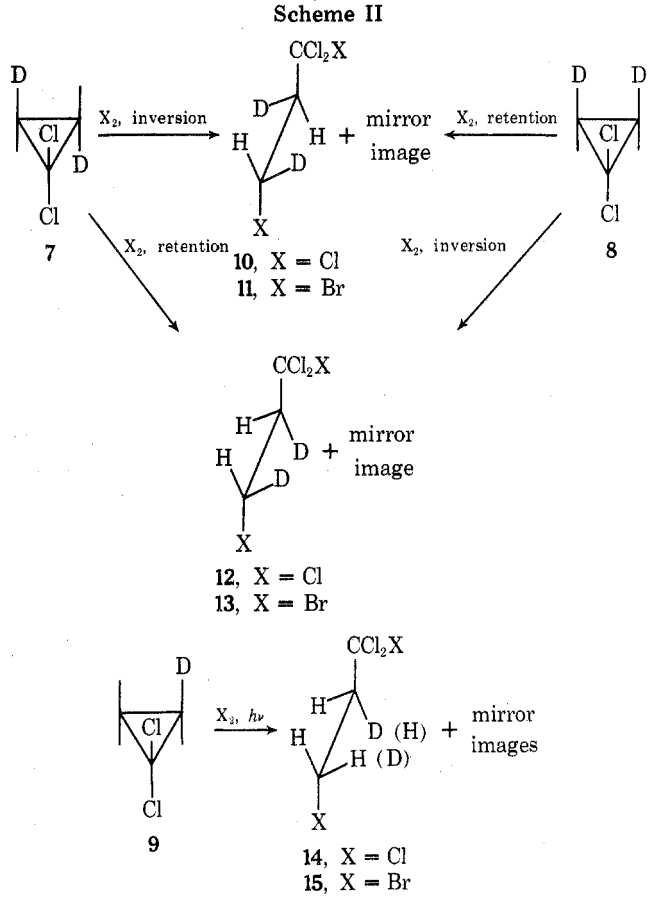


The known stability of **1** to ionic conditions[16c,31] strongly implied that the reactions with chlorine and bromine were radical in nature. This was conclusively proven by observing the relative amounts of products formed in the presence of known radical accelerators and inhibitors. Benzoyl peroxide and azobisisobutyronitrile (AIBN) were effective as accelerators, while benzoquinone, molecular oxygen, and darkness were examined for their inhibitory effects. The results of these studies are presented in Tables I and II.

Chlorination of **1** is markedly accelerated by peroxide or AIBN and is severely inhibited by quinone, oxygen, and darkness. Additionally a sample of **1** in carbon tetrachloride saturated with hydrogen chloride gave no evidence of reaction after 24 hr. Material balances are high indicating the absence of any appreciable side reactions. Similarly bromination of **1** is accelerated by peroxide and to a lesser degree by AIBN. The latter effect may be the result of increased cage recombination of AIBN in the more polar **1**.[32] The acceleration of photobrominations by molecular oxygen is well known,[33] although the nature of the effect is not well understood. Material balances are excellent, again indicating no appreciable side reactions.

In order to elucidate the stereochemistry of attack of both chlorine and bromine atoms on **1**, 1,1-dichloro-*trans*-2,3-dideuteriocyclopropane (**7**) and its cis isomer **8** as well as monodeuterated **9** were synthesized, photochlorinated, and photobrominated. The stereochemical possibilities are presented in Scheme II.

Scheme II



An effective synthetic approach to **7–9** would be addition of dichlorocarbene to (*E*)- and (*Z*)-ethylene-d_2 and ethylene-d_1, respectively. Although addition of dichlorocarbene to ethylene proceeds poorly,[34] two recent reports giving good yields have appeared.[35,36] The most promising route appeared to be that of Fields, Haszeldine, and Peters,[36] where pyrolysis of trichloromethyltrifluorosilane (**16**) at 140° in excess olefin gave excellent yields of the corresponding 1,1-dichlorocyclopropanes. Nearly complete ste-

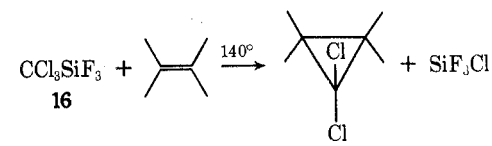


Table I
Effect of Added Modifiers on the Chlorination of 1,1-Dichlorocyclopropane (1) at 0–5°

Modifier added[a,b]	Light (±)	Time, min	% 2[c]	% 3[c]	% Cl_2 consumed[c]	Material balance of 1[c]
N_2	+	5	15.1	10.8[d]	25.9	93.9
N_2	+	10	31.0	44.3	75.3	93.5
N_2	+	30	32.6	47.7	80.3	97.1
N_2	−	1440	<1.5	<1.9	<1.5	98.1
O_2	+	10	2.2	<1.9	2.2	97.1
A	+	5	25.0	28.0	51.0	92.2
B	+	5	27.1	29.5	56.6	96.9
Q	+	5	4.7	<1.9	4.7	99.9
HCl	−	1440	<1.5	<1.9	<1.5	

[a] A = AIBN; B = benzoyl peroxide; Q = benzoquinone. [b] Modifiers A, B, and Q added 2–3 mol % based on chlorine. [c] All values are the average of at least two separate determinations. [d] A referee has pointed out that the change in 3/2 with the extent of chlorination is further evidence for formation of 3 and 4 from 2 (vide supra).

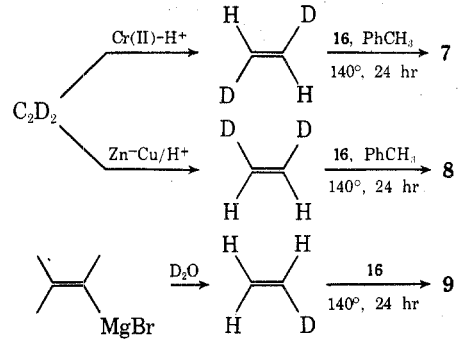
Table II
Effect of Added Modifiers on the Bromination of 1 at 35 ± 2°

Modifier added[a,b]	Light (±)	Time, hr	% 5[d]	Material balance of 1[d]
N_2	+	1	10.4	98.0
N_2	−[c]	22	2.8	93.4
O_2	+	1	82.7	96.0
O_2	−[c]	22	1.6	95.4
N_2	+	3	94.5	98.0
A	+	1	15.3	99.8
B	+	1	92.8	97.5
Q	+	1	5.2	100.4

[a] A = AIBN, B = benzoyl peroxide, Q = benzoquinone. [b] Modifiers A, B, and Q used at 2–3 mol % of bromine. [c] Reaction at 45°. [d] All values are the average of two separate determinations.

reospecific addition was observed for isomerizable olefins if 0.5–1.0 equiv of toluene was added to the reaction.[37] Reaction with ethylene gave 1 in 86% yield.

The appropriately deuterated ethylenes were prepared by previously described procedures[38] (see Experimental Section). The ir spectra of all acetylenes and ethylenes were in excellent agreement with those reported.[39,40] Pyrolysis of 16 in the presence of excess deuterated ethylene, and where necessary toluene, gave 7–9 in good yields. Although the reaction mixtures were frequently dark colored and contained some polymeric material, the only volatile products (GLC) were chloroform, 7–9, and, if added, toluene. Purification was accomplished by distillation and preparative GLC, yielding 7–9 as clear, colorless liquids, with GLC behavior identical with that of 1. The overall synthetic route is summarized below.



