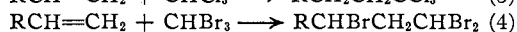
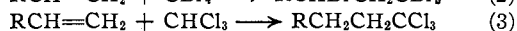
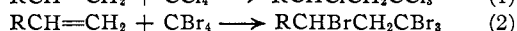
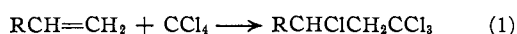


[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

## Reactions of Atoms and Free Radicals in Solution. X. The Addition of Polyhalomethanes to Olefins

BY M. S. KHARASCH, ELWOOD V. JENSEN AND W. H. URRY

In preliminary communications<sup>1</sup> we have described the addition of halogenated methanes to olefins to yield products containing one or more equivalents of the olefin to one equivalent of the halogenated methane. The present paper deals in detail with the additions of carbon tetrachloride, carbon tetrabromide, chloroform and bromoform to a number of olefins containing terminal double bonds (Table I). The mono-additions have been shown to follow the schemes indicated.



The additions of all these halogenated methanes to olefins are readily initiated by small amounts of diacyl peroxides or by light of the appropriate wave length.

uct (the one-to-one addition product) was always accompanied by a small amount of higher-boiling material (containing two or more equivalents of the olefin to one equivalent of carbon tetrachloride). With styrene, however (as has been previously observed<sup>2</sup>), the addition product consisted principally of a polymer containing chlorine. Carbon tetrabromide, on the other hand, gave practically quantitative yields of the one-to-one addition product even in the case of styrene. Furthermore, when a mixture of one equivalent of carbon tetrabromide and two equivalents of carbon tetrachloride was treated with a half-mole of an olefin, only the carbon tetrabromide addition product was formed.

The yields obtained from the addition of chloroform and bromoform to aliphatic olefins were markedly lower than those obtained from the addition of carbon tetrachloride or tetrabromide.

TABLE I  
ADDITION OF CARBON TETRACHLORIDE, CARBON TETRABROMIDE, CHLOROFORM AND BROMOFORM TO OLEFINS

Halide	Olefin	Reaction initiated by (mole % of olefin)	Product	Yield (% based on olefin)	
Carbon tetrachloride	Octene-1	Ac <sub>2</sub> O <sub>2</sub> 2	1,1,1,3-Tetrachlorononane	85	
	Octene-1	Bz <sub>2</sub> O <sub>2</sub> 6	1,1,1,3-Tetrachlorononane	75	
	Octene-1	Ultraviolet light	1,1,1,3-Tetrachlorononane	..	
	Octene-1	Visible light	No reaction		
	Styrene	Ac <sub>2</sub> O <sub>2</sub> 10	Polymer		
	Ethyl acrylate	Ac <sub>2</sub> O <sub>2</sub> 6	Polymer		
	Biallyl	Bz <sub>2</sub> O <sub>2</sub> 5	Octachlorooctane	ca. 29	
			Tetrachloroheptene	31	
		Biallyl	Ac <sub>2</sub> O <sub>2</sub> 6	Octachlorooctane	31
				Tetrachloroheptene	26
Carbon tetrabromide	Propylene	Bz <sub>2</sub> O <sub>2</sub>	Tetrachlorobutane	a	
	Ethylene	Bz <sub>2</sub> O <sub>2</sub>	Tetrachloropropane	a	
	Octene-1	Ac <sub>2</sub> O <sub>2</sub> 2	1,1,1,3-Tetrabromononane	b	
	Octene-1	Visible light	1,1,1,3-Tetrabromonane	88	
Chloroform	Styrene <sup>c</sup>	Visible light	1,1,1,3-Tetrabromo-3-phenylpropane	96	
	Ethylene <sup>c</sup>	Visible light	Tetrabromopropane	a	
Bromoform	Octene-1	Bz <sub>2</sub> O <sub>2</sub> 2	1,1,1-Trichlorononane	22	
	Biallyl	Ac <sub>2</sub> O <sub>2</sub> 8	Trichloroheptene	5	
Bromoform	Octene-1	Ac <sub>2</sub> O <sub>2</sub> 5	1,1,3-Tribromononane	31	
	Octene-1	Visible light	No reaction		
	Styrene	Bz <sub>2</sub> O <sub>2</sub> 5	Phenyl tribromopropane	10	
			Low mol. wt. polymers	10	

<sup>a</sup> The olefin vapor was bubbled into the reaction mixture at atmospheric pressure; under those conditions, most of the olefin escaped from the mixture. Presumably, all of the olefin which was absorbed did react in the expected manner. Better yields have been obtained by carrying out the reactions under pressure and in the absence of oxygen. <sup>b</sup> The yield was good, but the reaction was so vigorous that some of the product was lost through the condenser. <sup>c</sup> Reaction was carried out in carbon tetrachloride as a solvent.

