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Free-Radical Reactions of Diazomethane with Reactive Bromopolychloroalkanes

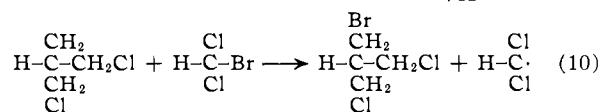
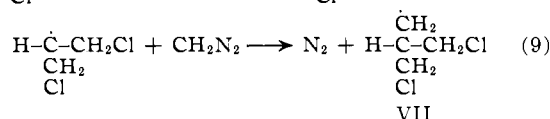
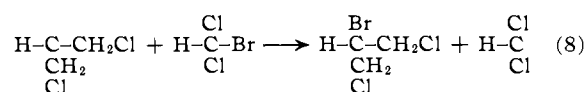
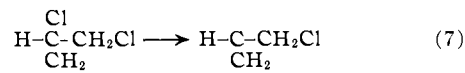
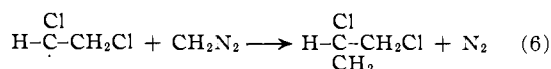
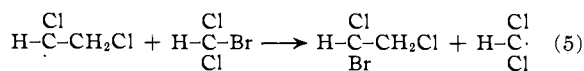
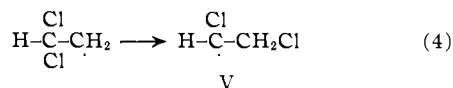
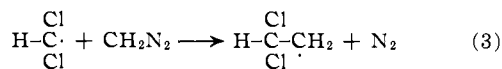
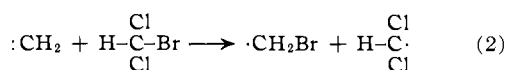
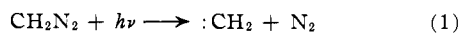
BY W. H. URRY AND NORMAN BILOW

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The reactions of diazomethane, introduced as the gas over extended periods (1.5–3 hr.), with bromopolychloromethanes (or 1-bromo-1,1-dichloroethanes) under irradiation give a series of products of successive interpositions of methylene—initially between chlorine and carbon, and finally between bromine and the same carbon. For these examples, the previously suggested free-radical chain mechanism must be modified to propose attack by intermediate radicals (only those produced by 1,2-shift of chlorine) upon either the bromochloroalkane or diazomethane. For example, with bromotrichloromethane, the products $\text{BrCl}_2\text{CCH}_2\text{Cl}$ (I), $\text{BrClC}(\text{CH}_2\text{Cl})_2$ (II), $\text{BrC}(\text{CH}_2\text{Cl})_3$ (III), and $\text{BrCH}_2\text{C}(\text{CH}_2\text{Cl})_3$ (IV) were obtained. High diazomethane concentration at low temperature gave the higher products (II, III, and IV) in preponderance, while with low diazomethane concentration at high temperature only the products I, II, and III were isolated.

The free radical reactions of diazomethane with polyhaloalkanes take various courses which depend upon: (1) the reactivity of the organic halide toward free radical attack, (2) the stability of intermediate free radicals, and (3) the reaction conditions. With unreactive halides, polymethylene is the dominant product (*cf.* 2-chloro-2-methylpropane¹); with halides of low reactivity (bromochloromethane), mixtures of products of the general formula $\text{ClCH}_2(\text{CH}_2)_x\text{Br}$ are formed; and with those of intermediate reactivity (*cf.* carbon tetrachloride¹), pentaerythrityl derivatives are obtained ($\text{CCl}_4 + 4\text{CH}_2\text{N}_2 \rightarrow 4\text{N}_2 + \text{C}(\text{CH}_2\text{Cl})_4$). The highly reactive polybromo- and polyiodomethanes give dibromo- or diiodomethane and related alkenes *via* β -elimination of bromine or iodine atoms from intermediate radicals ($\text{CBr}_4 + 2\text{CH}_2\text{N}_2 \rightarrow \text{CH}_2\text{Br}_2 + \text{Br}_2\text{C}=\text{CH}_2 + 2\text{N}_2$),² while the light-promoted reactions of halides of comparable reactivity reported here give products of attack of intermediate free radicals upon the polyhaloalkanes (Table I). Conditions (concentration of diazomethane and temperature) influence the relative yields of these products.

These recent results support the previously-postulated^{1,2} free radical, chain mechanism and emphasize the facility of the 1,2-shift of chlorine. It is most striking that the only intermediate products observed are those which result from attack upon the polyhalomethane by radicals produced *via* chlorine rearrangement (reactions 4 and 7 below). The postulated mechanism, modified to account for the formation of intermediate products in the reaction of diazomethane with bromodichloromethane, is



Chain initiation,³ by reactions 1 and 2 is suggested since these reactions may be induced by visible light which gives photochemical dissociation of diazomethane but does not so affect the polyhaloalkane. In our experiments in which a mercury resonance lamp (90% of radiation at 2537 Å.) was used, some initiation *via* photolysis of the bromopolychloroalkanes probably also occurred. The remaining reactions are chain propagating with the sequences of reactions 3 to 5 to give the 1:1 product; reactions 3, 4, 6, 7, and 8 to give the 2:1 product; and reactions 3, 4, 6, 7, 9, and 10 to give the 3:1 product.