Stereospecificity of the carbene addition was assumed from previous work,[36,37] and qualitative confirmation achieved spectroscopically. Spectroscopic differences between 7 and 8 are more apparent in the Raman than in the infrared. The Raman spectrum of 7 exhibits a medium-intensity band at 835 cm^{-1}, a peak present, but extremely weak, in the spectrum of 8. Similarly 8 has a medium-intensity band at 865 cm^{-1}, present, but extremely weak, in the spectrum of 7. The relative peak intensities indicate ca. 5% stereoisomeric impurity in each case.[41]

Distinction between erythro tetrahalopropanes 10–11 and threo isomers 12–13 obtained on halogenation of 7 or 8 should be provided by their ^1H NMR coupling constants.[42] The ^1H NMR of 2 has been reported[29b] as an AA'BB' spin system with J_{AB} = 10.9 and J_{AB} = 4.8 Hz. Deuterium substitution for $H_{A'}$ and $H_{B'}$ should reduce the spectra of 10–13 to AB spin systems with similar couplings. The erythro isomers 10–11 would be expected to exhibit the larger coupling.

Chlorination of 7 and 8 was carried out in carbon tetrachloride similar to chlorination of 1 (see Experimental Section). The 1,1,1,3-tetrachloropropane-2,3-d_2 obtained from chlorination of 7 gave the 60-MHz ^1H NMR spectrum shown in Figure 1a. The AB pattern is clearly evident, $J_{AB} \simeq 11$ Hz, and clearly is predominantly the erythro isomer, 10. Similarly chlorination of 8 gave threo isomer 12, $J_{AB} \simeq 5$ Hz. The ^1H NMR of 12 (Figure 1b) collapses to two broad multiplets as a result of the smaller coupling. Also isolated from both 7 and 8 was 1,1,1,3,3-pentachloropropane (17), presumed to be a mixture of 2,3-d_2 and 2-d_1. Chlorination of 9 gave 14 and pentachloropropane 18. The ^1H NMR of 14 indicated no appreciable isotope effect introduced by the single CHD functionality.

$CCl_3CHDCHCl_2$ (D) 17 $CCl_3CH_2CHCl_2$ (HD) (D) 18

Bromination of 7–9 was carried out exactly as described for 1. Both products 11, 13, and 15 as well as unreacted 7–9 were collected by preparative GLC. A Raman spectrum of recovered 8 gave no evidence of any isomerization. The ^1H NMR spectra of the 1,3-dibromo-1,1-dichloropropane-2,3-d_2 products from 7 and 8 were strikingly similar to those of 10 and 12, clearly indicating predominant inversion of configuration by the bromine atom.

Vicinal and geminal hydrogen–deuterium coupling in the 60-MHz ^1H NMR spectra made accurate determination of J_{AB} impossible, and more importantly eliminated any quantitative estimation of the amount of stereoisomeric impurity (e.g., a retention pathway). Spectral clarification of 10–13 was achieved using a 250-MHz spectrometer and deuterium decoupling. The decoupling frequency was chosen to optimize both the A and B portions simultaneously. The decoupled spectra of both 10 and 12 are shown in Fig-

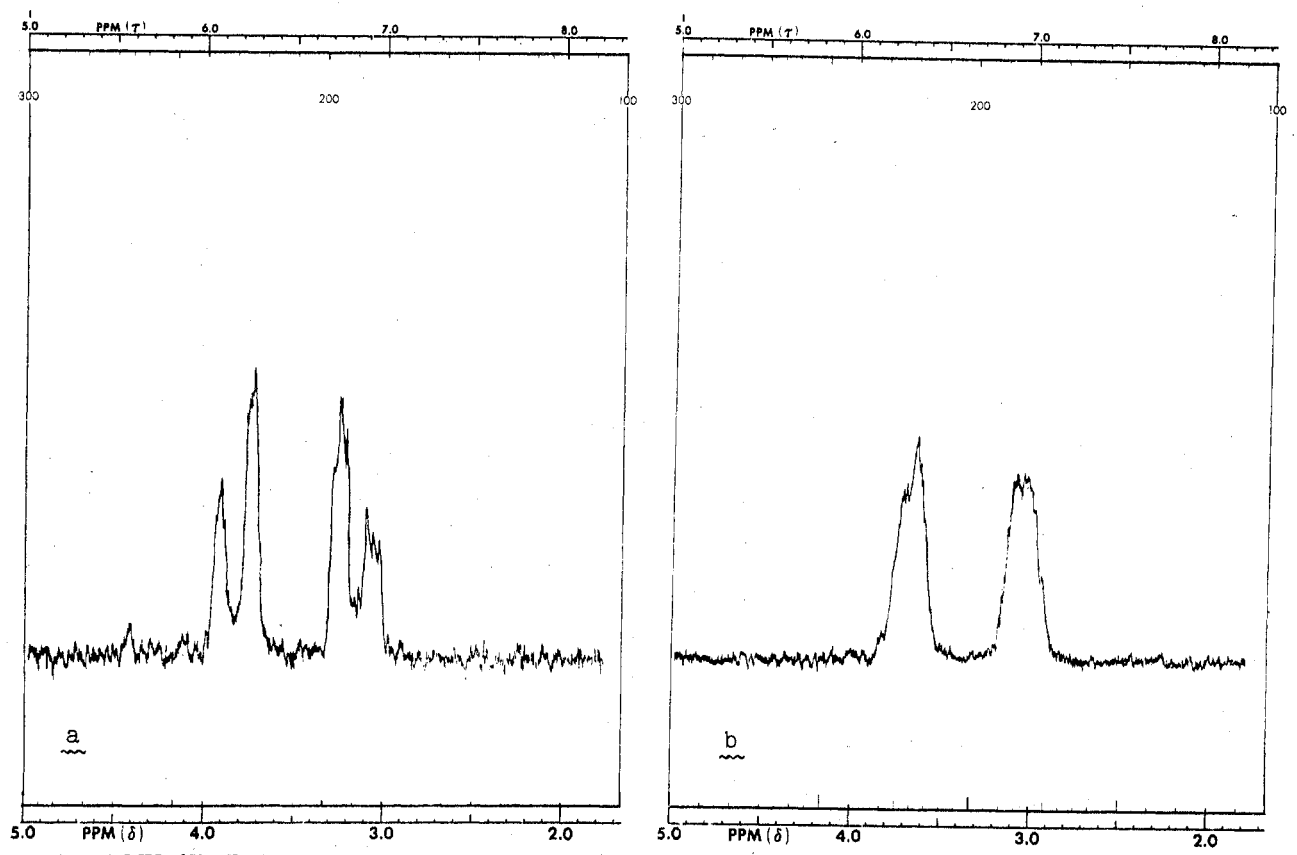


Figure 1. 60-MHz ^{1}H NMR spectra of (a) *erythro*-1,1,1,3-tetrachloropropane-*2,3-d*$_2$ (**10**); (b) *threo*-1,1,1,3-tetrachloropropane-*2,3-d*$_2$ (**12**).