In the addition reactions of carbon tetrachloride with aliphatic olefins, the main reaction prod-

Considerable quantities of higher-boiling materials were also formed. In the reaction of bromoform with styrene, only 10% of the one-to-one addition

(1) Kharasch, Jensen and Urry, *Science*, **102**, 128 (1945); *THIS JOURNAL*, **67**, 1864 (1945); **68**, 154 (1946); Kharasch, Urry and Jensen, *ibid.*, **67**, 1626 (1945).

(2) Breitenbach and Maschin, *Z. physik. Chem.*, **A187**, 175 (1940); see also Mayo, *THIS JOURNAL*, **65**, 2324 (1943).

product was obtained, although the molecular ratio of olefin to bromoform was one to four. The main product was a polymer. However, the molecular weight of this polymer was much lower than that of the polymer formed when the same molecular ratio of styrene and carbon tetrachloride was used.

**Proof of Structure of the One-to-One Addition Products.**—In all instances the molecular formulas of the products listed in Table I were established by analysis, molecular weight determination, and, if the material contained unsaturation, by titration with bromate-bromide reagent. The proof of skeletal structure of the compounds was obtained by the methods indicated below for a few representative cases.

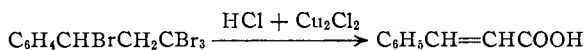
1. The product obtained from the reaction of carbon tetrachloride and octene-1 was shown to be 1,1,1,3-tetrachlorononane by the following series of reactions.



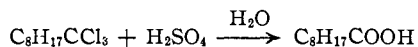
$\text{C}_8\text{H}_{13}\text{CH}=\text{CHCCl}_3 + \text{O}_3 \xrightarrow{\text{H}_2\text{O}} \text{C}_6\text{H}_{13}\text{CHO} + \text{Cl}_3\text{CHO}$   
Both the *n*-heptaldehyde and the chloral were isolated and identified.

2. The product from carbon tetrabromide and octene-1 was shown to be 1,1,1,3-tetrabromononane by a procedure similar to that described above.

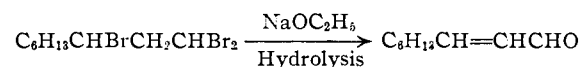
3. The reaction product of carbon tetrabromide and styrene was shown to be 1,1,1,3-tetrabromo-3-phenylpropane by its conversion to cinnamic acid.



4. The addition product formed from chloroform and octene-1 was shown to be 1,1,1-trichlorononane by conversion to pelargonic acid<sup>3</sup> and its *p*-toluidide. The melting point of this compound did not depress the melting point of an authentic sample of the *p*-toluidide of pelargonic acid.



5. The addition product formed from bromoform and octene-1 was shown to be 1,1,3-tribromononane by conversion to 2-nonenal by treatment with sodium ethoxide. The latter compound was identified by the melting point of its 2,4-dinitrophenylhydrazone.



6. The structures of the addition products formed from carbon tetrachloride and biallyl have not been definitely established. There can be little doubt, however, on the basis of the work described in this paper and other studies carried out by us, that the mono addition product of carbon tetrachloride to biallyl is 5,7,7,7-tetrachlorohep-

tene-1, and that the addition compound containing the two equivalents of carbon tetrachloride to one of biallyl is 1,1,1,3,6,8,8,8-octachlorooctane. There is also little doubt that the mono and di addition compounds of chloroform to biallyl are 7,7,7-trichloroheptene-1, and 1,1,1,7,7,7-hexachlorooctane, respectively.