Tentative conclusions with regard to chain termination reactions may be deduced from the observation that these reactions under the conditions investigated are of zero order in diazomethane.² This evidence suggests (argument below) that chain breaking involves interaction of two radicals of types V, VI, or VII ($\cdot\text{CHClCH}_2\text{Cl}$, $\text{ClCH}_2\dot{\text{C}}\text{HCH}_2\text{Cl}$, or $\cdot\text{CH}_2\text{CH}(\text{CH}_2\text{Cl})_2$, or their unrearranged precursors) by dimerization and/or disproportionation. The above reaction sequence resembles that of free radical olefin additions, a kinetic analysis of which has been made by Walling.⁴ He derived a complex kinetic equation by

(3) Presumably the bromoethyl radical reacts further to initiate another chain: (2a) $\cdot\text{CH}_2\text{Br} + \text{HCBBrCl}_2 \rightarrow \text{BrCH}_2\text{Br} + \text{H}\cdot\text{CCl}_2$. It is likely that methylene also reacts with the polyhaloalkane *via* typical carbene reactions (insertion reactions such as $\cdot\text{CH}_2 + \text{HCBBrCl}_2 \rightarrow \text{CH}_2\text{CBrCl}_2$ or HCCl_2CHCl) which give no radical products. This latter mechanism dominates in the photochemical reactions of methyl diazoacetate with polyhaloalkanes ($\text{BrCCl}_3 + \text{N}_2\text{CHCOOCH}_3 \rightarrow \text{BrCCl}_2\text{CHClCOOCH}_3 + \text{N}_2$; quantum yield, 0.9) although some products of free radical attack by the methoxycarbonyl carbene are also obtained ($\text{Br}_2\text{CHCOOCH}_3$, $\text{Cl}_3\text{CCOCH}_3$): N. Bilow, Ph.D. Thesis, University of Chicago, Chicago, Ill., 1956; J. W. Wilt, Ph.D. Thesis, University of Chicago, Chicago, Ill., 1954.

(4) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 243.

(1) W. H. Urry and J. R. Eiszner, *J. Am. Chem. Soc.*, **74**, 5822 (1952).(2) W. H. Urry, J. R. Eiszner, and J. W. Wilt, *ibid.*, **79**, 918 (1957).

TABLE I
 REACTIONS OF DIAZOMETHANE WITH BROMOPOLYCHLOROALKANES

Halide	Products				
	H	H	H	H	H
H CBrCl ₂	BrCCH ₂ Cl Cl 7%	ClCH ₂ CCH ₂ Cl Br 13%	ClCH ₂ CCH ₂ Cl Br 13%	ClCH ₂ CCH ₂ Cl CH ₂ Br 15%	
Cl BrCCH ₃ Cl	ClCH ₂ CCH ₃ Br 10%	ClCH ₂ CCH ₂ Cl CH ₃ 20%	ClCH ₂ CCH ₂ Cl CH ₂ Br 13%	ClCH ₂ CCH ₂ Cl CH ₂ Cl 18%	
Cl BrCCH ₂ Cl Cl	ClCH ₂ CCH ₂ Cl Br 7%	ClCH ₂ CCH ₂ Cl CH ₂ Cl 13%	ClCH ₂ CCH ₂ Cl Br 15%	ClCH ₂ CCH ₂ Cl CH ₂ Br 18%	
Cl BrCCl Cl	Cl BrCCH ₂ Cl Cl I 1%	Cl ClCH ₂ CCH ₂ Cl Br II 16%	Cl ClCH ₂ CCH ₂ Cl CH ₂ Cl III 15%	ClCH ₂ CCH ₂ Cl CH ₂ Cl IV 14%	ClCH ₂ CCH ₂ Cl CH ₂ Br V 0
At 5-15°: At 40-70°:	1% 13%	16% 26%	15% 18%	14% 0	

consideration of probable initiation, propagation, and three different chain termination reactions. However, if mutual interaction of two olefin-derived radicals is the dominant chain breaking reaction ($2M\cdot \rightarrow M-M$; conditions attained experimentally by using an excess of olefin), simpler kinetics result in which the reaction is first order in addend (here polyhalomethane) and of zero order in olefin. With a reagent as reactive as diazomethane toward free radical attack (see below) instead of olefin, such kinetics would be observed over a greater range in its concentration.⁵

With the application of this derivation to the reaction of diazomethane with bromodichloromethane, the kinetic equation becomes $d[CH_2N_2]/dt = k_d \cdot [BrCHCl_2](R_i/2k_t)^{1/2}$. Other assumptions implied are that the rate constants for the propagation reactions (k_d) are equal, that the rate of initiation (R_i) is constant, and that the rates of termination reactions may be represented by a single constant (k_t). This argument implies that under the conditions investigated the reaction is of first order in polyhalomethane, and that at lower diazomethane concentrations other kinetic orders would be observed.

The relative rates of reactions of the rearranged radical $H-C\dot{C}l(CH_2Cl)$ with polyhaloalkane (reaction 5) or with diazomethane (reaction 6) determine the relative yields of the 1:1 product and the higher homologs. A similar competition (reactions 8 vs. 9) decides the relative yields of the 2:1 and 3:1 products. The fact that all three products were obtained in comparable amounts indicates that these reaction rates were of the same order of magnitude under our experimental conditions. It is obvious, however, that the rate constants for the reactions of these radicals with diazomethane (6 and 9) must be much larger than those for their reaction with the polyhaloalkane (5 and 8) since the concentration of

diazomethane was very low—the polyhaloalkane in excess was used as reaction solvent.