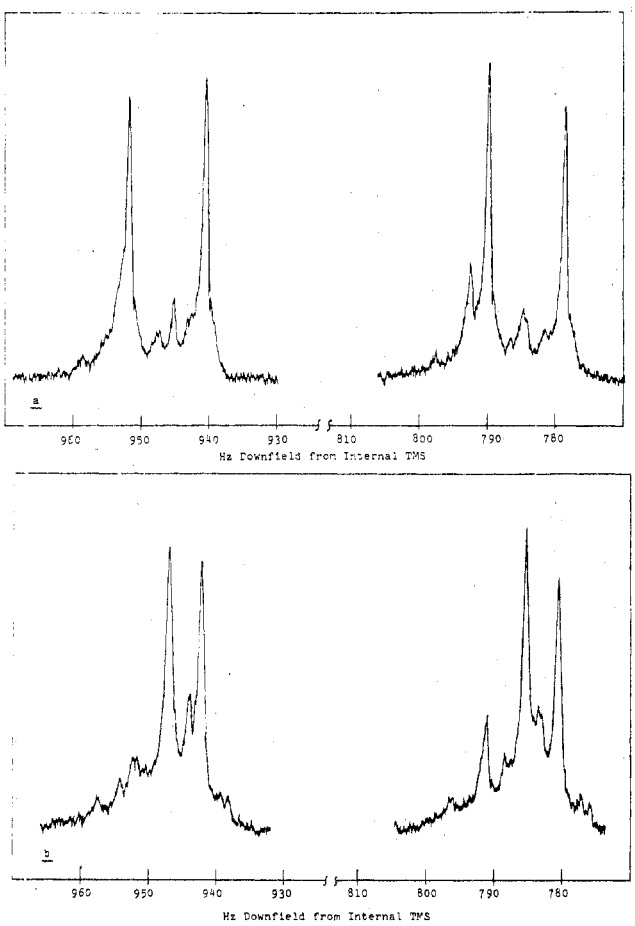
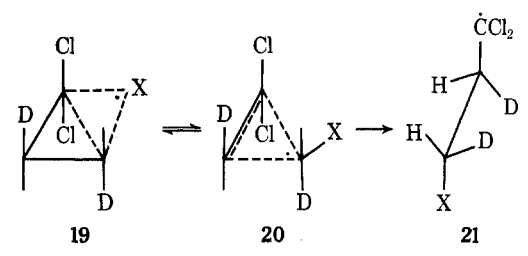


Figure 2. Deuterium-decoupled 250-MHz ^{1}H NMR spectra of (a) **10** and (b) **12.**

ure 2; isomer assignments, coupling constants (measured directly from the spectra), decoupling frequencies, and peak positions from internal Me_4Si are summarized in Table III.

The decoupled spectra of **10–13** are sufficiently distinct to observe traces of stereoisomeric impurity as well as monodeuterated **14** or **15.** Planimetry integration of each spectrum allowed calculation of the stereoisomeric ratios: **10/12,** and **12/10** for chlorination of **7–8** and **11/13** and **13/11** for bromination. These ratios were all found to be 0.96 ± 0.04, while the amount of **14** and **15** was 9.5 ± 2.0% in all cases. The observation of identical stereoisomeric ratios, within experimental error, for two radicals of considerably different energies, as well as the Raman evidence that **7** and **8** were not stereoisomerically pure, suggests that product stereoisomeric impurities arise by stereospecific reactions of **7** and **8** and not via a retention pathway.

Observation of essentially complete inversion by both chlorine and bromine atoms eliminates mechanisms resulting in retention of configuration. Thus formation of an edge-attached or corner-attached species, **19** and **20,** as intermediates or transition states does not occur to a detectable extent. Both would be expected to lead to ring-opened



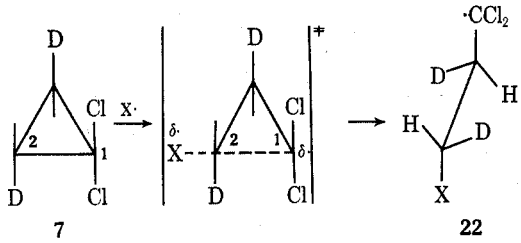
radical **21** resulting in retention of configuration, contrary to our experimental results.

Table III
^{1}H NMR Data (250 MHz) and Product Assignments for Chlorination and Bromination of 7–9

Reactant	Halogen	Product	J_{AB}, Hz	^{2}H decoupling frequency, Hz	Peak positions, Hz from internal Me_4Si	
7	Cl_2	10	11.2	38, 376, 652	940.5, 951.8	778.5, 789.7
8	Cl_2	12	4.7	38, 376, 650	942.2, 946.9	780.5, 785.3
9	Cl_2	14		38, 376, 650	938.6, 944.5	776.5, 783.9
					946.7, 952.4	791.7
					954.5	
7	Br_2	11	12.0	38, 376, 651	904.6, 892.6	820.4, 808.4
8	Br_2	13	4.6	38, 376, 650	901.3, 896.8	818.2, 813.6
9	Br_2	15		38, 376, 651	907.6, 905.7	806.7, 814.7
					904.4, 899.9	822.5
					896.7, 891.1	

Nonclassical radicals **19** and **20** would not be expected to lead to significantly increased radical stability.[43] Furthermore, neither leads to any significant release of ring strain, the obvious driving force of the reaction. Additionally **20** could suffer attack by halogen at C_3 resulting in formation of some 1,2,2,3-tetrahalopropane, none of which was detected in any experiment.

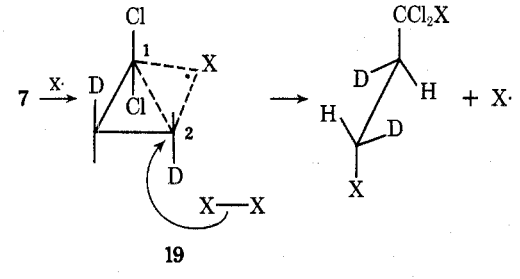
Inversion could occur via two pathways. The most likely in our opinion would be a one-step displacement process, proceeding via a transition state geometrically similar to that of an SN2 displacement. Attack of X· occurs at a minor lobe of the C_1–C_2 hybrid orbital, with concomitant cleavage of the C_1–C_2 bond. This would lead directly to ring-opened radical **22**, provides direct relief of ring strain,



7 22

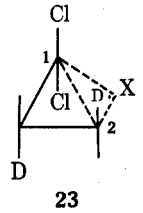
would not be expected to yield any 1,2,2,3-tetrahalopropane, and most importantly predicts the observed stereochemistry. Attack of halogen on **22** would be expected to occur nonstereospecifically.

A second mechanism also leading to inversion involves initial formation of edge-attached **19** which is then inverted at C_2 by halogen.



19

This latter mechanism appears unlikely, particularly based on the questionable existence of **19** (vide supra). If initial formation of **19** does occur, it would most likely exist as unsymmetrical **23**;[44] unpaired electron density in both



23

19 and **23** should be greatest at C_1. Reaction with halogen should be favored there, and lead to retention.

Nonetheless, attack by symmetrical reagents, chlorine and bromine, fails to distinguish between the partial or exclusive operation of either mechanism. A distinction could be effected, however, by reaction of **1** and, by analogy, **7–8**, with a generalized unsymmetrical addend AB. If B· serves as the chain carrier, then reaction of **1** by an SN2-like path (a) would give **24**, while a mechanism involving **19** or **23** (b) would yield **25**.