Although structural proofs based on postulated reaction mechanisms or analogies are inadmissible, we nevertheless believe it to be fairly safe to assign the structure 1,1,1,3-tetrachloropropane to the compound formed by the addition of carbon tetrachloride to ethylene and 1,1,1,3-tetrachlorobutane to the compound formed by the addition of carbon tetrachloride to propylene.

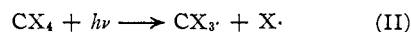
### Discussion

In the chain-reaction mechanism previously proposed<sup>1</sup> for the photochemical or peroxide-initiated additions of polyhalogenated methanes to olefins, it is assumed that the chains are initiated by and propagated through the homolytic scission of carbon-halogen bonds. Since the homolytic scission of a carbon-bromine bond requires less energy of activation than the similar scission of a carbon-chlorine bond, it follows that the addition of carbon tetrabromide should be both more readily initiated and more easily propagated than the corresponding addition of carbon tetrachloride. The difference should be particularly noticeable when the addition reaction is in competition with a concurrent chain reaction, such as polymerization.

When relatively reactive free radicals (such as free methyl radicals) are employed as chain initiators, the energy of activation of the reaction



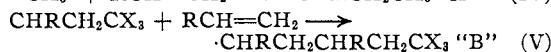
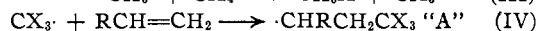
is probably small, whether X be bromine or chlorine. Hence, the reaction cited is initiated about as easily with carbon tetrachloride as with carbon tetrabromide.<sup>1</sup> That the expected difference between the two tetrahalides exists, however, is clearly demonstrated when the photochemical reaction



is employed as the chain initiator. Carbon tetrabromide additions to olefins are readily initiated by visible light, whereas carbon tetrachloride additions require ultraviolet light.<sup>4</sup> When less reactive (secondary or tertiary) free radicals act as chain propagators the greater lability of bromine as compared to chlorine in  $\text{CX}_4$  becomes evident. When the bromide is employed the proportion of addition product is much greater than when the chloride is used. This result may be explained in terms of the reaction schemes

(4) The beginning of the absorption continuum of carbon tetrachloride has been reported to be in ultraviolet region (2280, 2800 Å.—Saha, *C. A.*, **27**, 4733 (1933)); Lowry and Sass, *J. Chem. Soc.*, 622 (1926), while that of carbon tetrabromide approaches the violet and visible spectrum (3500 Å.—Henrici, *Z. Physik*, **77**, 35 (1932)).

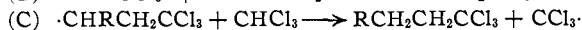
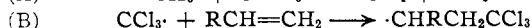
(3) Prins, *J. prakt. Chem.*, [2] **89**, 414 (1914).



The secondary free radical "A" is always less reactive than any primary aliphatic free radical. However, within this limit, the reactivity of "A" depends largely on the nature of the radical R. If R is properly chosen, "A" takes part readily in reaction V, but shows little tendency to take part in reaction VI. Under these conditions the radical "B" also reacts with a molecule of olefin more readily than with a molecule of the tetrahalide, particularly when the halogen is chlorine. Thus, high polymers containing many molecules of olefin per  $\cdot\text{CX}_3$  radical are formed. Reaction VI, on the other hand, leads to an addition product where the ratio is one-to-one. Increase in the concentration of the tetrahalide favors reaction VI at the expense of reaction V. When bromine is the halogen in  $\text{CX}_4$ , reaction VI is favored at the expense of V and a much larger yield of one-to-one addition product is formed. Here a ratio of two to four equivalents of carbon tetrabromide per equivalent of olefin in the reaction mixture is sufficient to ensure a high yield of the one-to-one product. However, when chlorine is the halogen in  $\text{CX}_4$ , a ratio of five to one hundred equivalents of carbon tetrachloride per equivalent of olefin in the reaction is necessary to obtain any considerable amount of the one-to-one product. The exact ratio depends on the nature of the radical R in the olefin  $\text{RCH}=\text{CH}_2$  used.