In general, a low concentration of diazomethane would favor the formation of the lower products while higher concentrations of it would give a greater proportion of the higher homologs. Experiments with bromotrichloromethane demonstrate this effect. In previous work,¹ only the 4:1 product 2-bromomethyl-2-chloromethyl-1,3-dichloropropane was isolated (38% yield) when diazomethane (0.25 mole) in ether (500 ml.) was added rapidly to illuminated bromotrichloromethane (2.25 moles). These conditions involved relatively high diazomethane and low bromotrichloromethane concentrations. In the present work (see Table I), diazomethane in nitrogen was passed slowly (over 1.5 hr.) into irradiated bromotrichloromethane. When the reaction mixture was cooled (5-15°) and the low reaction rate permitted accumulation of a relatively high concentration of diazomethane, the higher products were preponderant. However, when the reaction temperature was allowed to rise (60-70°) so that the high reaction rate kept the diazomethane concentration low, the 1:1, 2:1, and 3:1, but none of the 4:1, products were isolated. Presumably such effects could also be observed in experiments in which the rate of introduction of diazomethane is the only variable.

1,2-Shift of chlorine has been postulated recently to explain the experimental results with other reactions ($HBr + H_2C=CHCl_3 \rightarrow BrCH_2CHClCHCl_2$; $BrCCl_3 + H_2C=CHCl_3 \rightarrow Cl_3CCH_2CHClCBrCl_2 + Cl_3CCH_2CH=CCl_2 + ClCH_2CHClCBrCl_2$ ⁶; $Br_2 + Cl_3CCH_2CH_3 \rightarrow Cl_3CCHBrCH_3 + BrCCl_2CHClCH_3 + BrCCl_2CHBrCH_3$).⁷ In the latter two reactions, it is suggested that intermediate radicals of this type ($Cl_3C\dot{C}HR$) also undergo β -elimination of chlorine at the higher temperatures used (80-110°). It is likely, therefore, that all of the polyhalomethanes that have

(5) Presumably, the situation is similar in the autoxidations of aldehydes and hydrocarbons where for the same reasons the reactions become independent of oxygen pressure above a relatively low limit in its concentration (interaction of $2ROO\cdot$ radicals becomes the dominant chain-breaking event); see ref. 4, p. 419.

(6) A. N. Nesmeyanov, *et al.*, *Doklady Akad. Nauk S.S.S.R.*, **78**, 717 (1951); **81**, 199 (1951); *Quart. Rev.*, (London), **10**, 344 (1956).

(7) N. Bilow, Ph.D. Thesis, University of Chicago, Chicago, Ill., 1956.

TABLE II

Product of zinc dehalogenation	Reaction product	Product of alkoxide dehydrohalogenation
	$\begin{array}{c} \text{H} \\ \\ \text{BrCCH}_2\text{Cl} \\ \\ \text{Cl} \end{array}$	$\begin{array}{c} \text{Br} \\ \\ \text{C}=\text{CH}_2 \\ \\ \text{Cl} \end{array}$
$\begin{array}{c} \text{ClCH}_2\text{C}=\text{CH}_2 \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{ClCH}_2\text{CCH}_2\text{Cl} \\ \\ \text{Br} \\ \\ \text{Cl} \end{array}$	$\begin{array}{c} \text{ClCH}_2\text{C}=\text{CH}_2 \\ \\ \text{Br} \\ \\ \text{Cl} \end{array}$
	$\begin{array}{c} \text{ClCH}_2\text{CCH}_3 \\ \\ \text{Br} \\ \\ \text{Br} \end{array}$	$\begin{array}{c} \text{Cl} \\ \\ \text{C}=\text{CCH}_3 \text{ (cis and trans)} \\ \\ \text{H} \\ \\ \text{Cl} \end{array}$
$\begin{array}{c} \text{CH}_2=\text{CCH}_2\text{Cl} \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{ClCH}_2\text{CCH}_2\text{Cl} \\ \\ \text{CH}_3 \\ \\ \text{Cl} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{C}=\text{CCH}_2\text{Cl} \\ \\ \text{CH}_3 \\ \\ \text{Cl} \end{array}$
	$\begin{array}{c} \text{ClCH}_2\text{CCH}_2\text{Cl} \\ \\ \text{Br} \\ \\ \text{Br} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{C}=\text{CH}_2\text{Cl} \\ \\ \text{H} \\ \\ \text{Cl} \end{array}$
	$\begin{array}{c} \text{ClCH}_2\text{CCH}_2\text{Cl} \\ \\ \text{CH}_2\text{Cl} \\ \\ \text{Cl} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{C}=\text{CH}_2\text{Cl} \\ \\ \text{CH}_2\text{Cl} \\ \\ \text{Cl} \end{array}$
	$\begin{array}{c} \text{BrCCH}_2\text{Cl} \\ \\ \text{Cl} \end{array}$	$\begin{array}{c} \text{Cl} \\ \\ \text{C}=\text{CHCl} \\ \\ \text{Cl} \end{array}$

been shown to react with diazomethane *via* intermediate 1,2-shift of chlorine at low temperatures (0–40°) would give products of the elimination reaction at higher temperatures ($\text{CCl}_4 + 2\text{CH}_2\text{N}_2 \rightarrow \text{Cl}_2\text{CH}_2 + \text{Cl}_2\text{C}=\text{CH}_2 + 2\text{N}_2$). Conversely, it is also possible that 1,2-shifts of bromine or iodine may be observed in photochemical reactions of polybromo- or polyiodoalkanes with diazomethane at temperatures much lower than those used in previous studies. This anticipation is suggested by the experiments of Skell⁸ with the chlorination of *t*-butyl bromide at -78° [$(\text{CH}_3)_3\text{CBr} + (\text{CH}_3)_3\text{COCl} \xrightarrow{h\nu} (\text{CH}_3)_2\text{CClCH}_2\text{Br} + (\text{CH}_3)_3\text{COH}$].

