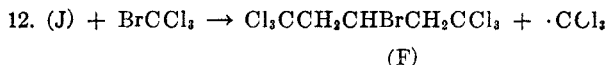
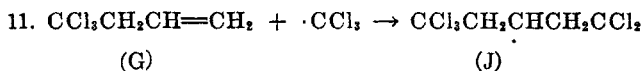
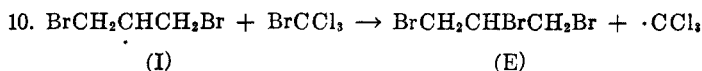
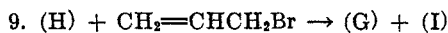
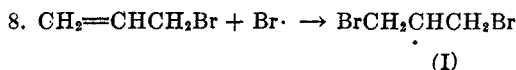
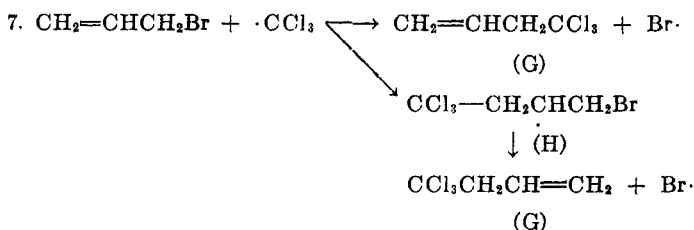
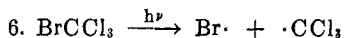




following series of reactions:



We are uncertain, at this time, whether product (G), namely 4,4,4-trichloro-1-butene, is formed by direct displacement of a bromine atom by the free trichloromethyl radical, by the addition of this free radical to the allyl bromide followed by elimination of a bromine atom,<sup>1</sup> or by interaction of (H) with allyl bromide to give (G) and (I) as indicated in step 9.

It is obvious, from a consideration of reactions 6 to 12 inclusive, that if instead of an excess of bromotrichloromethane one uses an excess of allyl bromide, that products (G), (4,4,4-trichloro-1-butene) and (E) (1,2,3-tribromopropane) should be the major reaction products. This was found to be the case.

The structure of 4,4,4-trichloro-1-butene was determined by ozonolysis of the compound, and identification of the formaldehyde and of the trichloropropionaldehyde. The latter compound, when treated with 2,4-dinitrophenylhydrazine, is first converted into dichloroacrolein, which then condenses with the 2,4-dinitrophenylhydrazine. The melting point of this substance was not depressed by the addition of an authentic sample of the 2,4-dinitrophenylhydrazine of  $\beta, \beta$ -dichloroacrolein.

#### EXPERIMENTAL

*Photochemical addition of bromotrichloromethane to allyl bromide.* A solution of allyl bromide, free of peroxides, (0.2 mole) and bromotrichloromethane (0.8 mole) was maintained at 25° in a water-bath and internally illuminated with a mercury vapor-neon fluores-

<sup>1</sup> The mechanism of this reaction is under investigation in this laboratory.

cent coil for 46 hours while a slow stream of nitrogen gas was passed through the solution. At the end of that time, no allyl bromide or other olefins could be demonstrated in the solution. The unreacted bromotrichloromethane was removed from the reaction mixture at 55 mm. pressure, and the residue was subjected to distillation at low pressure. The following fractions were collected:<sup>2</sup> Fraction I: 23 g.; b.p. 40–44° at 0.05 mm.;  $n_D^{20}$  1.5767. Fraction II: 2.5 g.; b.p. 44–61° at 0.05 mm.;  $n_D^{20}$  1.5589. Fraction III: 26.5 g.; b.p. 61–63° at 0.05 mm.;  $n_D^{20}$  1.5456. Residue: 3.2 g.

*Anal.* Fraction I. Calc'd for  $C_3H_5Br_3$ : C, 12.83; H, 1.79; Mol. wt. 280.8; Ag. eq. 93.6.  
Found: C, 13.42; H, 1.75; Mol. wt. 283; Ag. eq. 84.3.