Thus, when one equivalent of styrene (or *p*-chlorostyrene or vinyl naphthalene) is treated with five to fifty equivalents of carbon tetrachloride in the presence of one to five mole per cent. of a diacyl peroxide, polymerization products containing many units of styrene per  $\text{CX}_3$  unit are obtained almost exclusively. However, when styrene is treated with six moles of carbon tetrabromide and the reaction is initiated either by visible light or by a diacyl peroxide, the adduct formed is very largely (90%) the one-to-one product.

The additions of chloroform and of bromoform to olefins proceed by mechanisms similar to that just described. The product formed in the reaction of chloroform with octene-1 indicates that the first step is the removal of a hydrogen atom from chloroform to form a trichloromethyl radical. The reaction then proceeds as indicated

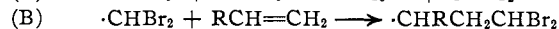


The fact that a hydrogen atom is removed by the attack of a free radical on chloroform is in agreement with the observation<sup>5</sup> that the decomposition

(5) Böeseken and Gelissen, *Rec. trav. chim.*, **43**, 869 (1924); Reijhart, *ibid.*, **46**, 72 (1927).

of benzoyl peroxide in chloroform leads to the formation of benzene but no chlorobenzene.

In bromoform, however, the bromine atoms are more labile than the hydrogen atom under attack by a free radical. The formation of methyl bromide from the reaction of bromoform with octene indicates that the first step is the removal of a bromine atom. The free radical then adds to the olefin as indicated.



The rather poor yields obtained in the additions of chloroform and bromoform to olefins are possibly due to the fact that the bonds in these substances are much less susceptible to attack than are the carbon-chlorine bonds in carbon tetrachloride or the carbon-bromine bonds in carbon tetrabromide, but probably, in part at least, to inhibitors incompletely removed by preliminary purification. This point is being further investigated.<sup>6</sup>

The additions of the halomethanes to olefins follow the same rules as those of other reagents, which add by a free radical mechanism<sup>7</sup>: hydrogen bromide,<sup>7a</sup> bisulfite,<sup>7b</sup> and mercaptans.<sup>7c</sup> In all of these instances, the first step in the addition is the formation of a new free radical of the lowest energy content (*i. e.*, a secondary or tertiary free radical).

### Experimental

**Apparatus.**—The experiments in which a diacyl peroxide was used to initiate the reaction were carried out in a three-necked flask of suitable capacity equipped with a dropping funnel, a thermometer and a reflux condenser, the outlet of which was connected to a trap cooled in ice-water and then to a trap cooled in Dry Ice. If the boiling point of the reaction mixture was below 80° at atmospheric pressure, the outlet from the traps was connected to a tube which dipped into a column of mercury of sufficient height to raise the boiling point of the mixture to 80°. In some experiments the effluent gases were passed through weighed tubes of soda-lime to determine the amount of carbon dioxide evolved in the decomposition of the diacyl peroxide. After the reactants had been placed in the flask the air in the apparatus usually was displaced with nitrogen.

The reactions employing visible light were carried out in a glass vessel containing a neon-type glass coil filled with mercury vapor. In some of the experiments, a coil coated with a fluorescent material was used. The vessel was equipped with a gas inlet tube and a reflux condenser. The reactions employing ultraviolet light were carried out in a quartz flask; a mercury vapor lamp was used as a light source.

**Reaction of Carbon Tetrachloride with Octene-1.**—Octene-1 (b. p. 121.2° (750 mm.);  $n_D^{20}$  1.4090) (37 g., 0.33 mole), carbon tetrachloride (154 g., 1.0 mole) and

(6) The decrease in reactivity of the halomethanes with decreasing number of halogen substituents is further illustrated by the yields obtained in the addition of  $\alpha$ -chlorinated acetic acids to octene. Thus, trichloroacetyl chloride gave a practically quantitative yield of the addition product; methyl dichloroacetate gave a good yield of the addition product, whereas methyl chloroacetate gave a poor yield of the addition product.