Extensive use was made of dehydrohalogenation reactions with sodium alkoxides and zinc dehalogenations as initial steps in the identifications of the bromopolychloroalkane products of these reactions (see Table II). Experience with these dehydrohalogenations with alkoxides suggest that the elimination always occurs in the expected manner. The hydrogen atom removed is the most acidic one—that attached to the carbon atom of the molecule that is substituted most thoroughly with haloalkyl groups and/or halogen atoms. Then, loss of bromine or chlorine on an adjacent carbon atom completes the elimination. If both bromine and chlorine are situated on carbon atoms adjacent to the one from which the proton is removed, dehydrobromination invariably occurs.

Experimental

Reagents.—The gaseous diazomethane used was prepared by a standard procedure. *N*-Methyl-*N*-nitrosourea was made⁹

(8) P. S. Skell, R. G. Allen, and N. D. Gilman, *J. Am. Chem. Soc.*, **83**, 504 (1961).

(9) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 461.

and stored (moist) in a refrigerator. A cold slurry of this nitrosomethylurea (120 g.) in water (63 ml.) was added to a solution of potassium hydroxide (150 g.) in water (125 ml.) which was stirred slowly and maintained at 0–5°. The diazomethane formed was swept by a slow stream of nitrogen into the reaction mixtures contained in a cylindrical vessel (250 ml.) which was illuminated internally by a coiled quartz mercury resonance lamp (quartz section 8 in. long). Exit gases passed through a condenser, a trap cooled to -80° or a sulfuric acid trap, and a Precision wet test meter.

The yield of diazomethane was determined by passing the product obtained as above into a solution of benzoic acid (48.19 g., 394 meq.) in ether (720 ml.). Analysis for unreacted benzoic acid (50.4 meq.) with standard sodium hydroxide solution (139.3 ml., 0.362 *N* required) indicated the yield of diazomethane (2.86 meq. per gram of moist nitrosomethylurea).

Commercially available polyhaloalkanes (Matheson Coleman and Bell) were distilled immediately before use: bromochloromethane (b.p. 68°, n_D^{20} 1.4839), bromodichloromethane (b.p. 91°, n_D^{20} 1.4978), bromotrichloromethane (b.p. 68° at 244 mm., n_D^{20} 1.4166), and 1,1,2-trichloroethane (b.p. 113–114°).

1-Bromo-1,1-dichloroethane (b.p. 98°, n_D^{20} 1.4822) and 1-bromo-1,1,2-trichloroethane were prepared by the bromination of 1,1-dichloroethane and 1,1,2-trichloroethane, respectively. For example, bromine (354 g., 2.0 moles) was added dropwise over 35 hr. to 1,1,2-trichloroethane (500 g., 3.74 moles) held under reflux with irradiation from a 150-w. spotlight. After 75 hr. the bromine was consumed, and the reaction temperature reached 115°. The cooled reaction mixture was washed with sodium bicarbonate solution (200 ml., 10%), sodium bisulfite solution (120 ml., 10%), and three times with water. Its distillation (dried CaCl_2) gave unreacted 1,1,2-trichloroethane and 1-bromo-1,1,2-trichloroethane (318 g., 69% yield, b.p. 152°, n_D^{20} 1.5217).¹⁰

The Reaction of Bromodichloromethane with Diazomethane.—Diazomethane (0.66 mole) in nitrogen was passed into bromodichloromethane (296 g., 1.80 moles) under irradiation over a period of 3 hr. After addition was complete, further irradiation (30 min.) was necessary before reaction ceased. Preliminary distillation (12-plate Fenske column) gave unreacted bromodichloromethane (235 g., b.p. 55° at 200 mm., n_D^{20} 1.4979). Continued distillation (50-plate Podbielniak column glass concentric tube) gave: (1) 1-bromo-1,2-dichloroethane, 8.66 g., 0.049 mole, b.p. 138°, 64° at 55 mm., n_D^{20} 1.5122, 7.4% yield based upon diazomethane; (2) 2-bromo-1,3-dichloropropane, 7.98 g., 0.042 mole, b.p. 179°, 62° at 10 mm., n_D^{20} 1.5191, 12.7%; (3) 2-bromomethyl-1,3-dichloropropane, 6.71 g., 0.033 mole, b.p. 58° at 2 mm., n_D^{20} 1.5136, 15%; (4) an unidentified product, 1.4 g., b.p. 80° at 1 mm., n_D^{20} 1.5242; and (5) a residue, 3.6 g.

The product, 1-bromo-1,2-dichloroethane (1) [*Anal.* Calcd. for $\text{C}_2\text{H}_3\text{BrCl}_2$: Cl + Br, 84.8; mol. wt., 178. Found: Cl + Br, 85.4; mol. wt., 181], was identical in physical properties and infrared spectrum with the substance obtained below, and its dehydrohalogenation gave 1-bromo-1-chloroethene. Its properties and infrared spectrum⁷ were different from those of 1-bromo-2,2-dichloroethane also prepared. Bromine (104 g., 0.65 mole) was added dropwise over a 5-hr. period of 1,2-dichloroethane (214 g., 2.15 moles) held under reflux by irradiation with two 100-w. Mazda bulbs. An additional 50 hr. of irradiation was required to complete the reaction. After it was washed with sodium bisulfite solution (3%, 100 ml.) and water, the reaction mixture (dried CaCl_2) was distilled to give 1-bromo-1,2-dichloroethane (69 g., 60%, b.p. 138°, 53° at 18 mm., n_D^{20} 1.5132, d_{25}^{25} 1.857).