$ACCl_2CH_2CH_2B$ $BCCl_2CH_2CH_2A$

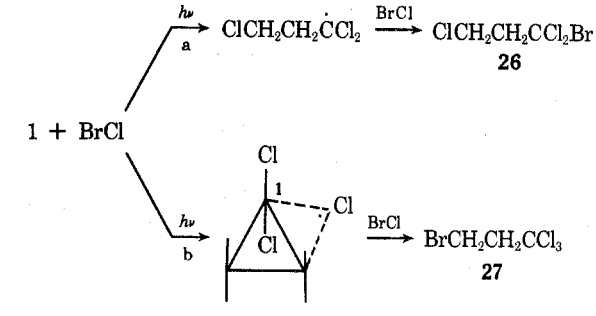
24 **25**

Reactions of **1** with bromotrichloromethane (A = Br, B = CCl_3) or trichloromethanesulfonyl chloride (A = Cl, B = CCl_3) under a variety of conditions (see Experimental Section) were unsuccessful. Formation of hexachloroethane in each case implied formation of the trichloromethyl radical, but no ring opening appears to occur.[45]

The use of bromine chloride to effect difficult brominations is well known,[33,46] and the mechanism is established to be initial hydrogen abstraction by chlorine atoms, followed by reaction of the generated radical with BrCl.

$$RH + Cl\cdot \xrightarrow{-HCl} R\cdot \xrightarrow{BrCl} RBr + Cl\cdot$$

The analogous reaction of **1** should yield 1-bromo-1,1,3-trichloropropane (**26**) via path a, or 3-bromo-1,1,1-trichloropropane (**27**) via path b.



Photolysis of a solution of **1**, bromine, and chlorine in mole ratios of 23.5:1:3 leads to a rapid reaction and formation of at least ten products (Experimental Section). The tetrahalopropanes isolated from the reaction were found to be **2**, **5**, and *only* **26**. An excess of chlorine served to divert bromine to BrCl, eliminating the possibility of bromine bridging (**19** or **23**, X = Br). Evidence supporting this conclusion is that **5**, while formed, possibly from **23**, more likely from **6b**, is formed as <1% of the total product peak areas in the GLC. There was no evidence by GLC for the presence of any **27** and 1% should have been detectable. We conclude, therefore, that attack of chlorine and bromine

atoms on 1 and 7–9 occurs with complete inversion of configuration, and that the mechanism of inversion does not involve a bridged radical species to any detectable degree. Our results appear to be in close agreement with those of Maynes and Applequist.[26]

Experimental Section

Melting points were taken on a Fisher-Johns apparatus and are corrected. Boiling points are uncorrected. Infrared spectra were recorded on a Beckman IR-20 spectrophotometer using 10% (v/v) solutions in carbon tetrachloride and carbon disulfide. Peak positions were calibrated with the 1601.8-cm^{-1} band of polystyrene. Vapor phase ir spectra were obtained with a standard 10-cm cell with sodium chloride windows. Laser Raman spectra were recorded using neat samples, on a Cary Model 81 spectrophotometer using a Spectra Physics Model Ar^+ laser at 4880 Å.

Proton magnetic resonance (^1H NMR) spectra were recorded on a Varian A-60 using 10% (v/v) solutions in carbon tetrachloride. Chemical shifts are reported in parts per million (δ) from internal tetramethylsilane. Spectra at 250 MHz and deuterium decoupling experiments were performed at the NMR Biomedical Facility, Carnegie Mellon University Pittsburgh, Pa.

Analytical and preparative GLC were performed using a Varian Aerograph A-90-P3 chromatograph. Columns all prepared on 60/80 mesh Chromosorb P as support were: A, 6 ft × 0.25 in. 20% SE-30; B, 12 ft × 0.25 in. 20% SE-30; C, 15 ft × 0.25 in. 10% Ucon 50-lb 550X; and D, 5 ft × 0.25 in. stainless steel, 20% SE-30.

Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany.

Antimony trifluoride (Alpha), methyltrichlorosilane (Dow Corning), and cyclopropane (National Cylinder Gas) were all used as received.

Carbon tetrachloride, THF, and bis(2-ethoxyethyl) ether (DEC) were distilled from and stored over calcium hydride. Commercial 1,1,1,3-tetrachloropropane (2) (Peninsular Chemresearch) and 1,1,1,3,3-pentachloropropane (3) (K and K Laboratories) were purified by preparative GLC using column B at 165 and 180°, respectively. Benzoyl peroxide[47a] and AIBN[47b] were purified by several recrystallizations.

1,1-Dichlorocyclopropane (1) was prepared by vapor phase chlorination of cyclopropane following the procedure described by Stevens.[16c] Purification by distillation and then preparative GLC on column A at 88° gave pure 1 with physical[16b,c] and spectral[48] properties identical with those reported.

Acetylene-d_2 and (*E*)- and (*Z*)-ethylene-d_2 were prepared following the general procedure described by Nicholas and Carroll.[38] The only modification: in the case of (*Z*)-ethylene-d_2, the partially reduced mixture was shaken for an additional 24 hr to effect complete reduction, not isolated and treated with fresh catalyst as described.[38] Any traces of unreduced acetylene-d_2 did not interfere in subsequent reactions. Ethylene-d_1 was prepared by addition of deuterium oxide to freshly prepared vinylmagnesium bromide.[49] Trichloromethyltrichlorosilane,[50] prepared by photochlorination of methyltrichlorosilane, was purified by short-path distillation.

Trichloromethyltrifluorosilane (16) was prepared by a modification of the procedure described by Meuller, Reichel, and Dathe.[51-53] Trichloromethyltrichlorosilane (0.25 mol) in xylene (50 ml) was added at −20° to an equimolar suspension of antimony trifluoride in xylene (50 ml) under a dry nitrogen atmosphere over a 2-hr period. After stirring at −20° for an additional 1 hr, a stream of dry nitrogen was used to sweep 16 into two dry ice–2-propanol traps as the mixture warmed over 2 hr to 25°. After 2 hr at 25° the mixture was warmed to 50° and maintained at 50° for 2 hr. The contents of both traps were combined and distilled through an 8-in. vacuum-jacketed Vigreux column into a dry ice cooled receiver, giving 16 in 75% yield, bp 44–45° (lit.[36,51] 43.5–45°). Purified 16 was stored in a tightly stoppered flask at −78° and was stable for at least 1 month. The liquid reacts vigorously with moist air and should be handled with considerable care.

Synthesis of Deuterated 1,1-Dichlorocyclopropanes 7–9. Reaction of deuterated ethylenes with 16 was carried out in a 3-l. flask, the top of which was sealed and two high-vacuum stopcocks fused into the neck. The ethylenes were dried by passage through a calcium sulfate drying tower and introduced into the reaction flask by vacuum transfer. Then 5.5–6.0 g (27–29 mmol) of 16 and toluene (1.0–1.2 g, 11–13 mmol), where necessary, were introduced by chilled syringe. The ratio of ethylene:16 is thus ca. 4.8:1 assuming ideality. The stopcocks were securely fastened and the flask heated at 140° for 22–24 hr, removed, and cooled to −20°. The liquid that condensed was drawn off and the flask washed with two 15-ml portions of DEC.

In the case of (*E*)- and (*Z*)-ethylene-d_2, the above procedure was repeated and the initially collected liquid and DEC washings were combined with those of the first run. Both the washings and crude liquid were then separately distilled, and material boiling to 100° collected. Isolation of 7 and 8 was then accomplished by preparative GLC of each distillate using column C at 110°. With ethylene-d_1 only the DEC washings were distilled, the distillate and initially isolated liquid then subjected to preparative GLC as described above to give 9.