(7) (a) Kharasch and Mayo, *THIS JOURNAL*, **55**, 2468 (1933); (b) Kharasch, May and Mayo, *J. Org. Chem.*, **3**, 175 (1938); (c) Kharasch, Read and Mayo, *Chem. & Ind.*, **57**, 752 (1930).

benzoyl peroxide (5 g., 0.02 mole) were heated together under an excess pressure of 15 cm. of mercury. Carbon dioxide was steadily evolved for about four hours, during which time the boiling point of the reaction mixture rose from 90 to 105°. The excess of carbon tetrachloride was then removed by distillation, and the residue was distilled *in vacuo*. The forerun contained a small amount of a white solid material. A fraction (72 g.) boiling at 75–85° (0.05 mm.) was collected and redistilled. The yield of redistilled product was 66 g. (75%); b. p. 78–79° (0.1 mm.);  $n_D^{20}$  1.4770.

*Anal.* Calcd. for  $C_9H_{16}Cl_4$ : Cl, 53.3; mol. wt., 266. Found: Cl, 53.0; mol. wt., 259. This material, as will be shown later, is 1,1,1,3-tetrachlorononane.

The residue (12.5 g.) was distilled in a molecular still. Three fractions were taken; these showed a progressive decrease in chlorine content from 46.8 to 41.0%. A compound consisting of two moles of octene and one mole of carbon tetrachloride contains 37.6% chlorine. Thus the high-boiling material probably is a mixture of  $C_8H_{16}Cl_4$  and  $C_{17}H_{32}Cl_4$ .

When acetyl peroxide instead of benzoyl peroxide was used to initiate the reaction of carbon tetrachloride with octene-1, the results were similar. The yield of 1,1,1,3-tetrachlorononane obtained was 85% of the calculated amount.

**Identification of the Carbon Tetrachloride-Octene-1 Addition Product (1,1,1,3-Tetrachlorononane).**—The main product from the reaction of carbon tetrachloride and octene-1 was shown to be 1,1,1,3-tetrachlorononane by the following series of reactions. The compound (53.2 g.), dissolved in absolute ethanol, was treated with an equimolecular quantity of potassium hydroxide dissolved in ethanol. Slight cooling with tap water was necessary to maintain the temperature of the reaction mixture at 25°. After the mixture had stood overnight, water was added. The oil which separated was taken up in low-boiling ligroin, and the ligroin was removed by evaporation. The residue was distilled at reduced pressure. The fraction (40 g.) boiling at 70–75° (0.6 mm.) is presumably 1,1,1-trichlorononene-2 ( $n_D^{20}$  1.4758).

A 5-g. sample of the supposed 1,1,1-trichlorononene was dissolved in ethyl acetate, was cooled to –73° and treated with ozone. After removal of the ethyl acetate *in vacuo*, the oily residue was treated with water. The mixture was allowed to stand at room temperature for twenty-four hours, and was finally heated to 60° for one hour. The mixture was extracted with low-boiling ligroin, and the ligroin extract was washed with water. When a portion of the ligroin solution was treated with 2,4-dinitrophenylhydrazine reagent, the 2,4-dinitrophenylhydrazone of *n*-heptaldehyde was obtained. After two crystallizations this material melted at 104.5–105.5° and did not depress the melting point of the 2,4-dinitrophenylhydrazone prepared from an authentic sample of *n*-heptaldehyde.

The aqueous phase remaining from the ligroin extraction was extracted with ether in a continuous extractor. The ether was evaporated and the oily residue was distilled from sulfuric acid. The distillate had the odor of chloral and rapidly absorbed water from the air to yield crystals of chloral hydrate. A further identification of this material was made by treating it with 2,4-dinitrophenylhydrazine. The compound obtained (m. p. 125–126°) has been reported to be the 2,4-dinitrophenylhydrazone of ethyl glyoxalate.<sup>8</sup> Similar treatment of an authentic sample of chloral hydrate produced a compound which had the same melting point. Furthermore, the melting point of the unknown compound showed no depression when mixed with about 10% of the compound derived from chloral.

**Reaction of Carbon Tetrachloride with Biallyl.**—A mixture of biallyl (41 g., 0.5 mole), carbon tetrachloride (318 g., 2.07 moles) and acetyl peroxide (3.4 g., 0.029 mole) was heated to reflux under an excess pressure of 15 cm. of mercury. After five hours heating, the boiling

point had risen from 85 to 96°. In the –80° cold trap, there was collected a small amount of methyl chloride.

*Anal.* Calcd. for  $CH_3Cl$ : mol. wt., 50.5. Found: mol. wt., 51.0.