Fraction 1 above (2.3 g., 0.013 mole) in *n*-propyl alcohol (2 ml.) was added to a solution of sodium propylate (from sodium, 0.3 g., and *n*-propyl alcohol, 7 ml.), and the product was distilled in a nitrogen atmosphere as it formed. Redistillation gave 1-bromo-1-chloroethene (0.85 g., b.p. 61–62°, n_D^{17} 1.4786).¹¹ The "authentic" 1-bromo-1,2-dichloroethane gave the same product in 88% yield in a similar experiment on a larger scale.

To obtain 1-bromo-2,2-dichloroethane for comparison, phosphorus tribromide (24 g., 0.089 mole) was added over a 30-min. period to 2,2-dichloroethanol (25 g., 0.22 mole, prepared by reduction of dichloroacetic acid with lithium aluminum hydride).¹² The reaction mixture was held at 80° for 30 min., and

(10) M. S. Kharasch, J. A. Norton, and F. R. Mayo, *J. Org. Chem.*, **8**, 53 (1938).

(11) C. L. Agre and W. Hilling, *J. Am. Chem. Soc.*, **74**, 3898 (1952).

then hydrobromic acid (48%, 15 ml.) was added. The mixture was cooled, water (30 ml.) was added, and it was extracted twice with ligroin (30 ml., 60°). The ligroin solution was extracted three times with concentrated sulfuric acid, twice with water, and dried over calcium chloride. It was distilled to give 1-bromo-2,2-dichloroethane (6 g., 16%, b.p. 138°, n_D^{20} 1.5097).

The product 2-bromo-1,3-dichloropropane (2) had physical properties and an infrared spectrum⁷ identical with the same substance prepared as described below; its dehalogenation gave 3-chloropropene, and its dehydrohalogenation gave 2-bromo-3-chloropropene. Over a 3-hr. period, phosphorus tribromide (28.7 g., 0.106 mole) was added to redistilled 1,3-dichloropropanol-2 (Eastman, 41 g., 0.32 mole). The reaction mixture was held at 40° until the addition was complete, and then it was heated (over 2 hr.) to 95°. Hydrobromic acid (40%, 10 ml.) was added, and the mixture was allowed to cool. Water (200 ml.) and ligroin (60°, 100 ml.) were added. The ligroin solution was separated and washed with concentrated sulfuric acid (3 times) and with water. After it was dried over calcium chloride, distillation gave 2-bromo-1,3-dichloropropane (10.5 g., 18%, b.p. 178°, 64° at 13 mm., n_D^{20} 1.5202, d_{25}^{28} 1.742).

Anal. Calcd. for $C_3H_5Cl_2Br$: Cl + Br, 78.7. Found: Cl + Br, 78.6.

When this product (2, 1 g.) was added to zinc (1 g.) in ethanol (4 ml.), rapid reaction occurred. Concurrent distillation through a fractionating column gave 3-chloropropene (0.2 g., b.p. 46°, n_D^{20} 1.4150). Its treatment with thiourea (0.05 g.) in boiling ethanol (1.6 ml.) for 5 min. and then addition of picric acid (0.05 g.) gave S-allylthiouonium picrate (m.p. 155°, mixture m.p. with authentic sample, 155°).¹³ As additional proof for the structure of 2-bromo-1,3-dichloropropane (2), it (3 g.) was treated with a solution of sodium hexylate (from sodium, 0.3 g., and hexanol, 10 ml.). A mixture of 2-bromo-3-chloropropene and hexanol (b.p. 60–70° at 200 mm.) was distilled as the reaction occurred. The mixture was used to prepare S(2-bromoallyl)thiouonium picrate (m.p. after 3 recrystallizations from ethanol, 168–169°) as described above.

Anal. Calcd. for $C_{10}H_{16}O_7N_5SBr$: Br, 18.8. Found: Br, 18.3.

The same isothiuronium picrate was obtained from the 2-bromo-3-chloropropene¹⁴ prepared by the same procedure as above from 1-chloro-2,3-dibromopropane (from addition to bromine to 3-chloropropene). The mixture melting point showed no depression.

2,3-Dichloropropene (b.p. 93°, n_D^{20} 1.4535),¹⁵ prepared by similar dehydrohalogenation of 1,2,3-trichloropropane, gave S(2-chloroallyl)thiouonium picrate (m.p. 174–175°).

Anal. Calcd. for $C_{10}H_{16}O_7N_5SCl$: Cl, 9.3. Found: Cl, 9.4.

3-Bromo-1,2-dichloropropane (b.p. 178°, 70° at 17 mm., n_D^{20} 1.5172, d_{25}^{28} 1.746) prepared as follows had different properties and infrared spectrum⁷ from those of fraction 2. Chlorine (56 g.) was slowly bubbled into a solution of allyl alcohol (48 g.) in carbon tetrachloride (70 ml.), vigorously stirred and held at 5–10°. Distillation gave 2,3-dichloropropanol-1 (44 g., 43%, b.p. 60° at 12 mm., n_D^{20} 1.4847). To this product (32 g., 0.248 mole), maintained at 70°, phosphorus tribromide (22 g., 0.081 mole) was added dropwise (0.5 hr.). When hydrogen bromide evolution ceased, hydrobromic acid (40%, 20 ml.) was added, and the mixture was held at reflux for 2 hr. It was then cooled, and water (50 ml.) and ligroin (60°, 10 ml.) were added. The organic solution was separated, washed with concentrated sulfuric acid (4 × 7 ml.), with water (2 × 25 ml.), and then it was dried (sodium sulfate). 3-Bromo-1,2-dichloropropane (15 g., 31%) was obtained by distillation.