From two runs with (*E*)-ethylene-d_2 using a total of 58 mmol of 16 and 26 mmol of toluene was obtained after preparative GLC 2.44 g (21.6 mmol, 37%) of 7: bp 75–76°; $d^{25}{}_4$ 1.235; $n^{25}D$ 1.4362; ir 1280, 1208, 1082, 970, 950, 920, 818, 700, 682, and 490 cm^{-1}; Raman 3060, 3020, 2285, 1208, 927, 872, 834, 490, and 272 cm^{-1}; ^1H NMR δ 1.43 ppm (s).

Similarly from (*Z*)-ethylene-d_2, 57 mmol of 16, and 27 mmol of toluene was obtained 2.33 g (20.6 mmol, 36%) of 8: bp 75–76°; $d^{25}{}_4$ 1.231; $n^{25}D$ 1.4358; ir 1288, 1210, 1122, 1090, 1072, 960, 950, 920, 815, 708, 682, and 492 cm^{-1}; Raman 3060, 3020, 2285, 865, 492, and 272 cm^{-1}; ^1H NMR δ 1.45 ppm (s).

Reaction of ethylene-d_1 and 16 (30 mmol) gave 1.4 g (13 mmol, 41%) of 9: bp 75–76°; $d^{25}{}_4$ 1.241; $n^{25}D$ 1.4382; ir 1432, 1320, 1220, 1120, 1090, 1052, 960, 952, 820, 705, 656, and 490 cm^{-1}; Raman 3062, 3020, 2285, 1222, 872, 496, and 272 cm^{-1}; ^1H NMR δ 1.44 (s).

Chlorination of 1. A solution of 1 (11.0 mmol) in carbon tetrachloride (1.5 ml) was added to 1.0 ml of chlorine-saturated carbon tetrachloride, 1.72 mmol of chlorine.[54] The solution was placed in a small ampoule, sealed, cooled to 0–5°, and irradiated with a 150-W GE "reflector spot" incandescent lamp placed 6 in. from the sample until colorless (10–35 min). Analysis of the reaction mixture by GLC using column A at 150° or B at 170° indicated four components in addition to unreacted 1. In order of increasing retention time these were shown to be a minor product, 2–3% of total product peak area, believed to be 1,1,2-trichlorocyclopropane, 2, 3, and 4. Yields of 2 and 3 varied from run to run, ranging between 32–36% 2 and 41–45% 3. Preparative GLC using column A at 150° gave pure 2 (18%), 3 (20%), and 4 (ca. 3%), identified by their physical[28] and spectral[29] properties and comparison to authentic samples.

Chlorination of 7–9. Owing to more limited quantities of 7–9, the following general procedure was employed. The dichlorocyclopropane (0.4 ml, 4.4 mmol) in 0.6 ml of carbon tetrachloride was treated with 0.6 ml of chlorine–carbon tetrachloride and chlorinated as described for 1. The reaction mixture was transferred to a small flask, carbon tetrachloride and unreacted 7–9 were carefully distilled off, and the mixture was then rechlorinated with 0.45 ml of chlorine solution. Redistilling, chlorinating a third time with 0.30 ml of chlorine solution (total chlorine 2.3 mmol), and redistilling left a high-boiling residue that was separated by preparative GLC on column A at 150°. Only 1,1,1,3-tetrachloropropanes 10, 12, and 14 and 1,1,1,3,3-pentachloropropanes 17 and 18 were collected.

Reaction of 7 as described yielded after preparative GLC 0.36 mmol (16%) of *erythro*-1,1,1,3-tetrachloropropane-2,3-d_2 (10): ir 1288, 1260, 1211, 1123, 1078, 1040, 950, 888, 800, 728, and 700 cm^{-1}; Raman 2960, 2225, 388, 242, and 227 cm^{-1}; ^1H NMR δ 2.98–3.32 (m, CCl_3–CHD) and 3.62–3.98 ppm (m, CHDCl). See Figure 1a.

Also isolated was 0.46 mmol (38%) of 1,1,1,3,3-pentachloropropane 17, its ^1H NMR indicating it to be a mixture of 2,3-d_2 and 2-d_1 isomers: ir 1257, 1211, 1108, 1027, 947, 930, 911, 899, 828, 790, 699, 654, and 562 cm^{-1}; Raman 2970, 2240, 705, 564, 388, 318, 277, 208, and 190 cm^{-1}; ^1H NMR δ 3.50–3.65 (m, CCl_3CH–) and 5.82–6.00 ppm (m, $CHCl_2$).

Chlorination of 8 was repeated a fourth time with 0.30 ml of chlorine solution (vide supra) to yield after preparative GLC 0.51 mmol (17%) of *threo*-1,1,1,3-tetrachloropropane-2,3-d_2 (12): ir 1315, 1285, 1092, 1012, 992, 940, 885, 800, 712, and 522 cm^{-1}; Raman 2995, 2960, 712, 558, 462, 388, 350, 242, and 224 cm^{-1}; ^1H NMR δ 2.88–3.23 (m, CCl_3CHD) and 3.53–3.88 ppm (m, CHDCl), see Figure 1b.

In addition 0.53 mmol (35%) of 17 was also isolated, and was identical in ir, Raman, and ^1H NMR with that obtained from 7.

Chlorination of 9 as described for 7 gave after preparative GLC 0.30 mmol (13%) of 1,1,1,3-tetrachloropropane-2- and -3-d_1 (14): ir 1455, 1435, 1312, 1292, 1263, 1215, 1081, 1050, 1031, 1015, 945, 900, 830, 800, 741, 712, 680, 660, 570, and 540 cm^{-1}; Raman 2980, 2945, 2225, 716, 572, 560, 390, 250, and 228 cm^{-1}; ^1H NMR δ 3.00–3.30 (m, CCl_3CHD) and 3.67–4.00 ppm (m, CHDCl).

In addition 0.45 mmol (36%) of 1,1,1,3,3-pentachloropropane **18** was isolated, presumed to be a mixture of *2*- and *3*-d_1 and d_0: ir 1418, 1218, 1090, 1022, 978, 935, 917, 900, 830, 792, 710, 660, and 565 cm^{-1}; Raman 2950, 2245, 830, 722, 708, 580, 566, 381, 318, 278, 208, and 190 cm^{-1}; ^1H NMR δ 3.47–3.40 (m, CCl_3CH) and 5.85–6.05 ppm (m, $CHCl_2$).

In all cases, the GLC behavior of 1,1,1,3-tetrachloropropanes **10, 12,** and **14** and 1,1,1,3,3-pentachloropropanes **17** and **18** was identical with that of their undeuterated analogues **2** and **3** on all columns tested.