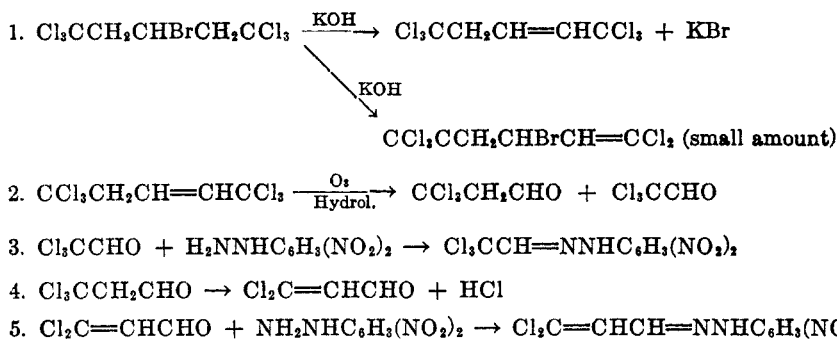
These data suggested that Fraction I was 1,2,3-tribromopropane mixed with a small quantity of the compound of Fraction III. For this reason, about 20 g. of this material was carefully redistilled at low pressures, and about 10 g. of material collected which had the index of refraction 1.5840 at 20°, and the melting point 15–16°. The melting point of this material was not depressed by admixture with an equal quantity of an authentic sample of 1,2,3-tribromopropane. The rest of the distillate had the index 1.5830 at 20°.

From the analyses of Fraction III it appears to be a hexachlorobromopentane contaminated with small quantities of 1,2,3-tribromopropane.

*Anal.* Fraction III. Calc'd for  $C_5H_5Cl_5Br$ : C, 16.79; H, 1.41; Ag. eq. 51.1 Mol. wt. 358.  
Found: C, 16.43; H, 1.52; Ag. eq. 52.2; Mol. wt. 344.

Fraction II is probably a mixture of 1,2,3-tribromopropane and the hexachlorobromopentane.

*Identification of fraction III, (1,1,1,5,5,5-hexachloro-3-bromopentane).* The structure of the 1,1,1,5,5,5-hexachloro-3-bromopentane was established by the following series of reactions:



A mixture of 19 g. of Fraction III and 3.2 g. of potassium hydroxide in 60 ml. of absolute alcohol was allowed to stand for 24 hours at room temperature. The reaction mixture was then cooled, and the solid which separated (5.1 g.) was collected. The alcohol was removed from the filtrate at reduced pressure and the residue thus obtained was dissolved in ether, washed with water, and the ether solution dried with sodium sulfate. The residue was subjected to distillation at low pressures. The following fractions were collected: Fraction I: 1.2 g.; b.p. 39–40° at 0.03 mm.;  $n_D^{20}$  1.5330; Ag. eq. 56.5; Mol. wt. 255. Fraction II: 0.45 g.; b.p. 40–44° at 0.03 mm.;  $n_D^{20}$  1.5350. Fraction III: 8 g., b.p. 75–76° at 0.04 mm.;  $n_D^{20}$  1.5413.

The analysis and the molecular weight of Fraction III indicate that it is a pure sample of 1,1,1,5,5,5-hexachloro-3-bromopentane.

*Anal.* Calc'd for  $C_5H_5Cl_5Br$ : Ag. eq. 51.1; Mol. wt. 358.  
Found: Ag. eq. 51.3; Mol. wt. 357.

<sup>2</sup> To prevent superheating of the material, a slow stream of nitrogen gas was used. The bubbles produced were extremely small.

Fraction I (Mol. wt. 255) was dissolved in ethyl acetate, and ozone was passed through the solution. Upon removal of the solvent at reduced pressure, 45°, water was added to the residue, and the whole was heated on a steam-bath for 2.5 hours, and then allowed to cool. The water layer was separated from the oil layer by filtration through a filter paper wet with water, and treated with an alcoholic solution of 2,4-dinitrophenylhydrazine. The precipitate which separated was boiled with a few ml. of absolute alcohol. The compound decomposed at 305–306° (unc.). The decomposition point of the 2,4-dinitrophenylhydrazone of chloral is recorded in the literature to be 315°.

The alcoholic filtrate (after removal of the 2,4-dinitrophenylhydrazone of chloral) was allowed to cool. A solid, which upon crystallization melted at 159°, separated. This material was the 2,4-dinitrophenylhydrazone of  $\beta,\beta$ -dichloroacrolein (1).

*Peroxide-induced addition of bromotrichloromethane to allyl bromide.* A solution of allyl bromide (0.3 mole) and bromotrichloromethane (1 mole) was heated to 70° in a flask equipped with a reflux condenser and stirrer. Acetyl peroxide (0.8 g.), dissolved in bromotrichloromethane (0.4 mole) was slowly added to the reaction mixture (45 min). The whole mixture was then maintained at 70° for ten hours. At that time no test for allyl bromide could be demonstrated in the solution. The reaction mixture was worked up in a manner similar to that described for the light-induced addition of bromotrichloromethane to allyl bromide.