Anal. Calcd. for $C_3H_5BrCl_2$: Cl + Br, 78.6. Found: Cl + Br, 78.4.

1,3-Diiodo-2-iodomethylpropane was prepared from the 2-bromomethyl-1,3-dichloropropane (3).

Anal. Calcd. for $C_4H_7BrCl_2$: Cl + Br, 73.2; mol. wt., 206. Found: Cl + Br, 74.2; mol. wt., 218.

A solution containing 3 (0.63 g.), sodium iodide (2.4 g.), and acetone (12 ml.) was heated in a bomb tube at 120° for 65 hr. The reaction mixture was diluted with chloroform (60 ml.),

filtered, and washed twice with water (25-ml. portions) and with sodium iodide solution (10%, 6 × 25 ml.). The chloroform solution was dried (calcium chloride) and distilled. The residual oil was recrystallized six times from absolute ethanol to give a white solid (m.p. 30°). This formation of a triiodide supports the structure given for 3 since it is apparent that it does not have vicinal halogens.

Anal. Calcd. for $C_4H_7I_3$: I, 87.4; mol. wt., 436. Found: I, 87.3; mol. wt., 401.

The Reaction of 1-Bromo-1,1-dichloroethane with Diazomethane.—As previously described, diazomethane (0.50 mole) in nitrogen was bubbled into 1-bromo-1,1-dichloroethane (326 g., 1.83 moles) over a 3-hr. period. Irradiation during the addition and for a subsequent period (0.5 hr.) was necessary to complete the reaction. The reaction mixture was distilled (12-plate Fenske column) to remove part of the unreacted 1-bromo-1,1-dichloroethane (253 g., b.p. 98°, n_D^{20} 1.4822). Continued distillation (10-plate tantalum wire spiral column) gave more of the polyhaloethane (43 g.) and three products: (1) 2-bromo-1,2-dichloropropane, 9.84 g., 0.051 mole, 10.3%, b.p. 84° at 88 mm., n_D^{20} 1.4970; (2) 2-bromo-1,3-dichloro-2-methylpropane, 10.42 g., 0.051 mole, 20.4%, b.p. 109° at 84 mm., n_D^{20} 1.5075; and (3) 2-bromomethyl-1,3-dichloro-2-methylpropane, 4.53 g., 0.021 mole, 12.6%, b.p. 117° at 38 mm., n_D^{20} 1.5054.

Structural evidence for the 2-bromo-1,2-dichloropropane (1) resulted from its dehydrobromination to *cis*- and *trans*-1,2-dichloropropenes.

Anal. Calcd. for $C_3H_5BrCl_2$: Cl + Br, 78.6; mol. wt., 192. Found: Cl + Br, 77.7; mol. wt., 198.

A solution of 1 (2 g., 0.01 mole) in pentanol (1 g.) was slowly added (1 hr.) to a sodium pentylate solution (from sodium, 0.24 g., and pentanol, 5 g.). The mixture was held at reflux (1 hr.) and then distilled through the tantalum column to give *trans*-1,2-dichloropropene (0.22 g., b.p. 75°, n_D^{20} 1.4438; reported¹⁵ b.p. 74.2°, n_D^{20} 1.4431) and *cis*-1,2-dichloropropene (0.22 g., b.p. 94°, n_D^{20} 1.4458; reported¹⁵ b.p. 92.5°, n_D^{20} 1.4462). A mixture of these dichloropropenes (0.45 g., 0.0055 mole) was hydrogenated with an equivalent of hydrogen (105 ml. STP, 0.0054 mole) over Adams catalyst (0.05 g.). The product obtained had vicinal chlorine atoms since iodine was liberated in its reaction with sodium iodide in acetone.

The structure of 2-bromo-1,3-dichloro-2-methylpropane (2) was confirmed by its zinc dehalogenation to give 3-chloro-2-methylpropene, and its dehydrobromination to give 1,3-dichloro-2-methylpropene.

Anal. Calcd. for $C_4H_7BrCl_2$: Cl + Br, 73.3; mol. wt., 206. Found: Cl + Br, 73.0; mol. wt., 217.

To a mixture of zinc powder (1.5 g.) and propanol (6 ml.) under reflux in a reaction flask attached to the tantalum column, substance 2 (1.5 g.) was added dropwise. Rapid reaction occurred, and a mixture of propanol and the product was distilled as it formed. Redistillation gave 3-chloro-2-methylpropene (0.4 g., b.p. 73°) which gave S-methylthiouonium picrate (m.p. 171° after 4 recrystallizations from ethanol; mixture m.p. with an authentic sample gave no depression). A solution of 2 (2 g., 0.01 mole) in octanol (2 ml.) was added slowly to a solution of sodium octylate (from sodium, 0.22 g., with octanol, 2 ml.). After the reaction mixture had been stirred overnight, it was distilled to give 1,3-dichloro-2-methylpropene (*cis*, *trans*, or mixture of the two; 0.8 g., 66%, b.p. 130°, 83° at 163 mm., n_D^{20} 1.4742; reported¹⁶ b.p. 132°, n_D^{20} 1.4744). Its infrared spectrum had absorption peaks at 1380 and 1446 cm^{-1} but none at 880–898 cm^{-1} . The product, therefore, has a methyl group but no terminal methylene.

Anal. Calcd. for $C_4H_8Cl_2$: Cl, 56.7. Found: Cl, 57.1.