Bromination of 1. When a solution of bromine (0.64 mmol) in **1** (6.0 mmol) was irradiated at 35°, the color faded within 1–2 hr. Analysis of the reaction mixture by GLC, column D, 170° (copper columns caused extensive decomposition) indicated three minor products totaling ca. 5% of total product peak areas and a major product shown to be **5.** Two of the minor components are likely due to thermal decomposition of **5** as purified samples of **6** also show two minor peaks and **5** on reinjection. Yields of **5** (GLC) were shown (Table II) to be as high as 94%. Preparative GLC of the reaction mixture gave **5** in 65% isolated yield, as a clear, colorless liquid with an odor similar to that of **2**: $n^{25}D$ 1.5422 (lit.[55] $n^{20}D$ 1.5450); ir 1217, 1153, 800, 785, 679, and 647 cm^{-1}; Raman 2985, 2940, 650, 579, 369, 339, 290, 228, and 169 cm^{-1}; ^1H NMR δ 3.00–3.33 (m, CCl_2BrCH_2) and 3.40–3.73 (m, CH_2Br).

Anal. Calcd for $C_3H_4Br_2Cl_2$: C, 13.29; H, 1.49; Br 59.03; Cl, 26.19. Found: C, 13.25; H, 1.39; Br, 58.97; Cl, 26.19.

Bromination of **7–9** was accomplished similarly using 5.5 mmol of cyclopropane and 0.58 mmol of bromine. Both unreacted **7–9** and products **11, 13,** and **15** were isolated by preparative GLC on column D at 170°.

Thus **7** gave 0.39 mmol (67%) of *erythro*-1,3-dibromo-1,1-dichloropropane-*2,3*-d_2 (**11**) after preparative GLC: ir 1283, 1180, 1028, 945, 850, 781, 742, 712, 690, and 630 cm^{-1}; Raman 632, 364, 338, 289, 275, 225, and 169 cm^{-1}; ^1H NMR δ 2.97–3.35 (m, CCl_2BrCHD) and 3.40–3.73 ppm (m, $CHDBr$).

Bromination of **8** followed by preparative GLC yielded 0.32 mol (55%) of *threo*-1,3-dibromo-1,1-dichloropropane-*2,3*-d_2 (**13**): ir 1200, 1085, 1008, 988, 940, 850, 782, 740, 708, 688, and 631 cm^{-1}; Raman 634, 364, 338, 290, 276, 225, and 168 cm^{-1}; ^1H NMR δ 3.07–3.38 (m, CCl_2BrCHD) and 3.40–3.68 ppm (m, $CHDBr$).

Finally, bromination of **9** gave 0.35 mmol (59%) of **15** as a mixture of *2*- and *3*-d_1 isomers: ir 1284, 1230, 1180, 1072, 1005, 937, 863, 805, 785, 740, 725, 710, and 632 cm^{-1}; Raman 2985, 632, 368, 339, 292, 228, and 169 cm^{-1}; ^1H NMR δ 3.00–3.38 (m, CCl_2BrCHD) and 3.41–3.70 ppm (m, $CHBr$).

Reaction of 1 with Bromine–Chlorine Mixtures. Photolysis of **1** (5.5 mmol) in a solution of bromine (0.23 mmol) in 0.40 ml of chlorine-saturated carbon tetrachloride (0.70 mmol of Cl_2) at 20° resulted in a complete loss of color within 20 min. Analysis of the reaction mixture by GLC on column D at 145° indicated at least ten components. In order of increasing retention time they were two trace products not identified but likely 1,1,2-trichloro- and 1,1-dichloro-2-bromocyclopropane; **2,** 1-bromo-1,1,3-trichloropropane (**26**), **3, 4, 5,** and three higher boiling components. Identification of **2–5** was initially confirmed by coinjection with authentic samples. After unreacted **1** and carbon tetrachloride were carefully distilled off, preparative GLC allowed spectroscopic (ir) verification. The three highest boiling components were not specifically identified but the ir and ^1H NMR of two of them strongly indicated that they were 1,1,1,3,3-pentahalopropanes. The other had ir very similar to that of **4** and is likely a 1,1,1,2,3-pentahalopropane.

The identity of **26,** isolated in ca. 20% yield, is based upon its ir, Raman, and ^1H NMR spectra and elemental analysis: $n^{20}D$ 1.5147; ir 1446, 1425, 1240, 1254, 1173, 1070, 1025, 970, 822, 795, 720, 703, 560, and 530 cm^{-1}; Raman 2979, 2943, 1434, 1068, 1025, 825, 799, 721, 677, 534, 376, 345, 303, 289, 232, and 211 cm^{-1}; ^1H NMR δ 2.92–3.27 (m, CCl_2BrCH_2) and 3.61–3.80 ppm (m, CH_2Cl). The refractive index of **27** is reported[56] to be $n^{20}D$ 1.5127.

Anal. Calcd for $C_3H_4BrCl_3$: C, 15.90, H, 1.76; Br, 35.30; Cl, 47.02. Found: C, 15.88; H, 1.67; Br, 35.16; Cl, 46.80.

Attempted Reactions of 1 with Trichloromethyl Radicals. A. Bromotrichloromethane. Heating a solution of **1** (5.5 mmol) and bromotrichloromethane (42 mmol) with 50 mg of benzoyl peroxide at 105° for either 2 or 8 hr yielded no products. Only starting materials and a trace of bromobenzene were observed (GLC, ^1H NMR).

In a second experiment, four solutions of **1** and bromotrichloromethane were prepared providing mole ratios of 1:bromotrichloromethane of 1:1, 1:1, 1:2, and 1:0.5. Benzoyl peroxide (50 mg) was added to the latter three solutions and all were irradiated at 95° for 22 hr, cooled, and analyzed by GLC, column D at 145°. The only observable products in samples with added peroxide were bromobenzene and hexachloroethane and in one case (1:2) a trace of **5.**[45] The sample without peroxide gave an extremely weak peak with retention time identical with that of **5.**[45]

B. Trichloromethanesulfonyl Chloride. A solution of **1** (6.6 mmol) and trichloromethanesulfonyl chloride (5.6 mmol) and 50 mg of benzoyl peroxide were heated at reflux for 8 hr. Analysis by GLC, column D, 145°, indicated only starting materials, chlorobenzene, and hexachloroethane. Extending the reaction time to 16 hr gave identical results.

Chlorination and Bromination of 1 in Presence of Added Modifiers. A solution of **1** (11.0 mmol) in carbon tetrachloride (1.5 ml) was added to a small flask and deoxygenated with nitrogen, bubbled into the solution via a small capillary. Then, in a darkened room, 1.0 ml of chlorine-saturated carbon tetrachloride (1.72 mmol) was added. Aliquots of 0.70 ml were then added to each of five nitrogen-flushed ampules. Three of the ampules contained preweighed quantities, 2–3 mol % based on chlorine, of benzoyl peroxide, AIBN, and benzoquinone. The other two ampules contained no additional modifiers. All the ampules were sealed and those with modifiers and one without were irradiated at 0–5° for 5 min. The remaining ampule was wrapped in aluminum foil and stored in the dark at 5° for 24 hr.

The effect of oxygen was ascertained by saturating the solution of **1** with oxygen prior to addition of chlorine. The ampule and one treated with nitrogen were then irradiated for 10 min, at which time the nitrogen-treated sample was colorless.