Only two products were isolated, namely 1,2,3-tribromopropane and 1,1,1,5,5,5-hexachloro-3-bromopentane. Furthermore from a comparison of the index of refraction of the reaction mixture and the curve of the index of refraction of the pure 1,2,3-tribromopropane, and pure 1,1,1,5,5,5-hexachloro-3-bromopentane, it would appear that at most only insignificant quantities of the adduct of bromotrichloromethane and allyl bromide are formed in the reaction.

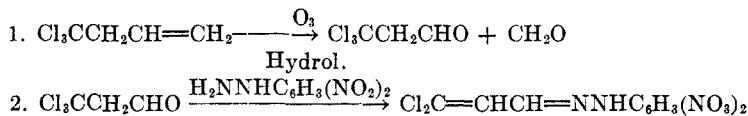
*Photochemically-induced reaction of bromotrichloromethane and allyl bromide in the presence of an excess of the latter reagent.* A solution of freshly distilled allyl bromide (1.1 mole) and bromotrichloromethane (0.33 mole) was maintained at 30–40° and internally illuminated with a mercury vapor-neon fluorescent coil for eleven hours. The air in the apparatus was displaced by nitrogen.

Most of the unreacted allyl bromide was removed by distillation at ordinary temperatures. The residue was distilled through a Vigreux column (6"), and the following fractions were collected: Fraction I: 25.5 g.; b.p. 36–43° at 0.04 mm.;  $n_D^{20}$  1.5681. Fraction II. Material which collected in cold-trap (CO<sub>2</sub>) 65.2 g.;  $n_D^{20}$  1.4895. Residue, 1 g. Fraction I has been demonstrated to be a mixture of four parts of 1,2,3-tribromopropane and one part of the "dimer" of allyl bromide (2). The material caught in the cold-trap was fractionated at ordinary pressure, and the fraction boiling at 123–131° was collected. Upon distillation of this material the fraction boiling at 128–129° was collected. This material had the index of refraction 1.4678 and was considered to be pure 4,4,4-trichloro-1-butene.

*Anal.* Calc'd for C<sub>4</sub>H<sub>5</sub>Cl<sub>3</sub>: C, 30.1; H, 3.15; Ag. eq. 53.2.

Found: C, 29.6; H, 3.22; Ag. eq. 53.6.

*Identification of the structure of 4,4,4-trichloro-1-butene (C<sub>4</sub>H<sub>5</sub>Cl<sub>3</sub>).*



The material (C<sub>4</sub>H<sub>5</sub>Cl<sub>3</sub>) (6.9 g.) was dissolved in ethyl acetate cooled to –70°, and ozone (8%) was passed through the mixture, until no further absorption took place. The solvent was removed at room temperature, and the ozonide was decomposed by warming with water on a steam-bath (3 hours). The layers were separated, and the water layer discarded. The oil layer was mixed with an alcohol-water solution of 2,4-dinitrophenylhydrazine and warmed for 15–30 minutes. Upon cooling, a solid separated, which was crys-

tallized twice from small quantities of alcohol. The melting point of the substance from the second crystallization was 158–159°, indicating that it was the 2,4-dinitrophenylhydrazone of  $\beta,\beta$ -dichloroacrolein. The material did not depress the melting point of an authentic sample of the 2,4-dinitrophenylhydrazone of  $\beta,\beta$ -dichloroacrolein (1).

Another sample of the compound  $C_2H_2Cl_2$  was dissolved in carbon tetrachloride and ozonized at  $-12^\circ$ . The liberated formaldehyde was caught in two tubes containing water. Upon addition of a methanol solution of methone to the contents of the two tubes a heavy precipitate resulted. This material melted at 189.5°, which indicates that it is a quite pure sample of the methone derivative of formaldehyde.

#### SUMMARY

1. In photochemical or peroxide-induced reactions of allyl bromide and an excess of bromotrichloromethane the products are 1,2,3-tribromopropane and 1,1,1,5,5,5-hexachloro-3-bromopentane.

2. In photochemical or peroxide-induced reactions of bromotrichloromethane and an excess of allyl bromide, the products are 1,2,3-tribromopropane and 4,4,4-trichloro-1-butene.

3. The structures of the new compounds formed have been determined by conventional methods.

4. A mechanism which accounts for the products formed is suggested.

CHICAGO 37, ILL.

#### REFERENCES

- (1) KHARASCH, REINMUTH, AND URRY, *J. Am. Chem. Soc.*, **69**, 1105 (1947).
- (2) KHARASCH AND BÜCHI, Unpubl. work.