The excess carbon tetrachloride was distilled from the reaction mixture, and the residue was fractionated under reduced pressure. A fraction boiling at 50–60° (0.4 mm.) was collected. Upon distillation this material yielded 31 g. of tetrachloroheptene; b. p. 57–59° (0.4 mm.),  $n_D^{20}$  1.4913.

*Anal.* Calcd. for  $C_7H_{10}Cl_4$ : Cl, 60.1; mol. wt., 236. Found: Cl, 59.7; mol. wt., 226.

A sample of this material was titrated for unsaturation by the standard technique. The results indicated one double bond for a molecular weight of 251.

The residual portion of the reaction mixture (85 g.) was distilled in a molecular still. Successive portions of the distillate (60 g.) showed a progressively decreasing chlorine content from 69.2 to 63.8%. On standing, fine white needles were formed by partial crystallization of the distillate. These were washed quickly with a little methyl alcohol and dried. This material (m. p. 72–74°) appeared to be octachlorooctane.

*Anal.* Calcd. for  $C_8H_{10}Cl_8$ : Cl, 72.8. Found: Cl, 72.6.

The residue from the molecular distillation (25.0 g.) appeared to consist of a compound containing more than one molecule of biallyl for each two molecules of carbon tetrachloride. The molecular weight of this substance was 695, and its chlorine content 62.0%.

When benzoyl peroxide (6 g., 0.026 mole) was heated with a mixture of carbon tetrachloride (231 g., 1.5 mole) and biallyl (41 g., 0.5 mole) the reaction proceeded in a manner similar to that described for the case when acetyl peroxide was used. The products were tetrachloroheptene (36 g., 31%) and 77 g. of a higher-boiling substance which appeared to consist of octachlorooctane mixed with material of higher molecular weight.

**Reaction of Carbon Tetrachloride with Styrene.**—A mixture of redistilled styrene (21 g., 0.2 mole), carbon tetrachloride (185 g., 1.2 mole) and acetyl peroxide (1.2 g., 0.01 mole) was heated for eight hours under *ca.* 920 mm. of mercury pressure. Then another 1.2 g. of acetyl peroxide in a small amount of carbon tetrachloride was added and heating was continued for six hours longer. After removal of the carbon tetrachloride there remained 26 g. of a white, tacky material containing 7.6% chlorine. This value indicates that the material contains an average of about 16 styrene units for each molecule of carbon tetrachloride.

**Reaction of Carbon Tetrachloride with Propylene.**—Carbon tetrachloride (400 g., 2.6 moles) and benzoyl peroxide (2.0 g., 0.083 mole) were placed in an apparatus similar to that used in the previous experiments with the exception that it was equipped with gas inlet tube containing a fritted glass disc. Propylene was slowly passed into the reaction mixture which was maintained at 80°. Some propylene escaped from the reaction mixture and was condensed in the cold trap. After three hours the excess carbon tetrachloride was removed by distillation and the residue was distilled at reduced pressure. A fraction (4.5 g.) was obtained which appeared to be tetrachlorobutane; b. p. 65–69° (20 mm.),  $n_D^{20}$  1.4852.

*Anal.* Calcd. for  $C_4H_6Cl_4$ : Cl, 72.5. Found: Cl, 71.0.

**Reaction of Carbon Tetrachloride with Ethylene.**—The reaction of carbon tetrachloride and ethylene was carried out in a manner similar to that described for propylene. Ethylene was passed into a hot mixture of carbon tetrachloride and benzoyl peroxide for ten hours, during which period more benzoyl peroxide was occasionally added. By distillation of the reaction mixture there was isolated a fraction (10 g.) boiling at 40 to 65° (32 mm.). This appeared to be a mixture of tetrachloropropane and chlorobenzene. By distillation at atmospheric pressure, there was obtained a quantity of tetrachloropropane (b. p. 155°;  $n_D^{20}$  1.4825). Much better yields were obtained

(8) Chattaway and Bennet, *J. Chem. Soc.*, 2851 (1927).

by carrying out this reaction at about 2-3 atmospheres ethylene pressure. It is also important to displace all of the oxygen in the system by an inert gas, preferably nitrogen.