Product Analysis. Samples were analyzed for **2** and **3** by analytical GLC using column B at 170°. Millimoles of product formed in each sample was determined by comparison of peak areas (planimetry integration) with standard solutions of **2** and **3.** Control experiments established that peak area was linear with respect to concentration and injection size within 1.5%. The minimum extent of reaction was determined by diluting the standards until a 40-μl injection gave a small but repeatable peak at recorder attenuation 2. A yield of **2** of 1.5%, based on chlorine, could have been detected and 1.9% of **3.**

When the irradiation of a series of samples was completed, they were stored at 3° in a darkened room prior to analysis. Standard solutions were injected, then each ampule was opened in a darkened room and the contents washed into a 1.0-ml volumetric flask and diluted to the mark with carbon tetrachloride. The solution was mixed thoroughly and a 25-μl injection made. In cases of severe inhibition a 40-μl injection was also made. Millimoles of **2** and **3** in each sample were calculated from the relative peak areas and standard solution concentrations.

Unreacted **1** in each sample was determined by ^1H NMR using *p*-xylene as an internal standard. A carefully weighed amount of *p*-xylene (ca. 0.10 g) and 0.50 ml of the sample solutions prepared for GLC analysis were mixed thoroughly and the singlets of **1** and methyl groups of *p*-xylene were scanned and integrated a minimum of five times, and millimoles of **1** calculated. All of the above operations were conducted in a darkened room and there was no evidence of chlorination of the xylene.

B. Bromination. The overall procedure was virtually identical with that described for the chlorination, except that irradiation times were 1 hr at 35 ± 2°. In each run a solution of 2.3 mmol of bromine in 22 mmol of **1** was used.

The amount of **5** in each sample was also determined by analytical GLC using column D at 170°. Peak areas were compared to those of standard solutions of **5** in carbon tetrachloride. Control experiments again verified the linearity, within ±1.0%, of peak areas with sample concentrations and injection size. It was also shown that as little as 0.70% of **5** could have been detected.

Attempts to determine unreacted **1,** however, were complicated by rapid bromination of *p*-xylene by residual bromine, even in a darkened room. The following general procedure was thus employed. At the completion of the GLC analysis the solution was added to 1.0 ml of 1 *M* sodium bisulfite and shaken until colorless. The organic layer was withdrawn and dried over potassium carbonate. Then 0.20-ml aliquots of the above were added to *p*-xylene and the integrals recorded, and the amount of unreacted **1** calculated. This procedure was checked by preparing a solution of **1** and bromine as if no reaction had occurred. Work-up and analysis indicated 98% of **1** present, indicating no loss due to reaction with bisulfite and/or solubility.

For both chlorination and bromination studies, at least two separate and independent studies of added modifiers were made. The averages of these runs are presented in Tables I and II.

Acknowledgment. The authors are indebted to Dr. Joseph Dadok of Mellon Institute for help in performing the 250-MHz ^{1}H NMR and deuterium decoupling studies, and to Dr. William Fately and Mr. David Pensenstadler, both formerly of Mellon Institute, and Dr. John Freeman of Monsanto Physical Sciences Center for their help in obtaining the laser Raman spectra.

Registry No.—**1**, 2088-35-9; **5**, 53074-35-4; **7**, 57325-47-0; **8**, 35293-28-8; **9**, 57377-84-1; **10**, 57325-48-1; **11**, 57325-49-2; **12**, 57325-50-5; **13**, 57325-51-6; **14** isomer A, 57377-85-2; **14** isomer B, 57377-86-3; **15** isomer A, 57377-87-4; **15** isomer B, 57377-88-5; **16**, 17760-13-3; **17** isomer A, 57325-52-7; **17** isomer B, 57325-53-8; **18** isomer A, 42292-07-9; **18** isomer B, 23153-23-3; **26**, 57325-54-9; (*E*)-ethylene-d_2, 1517-53-9; (*Z*)-ethylene-d_2, 2813-62-9; ethylene-d_1, 2680-00-4; chlorine, 7782-50-5; bromine, 7726-95-6.