Product 3 was hydrolyzed to give 2-hydroxymethyl-2-methylpropanediol-1,3 and was converted to a trisiodo compound, presumably 2-iodomethyl-1,3-diiodopropane, to support its identification as 2-bromomethyl-1,3-dichloro-2-methylpropane.

Anal. Calcd. for $C_5H_9BrCl_2$: Cl + Br, 68.6; mol. wt., 220. Found: Cl + Br, 68.2; mol. wt., 224.

A sample of 3 (1.72 g.) was subjected to a series of hydrolysis attempts: (1) at reflux (70 hr.) with potassium hydroxide (2.6 g.) in methanol-water (2 ml.:6 ml.); (2) methanol was removed and propanol (5 ml.) and more potassium hydroxide (2 g.) were added (reflux, 90 hr.); (3) the lower organic phase was separated and treated at reflux with silver acetate (5 g.) in ethanol; and then (4) the supernatant liquid was decanted from tar and was

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heated at reflux with potassium hydroxide (4 g.) in water (5 ml., 72 hr.). The ethanol was removed, and the remaining aqueous solution was passed over a cation-exchange resin. Silica precipitated in the column. Evaporation of the water gave a white solid which was extracted with hot ethanol. When the ethanol solution was evaporated, 2-hydroxymethyl-2-methylpropanediol-1,3 (0.04 g., 4%, m.p. 202–203° after two recrystallizations with ethanol) was obtained. The melting point of a mixture with authentic material (Heyden, m.p. 203–203.5° after 3 recrystallizations from ethanol) showed no depression. The reaction of 3 (0.5 g.) with sodium iodide (2.5 g.) in acetone (8 ml.) in a sealed tube at 125° for 5 days gave product which did not crystallize. Analysis of the crude material (89 I, C₃H₉I₃: I, 85).

The Reaction of 1-Bromo-1,1,2-trichloroethane with Diazomethane.—Diazomethane (0.49 mole) was passed into irradiated 1-bromo-1,1,2-trichloroethane (315 g., 1.48 moles) over 3 hr. (0.5 hr. of subsequent irradiation needed). The reaction mixture was distilled (3.5 ml./hr.) through a 12-plate Fenske column to give unreacted 1-bromo-1,1,2-trichloroethane (278 g., b.p. 97° at 142 mm., n_D^{20} 1.5217). The distilland partly solidified upon cooling. Volatile products in it were evaporated (2 mm. pressure) into a trap cooled to –80°. The remaining solid (16.2 g.) was recrystallized 3 times from ethanol and then sublimed (80°, 2 mm.) to give 2-bromomethyl-2-chloromethyl-1,3-dichloropropane (5.0 g., m.p. 103–104°, mixture m.p. with an authentic sample 103–104°).¹ Filtrates from the recrystallizations were combined, the ethanol was distilled, and the remaining liquid was combined with that collected in the –80° trap in the above evaporation. Distillation of the mixture gave: (1) 2-bromo-1,2,3-trichloropropane, 7.3 g., 0.032 mole, 6.6%, b.p. 186°, 112° at 92 mm., n_D^{20} 1.5238; (2) 2-bromo-2-chloromethyl-1,3-dichloropropane, 7.6 g., 0.032 mole, 13%, b.p. 119° at 27 mm., n_D^{20} 1.5349; and additional 2-bromomethyl-2-chloromethyl-1,3-dichloropropane, 1.3 g., total yield 6.3 g., 16%.

The identification of 1 as 2-bromo-1,2,3-trichloropropane is based upon the identity of its physical properties and infrared spectrum^{7,14} with those of this polyhalopropane prepared as described below, its dehydrobromination to 1,2,3-trichloropropene, and its analysis.

Anal. Calcd. for C₃H₄Cl₃Br: Cl + Br, 82.3; mol. wt., 226. Found: Cl + Br, 82.3; mol. wt., 220.

Bromine (42 g., 0.26 mole) was added dropwise to 1,2,3-trichloropropane (Shell Oil Co., 147 g., 1.0 mole) irradiated with two 100-w. bulbs. After the bromine color had discharged, the reaction mixture was worked up as described for previous brominations. Distillation gave 2-bromo-1,2,3-trichloropropane (29 g., 49%, b.p. 186°, 116° at 95 mm., n_D^{20} 1.5233). 1,2,3-Trichloropropene (0.8 g., 42%, b.p. 140°, n_D^{16} 1.5003)¹⁴ was distilled as it formed in the reaction of product 1 (2.88 g., 0.0127 mole) in octanol (4 ml.) with a solution of sodium octylate (from sodium, 0.29 g., with octanol, 8 ml.). By the procedure previously described, it was converted to S(2,3-dichloroallyl)isothiuronium picrate (m.p. 180–181° from ethanol, mixture m.p. 180–181°).

Anal. Calcd. for C₁₀H₉O₇N₅SCl₂: Cl, 17.1. Found: Cl, 17.2.

1,3-Dichloro-2-chloromethylpropene was produced in the dehydrobromination of 2-bromo-2-chloromethyl-1,3-dichloropropane (2).

Anal. Calcd. for C₄H₅Cl₃Br: Cl + Br, 77.5; mol. wt., 240. Found: Cl + Br, 77.4; mol. wt., 248.

In a reaction flask attached to the tantalum column, a solution of sodium nonylate (from sodium, 0.55 g., with nonanol, 16 ml.) was added (1.5 hr.) to 2 (5.7 g., 0.025 mole) in nonanol (7 ml.); the product was distilled under vacuum (72 mm.) as it formed. Redistillation gave 2-chloromethyl-1,3-dichloropropene (2.57 g., 70%, b.p. 61° at 10 mm.,¹⁷ n_D^{20} 1.5015).