References and Notes

(1) For a preliminary report see J. H. Incremona and C. J. Upton, *J. Am. Chem. Soc.*, **92**, 301 (1972). Abstracted from the Ph.D. thesis of C.J.U., Duquesne University, 1973.
(2) Address correspondence to Detergent and Phosphates Division, Monsanto Co., St. Louis, Mo. 63166.
(3) W. A. Pryor, *Chem. Eng. News*, **49**, 34 (June 7, 1971).
(4) K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions", Wiley, New York, N.Y., 1971.
(5) (a) E. Gorin, W. Kauzman, J. Walter, and H. Erying, *J. Chem. Phys.*, **7**, 633 (1939); (b) A. F. Trotman-Dickenson, *Adv. Free-Radical Chem.*, **1**, 1 (1965).
(6) J. A. Berson, *Angew. Chem., Int. Ed. Engl.*, **1**, 779 (1968).
(7) R. A. Ogg and M. Polanyi, *Trans. Faraday Soc.*, **31**, 482 (1935).
(8) (a) R. A. Herrman and R. M. Noyes, *J. Am. Chem. Soc.*, **78**, 5764 (1956); (b) J. E. Bujake, M. W. T. Pratt, and R. M. Noyes, *ibid.*, **83**, 1547 (1961); (c) N. Nakashima and R. M. Noyes, *Int. J. Chem. Kinet.*, **1**, 391 (1969).
(9) (a) For an overall discussion of this reaction see W. A. Pryor, "Free Radicals", McGraw-Hill, New York, N.Y., 1966, pp 190–191. (B) Also M. L. Poutsma in "Free Radicals", J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, pp 142–143.
(10) Other pertinent references concerning atomic reactions of alkyl iodides include (a) J. H. Sullivan, *J. Phys. Chem.*, **65**, 722 (1961); (b) S. W. Benson and H. E. O'Neil, *J. Chem. Phys.*, **34**, 514 (1961); (c) S. W. Benson, *ibid.*, **38**, 1945 (1963).
(11) (a) A. J. Kassman and D. S. Martin Jr., *J. Am. Chem. Soc.*, **91**, 6237 (1969); (b) D. Clark, H. D. Pritchard, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 2633 (1954).
(12) (a) N. Davidson and J. H. Sullivan, *J. Chem. Phys.*, **17**, 176 (1949); (b) J. H. Sullivan and N. Davidson, *ibid.*, **19**, 143 (1951).
(13) L. S. Slaugh, *J. Am. Chem. Soc.*, **83**, 2734 (1961).
(14) W. S. Trahanovsky and M. P. Doyle, *J. Org. Chem.*, **32**, 146 (1967).
(15) (a) L. S. Kaplan, *J. Am. Chem. Soc.*, **89**, 1753 (1967); (b) L. S. Kaplan and R. Drury, *ibid.*, **95**, 2213 (1973); (c) L. S. Kaplan, *J. Org. Chem.*, **32**, 4059 (1967). For alternative arguments see ref 4 and 9b.
(16) (a) G. Gustavson, *J. Prakt. Chem.*, **42**, 495 (1890); (b) J. D. Roberts and P. G. Dirstine, *J. Am. Chem. Soc.*, **67**, 1281 (1945); (c) P. G. Stevens, *ibid.*, **68**, 620 (1946); (d) C. Walling and P. S. Fredricks, *ibid.*, **84**, 3326 (1962); (e) A. J. Davidson and A. T. Bottini, *J. Org. Chem.*, **34**, 3642 (1969); (f) D. E. Applequist, G. P. Fanta, and B. Hendrickson, *J. Am. Chem. Soc.*, **82**, 2368 (1960).
(17) (a) R. A. Ogg and W. J. Priest, *J. Am. Chem. Soc.*, **60**, 217 (1938); (b) M. S. Kharasch, M. Z. Fineman, and F. R. Mayo, *ibid.*, **61**, 2139 (1939); (c) S. J. Cristol and R. T. LaLonde, *ibid.*, **80**, 4355 (1958); (d) R. T. LaLonde and A. D. Debboli, *J. Org. Chem.*, **37**, 1094 (1972).
(18) (a) R. A. Ogg and W. J. Priest, *J. Chem. Phys.*, **7**, 736 (1939); (b) *J. Am. Chem. Soc.*, **60**, 217 (1938).
(19) J. B. Levy and R. C. Kennedy, *J. Am. Chem. Soc.*, **96**, 4791 (1974).
(20) (a) J. Meinwald and J. K. Crandall, *J. Am. Chem. Soc.*, **88**, 1292 (1966); (b) S. J. Cristol, J. K. Harrington, and M. S. Singer, *ibid.*, **88**, 1529 (1966).
(21) (a) S. J. Cristol, W. Y. Lim, and A. R. Dahl, *J. Am. Chem. Soc.*, **92**, 4013 (1970), and references cited therein. (b) See also C. H. Depuy and R. H. McGirk, *ibid.*, **96**, 1121 (1974); C. H. Depuy, A. H. Andrist, and P. C. Funfschilling, *ibid.*, **96**, 948 (1974).
(22) D. E. Applequist and R. Searle, *J. Am. Chem. Soc.*, **86**, 1389 (1964).
(23) M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 4293 (1965).
(24) B. B. Jarvis, *J. Org. Chem.*, **35**, 924 (1970).
(25) (a) K. J. Shea and P. S. Skell, *J. Am. Chem. Soc.*, **95**, 6728 (1973). (b) See also A. C. Udding, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 1345 (1968).
(26) G. G. Maynes and D. E. Applequist, *J. Am. Chem. Soc.*, **95**, 856 (1973).
(27) (a) J. Z. Chrzastowski, C. J. Cooksey, M. D. Johnson, B. L. Lockman and P. N. Steggles, *J. Am. Chem. Soc.*, **97**, 932 (1975); (b) J. H. Espenson and T. D. Sellers, *ibid.*, **96**, 94 (1974); (c) J. H. Expenson and J. S. Shveima, *ibid.*, **95**, 4468 (1973).
(28) (a) M. S. Kharasch and E. V. Jensen, *J. Am. Chem. Soc.*, **69**, 1100 (1947); (b) M. Joyce, E. Hanford, and J. Harmon, *ibid.*, **70**, 2529 (1948); (c) H. G. Haring and G. Gerding, *Recl. Trav. Chim. Pays-Bas*, **74**, 841 (1955).
(29) (a) A. B. Dempster, K. Price and N. Sheppard, *Spectrochim. Acta, Part A*, **25**, 1381 (1969); (b) *ibid.*, **27**, 1563 (1971).
(30) Y. I. Rothstein and N. G. Sokolouskaya, *Zh. Org. Khim.*, **7**, 26 (1971); *J. Org. Chem. USSR (Engl. Transl.)*, **7**, 24 (1971).
(31) H. Hart and G. Levitt, *J. Org. Chem.*, **24**, 1261 (1959).
(32) See ref 9a, pp 129–133.
(33) (a)C. Walling, "Free Radicals in Solution", Wiley, New York, N.Y., 1957, pp 356–381; (b) M. S. Kharasch, P. C. White, and F. R. Mayo, *J. Org. Chem.*, **3**, 33 (1938).
(34) (a) W. Von E. Doering and W. A. Henderson, *J. Am. Chem. Soc.*, **80**, 5724 (1958); (b) G. C. Robinson, *Tetrahedron Lett.*, 1749 (1965); (c) W. Kirmse "Carbene Chemistry", Academic Press, New York, N.Y., 1964, pp 145–150.
(35) D. Seyferth, R. Minasz, A. J. H. Treiber, J. M. Burlitch, and S. R. Dowd, *J. Org. Chem.*, **28**, 1163 (1963).
(36) R. Fields, R. N. Haszeldine, and D. Peters, *J. Chem. Soc. C*, 167 (1969).
(37) A recent report indicates that toluene may not be necessary in preventing isomerization: J. M. Birchall, G. N. Gilmore, and R. N. Haszeldine, *J. Chem. Soc., Perkin Trans. 1*, 2530 (1975).
(38) P. P. Nicholas and R. T. Carroll, *J. Org. Chem.*, **33**, 2345 (1968).
(39) (a) G. Herzberg, "Infared and Raman Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1945, pp 288–293; (b) R. M. Talley and A. H. Neilson, *J. Chem. Phys.*, **22**, 2030 (1954); (c) H. C. Allen Jr., E. D. Tidwell, and E. K. Plyer, *J. Am. Chem. Soc.*, **78**, 3034 (1956).
(40) (a) W. J. Lehman, *J. Mol. Spectrosc.*, **7**, 1 (1961); (b) R. L. Arnett and B. L. Crawford, *J. Chem. Phys.*, **18**, 118 (1950).
(41) The lack of a significant infared spectral difference between **7**–**8** is in contrast to the 1,2-dideuterated cyclopropane isomers: E. W. Schlag and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **82**, 5996 (1960).
(42) F. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, N.Y., 1966, pp 132–141, and references cited therein.
(43) (a) C. Walling in "Molecular Rearrangements", P. DeMayo, Ed., Wiley-Interscience, New York, N.Y. 1963, pp 407–455; (b) J. C. Martin and J. W. Timberlake, *J. Am. Chem. Soc.*, **92**, 978 (1970), and references cited therein.
(44) (a) P. S. Skell and K. J. Shea in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, pp 809–849. (b) See also L. Kaplan, "Bridged Free Radicals", Marcel Dekker, New York, N.Y., 1972.
(45) Similar results have been reported for phenylcyclopropane; see R. T. LaLonde, P. B. Ferrara, and A. D. Debboll, *J. Org. Chem.*, **37**, 1094 (1972).
(46) J. L. Speier, *J. Am. Chem. Soc.*, **73**, 826 (1951).
(47) (a) K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1946); (b) G. S. Hammond, L. S. Mahony, and U. S. Nandi, *Ibid.*, **85**, 737 (1963).
(48) (a) V. Slabey, *J. Am. Chem. Soc.*, **74**, 4928 (1952); (b) J. M. Freeman and P. J. Robinson, *Can. J. Chem.*, **49**, 2533 (1971).
(49) D. Seyferth, *Org. Synth.* **39**, 10 (1959).
(50) P. A. DiGiorgio, L. H. Sommer, and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 3512 (1948).
(51) R. Mueller, S. Reichel, and C. Dathe, *Chem. Ber.*, 1673 (1964).
(52) We experienced no difficulty or inconsistency with this modified procedure. Other workers[37] have reported some difficulty with the published procedure[51] and have devised an alternate synthesis.
(53) This reagent is now commercially available from PCR Inc., Gainesville, Fla.
(54) W. F. Linke, "Solubilities of Inorganic and Metal Organic Compounds", Vol. I., American Chemical Society, Washington, D.C., 1958, p 786.
(55) Y. N. Kost and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR., Otd. Khim. Nauk.*, 1252 (1951); *Chem. Abstr.*, **56**, 1328 *i* (1963).
(56) M. S. Kharasch, O, Reinmuth, and W. H. Urry, *J. Am. Chem. Soc.*, **69**, 1105 (1947).