Anal. Calcd. for C₄H₅Cl₂: Cl, 66.7. Found: Cl, 67.7.

The latter (2.57 g., 0.0161 mole) and thiourea (2.5 g., 0.033 mole) in ethanol (20 ml.) were heated under reflux (10 min.), and then a solution of picric acid (4.7 g., 0.021 mole) in ethanol

(80 ml.) was added. The expected bisothiuronium dipicrate (5.55 g., 80%, m.p. 231° after precipitation from its saturated solution in ethanol with ligroin) was obtained. The reactivity of this trichloroalkene confirms the postulated structure with two allylic chlorine atoms.

Anal. Calcd. for C₁₈H₁₇O₁₄N₁₀S₂Cl: Cl, 5.2. Found: Cl, 5.1.

The Reaction of Bromotrichloromethane with Diazomethane at Low Temperature.—Diazomethane (0.29 mole) was passed in a stream of nitrogen (1.5 hr.) into bromotrichloromethane (350 g., 1.77 moles) with the reaction temperature held at 5–15°. No irradiation other than room light (daylight and phosphorescent tubes) was used. After a brief induction period, the reaction became rapid. The reaction mixture retained a deep yellow color during the reaction; but, when nitrogen evolution ceased about 45 min. after diazomethane addition was completed, it became colorless. Gases from the reaction vessel were passed through a sulfuric acid trap (to remove diazomethane), a –80° trap, a trap cooled with liquid nitrogen, and then into a Precision wet test meter. Nothing condensed in the –80° trap, but a small amount of white solid appeared in the –196° trap. It probably contained ethylene since it vaporized on warming, and its reaction with bromine in carbon tetrachloride gave a product which when treated with sodium iodide in acetone gave iodine. The latter product was shown to be 1,2-dibromoethane by its conversion to the expected bisothiuronium dipicrate (m.p. 260° after two treatments with boiling ethanol).¹³

The reaction mixture was distilled through the 12-plate Fenske column to give recovered bromotrichloromethane (320 g., b.p. 78° at 360 mm., n_D^{20} 1.5059). Distillation was continued in the tantalum column to give: (1) a mixture (5.94 g., b.p. 104–116° at 44 mm., n_D^{20} 1.5211; infrared spectrum⁷ identical with that of a known mixture of the following two organic halides, 12:88) of 1-bromo-1,1,2-trichloroethane (0.71 g., 0.0034 mole, 1.2%) and 2-bromo-1,2,3-trichloropropane (5.23 g., 0.0231 mole, 16%); (2) 2-bromo-2-chloromethyl-1,3-dichloropropane (3.49 g., 0.0145 mole, 15%, b.p. 122° at 28 mm., n_D^{20} 1.5338; further, infrared spectrum identical⁷ with that of same substance obtained in previous experiment); (3) 2-bromomethyl-2-chloromethyl-1,3-dichloropropane (2.55 g., 0.0101 mole, 14%, m.p. 103–104°, mixture m.p. with authentic sample gave no depression); and (4) a residue (0.3 g.).

The Reaction of Bromotrichloromethane with Diazomethane at Higher Temperature.—Into bromotrichloromethane (423 g., 2.14 moles), irradiated in the described reaction vessel, was passed diazomethane (0.34 mole). No attempt was made to cool the reaction mixture, and hence it rose to 70° during the reaction. At no time was the yellow color of diazomethane apparent. After the removal of part of the unreacted bromotrichloromethane (336 g., b.p. 80° at 35 mm.) by distillation (4.6 ml./hr.) through the Fenske column, distillation with the tantalum column gave the remaining solvent, and the following products: (1) 1-bromo-1,1,2-trichloroethane, 9.05 g., 0.0427 mole, 12.6%, b.p. 95° at 100 mm., n_D^{20} 1.5211; (2) 2-bromo-1,2,3-trichloropropane, 9.95 g., 0.044 mole, 26%, b.p. 106° at 55 mm., n_D^{20} 1.5265; and (3) 2-bromo-2-chloromethyl-1,3-dichloropropane, 3.49 g., 0.0145 mole, b.p. 115° at 28 mm., n_D^{20} 1.5350. Tar (0.45 g.) and an oil (1.61 g., n_D^{20} 1.55) remained in the distilling flask. The physical properties and infrared spectra⁷ of products 1, 2, and 3 were the same as corresponding ones obtained in the 1-bromo-1,1,2-trichloroethane–diazomethane experiment.

A careful search was made for the 4:1 product 2-bromomethyl-2-chloromethyl-1,3-dichloropropane. For example, the column "hold-up" from the above distillation (1.85 g.) was treated with sodium iodide (11 g.) in acetone (30 ml.) in a sealed tube at 120° for 76 hr. None of the very insoluble 2,2-diiodomethyl-1,3-diodopropane was found. However, iodine (11 meq. by thiosulfate titration) was obtained to indicate that the major component had vicinal halogen and was probably product 3 (1.32 g., 0.0055 mole; total yield 4.82 g., 0.020 mole, 17.7%). Product 1, 1-bromo-1,1,2-trichloroethane (3.9 g., 0.018 mole), was identified further by its conversion to trichloroethene (1.56 g., 0.012 mole, 67%, b.p. 87°, n_D^{20} 1.4778; lit. b.p. 88°, n_D^{20} 1.4780) in its reaction (80°, 1 hr.) with sodium hexylate (from sodium, 0.39 g., with hexanol, 12 ml.).

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