**Reaction of Carbon Tetrabromide with Octene-1.**—A mixture of octene-1 (56 g., 0.5 mole) and carbon tetrabromide (600 g., 1.8 mole) was warmed to 75°, whereupon the carbon tetrabromide dissolved. The warm solution was illuminated with visible light for seven hours during which time it was stirred occasionally by bubbling a little nitrogen through it. The excess carbon tetrabromide was removed by distillation at reduced pressure; only a trace of unchanged octene could be recovered. The residue (205 g.) was distilled *in vacuo*. There was obtained 196 g. (88%) of tetrabromononane, b. p. 125-130° (0.2 mm.);  $n_{D}^{20}$  1.5484.

*Anal.* Calcd. for  $C_9H_{16}Br_4$ : Br, 72.1; mol. wt., 444. Found: Br, 72.8; mol. wt., 441.

When a mixture of octene-1 (92 g.), carbon tetrabromide (503 g.) and acetyl peroxide (2 g.) was warmed to 80°, a vigorous reaction occurred and part of the material boiled out of the reaction flask. Distillation of the remainder of the mixture yielded tetrabromononane (105 g.), identical with the product described above.

**Reaction of Carbon Tetrabromide with Styrene.**—A mixture of styrene (10 g., 0.1 mole), carbon tetrabromide (203 g., 0.61 mole), and carbon tetrachloride (173 g., 1.12 moles) was illuminated with visible light for four hours during which time the temperature was maintained at 90°. The carbon tetrachloride was removed by distillation at atmospheric pressure and most of the excess carbon tetrabromide was removed by distillation at reduced pressure. The last traces of carbon tetrabromide were removed by sublimation *in vacuo*. The residue, a brown oil weighing 46 g., was distilled in a small Claisen flask. After a small forerun the main fraction was collected; it boiled at 112-124° (0.1 mm.). On standing a short time the distillate crystallized to form a white solid m. p. 57-59°. The yield of product, which was shown to be 1,1,1,3-tetrabromo-3-phenylpropane, was 41.8 g. (96%).

*Anal.* Calcd. for  $C_9H_8Br_4$ : Br, 73.4. Found: Br, 73.3.

**Identification of the Carbon Tetrabromide-Styrene Addition Product (1,1,1,3-Tetrabromo-3-phenylpropane).**—The identity of the product from the reaction of carbon tetrabromide with styrene was confirmed by converting it to cinnamic acid by the following method. A portion of the product was refluxed for twelve hours with 18% hydrochloric acid and a small amount of cuprous chloride. At the end of that time, an equal volume of water was added and the mixture allowed to stand overnight. The brown tar which had formed was then extracted with boiling water. From the water there separated on cooling crystals of cinnamic acid (m. p. 131.5-132.5°) which did not depress the melting point of an authentic sample of cinnamic acid.

**Reaction of Carbon Tetrabromide with Ethylene.**—A mixture of carbon tetrabromide (213 g., 0.64 mole) and carbon tetrachloride (177 g., 1.15 moles) was illuminated with visible light. Ethylene was slowly bubbled into the mixture for seven hours during which time the temperature was maintained at 40°, and a 14 cm. pressure head of mercury was attached to the outlet of the apparatus. The carbon tetrachloride was removed by distillation at atmospheric pressure and the excess carbon tetrabromide by sublimation *in vacuo*. The brown oily residue was distilled *in vacuo*. There was obtained a colorless oil which appeared to be tetrabromopropane; b. p. 65-68° (0.3 mm.);  $n_{D}^{20}$  1.6090.

*Anal.* Calcd. for  $C_3H_4Br_4$ : Br, 90.0. Found: Br, 89.2.

**Reaction of Chloroform with Octene-1.**—Octene-1 (28 g., 0.25 mole), chloroform (120 g., 1 mole) and benzoyl peroxide (0.5 g.) were mixed and heated under 20 cm. excess pressure for ten hours during which time the boiling point of the mixture rose from 80 to 92°. After four hours,

an additional amount of benzoyl peroxide (1.0 g., total 0.006 mole) was added. On distillation of the reaction mixture about 15 g. of unchanged octene was recovered; on further distillation, a fraction boiling at 65-75° (0.1 mm.) was obtained. When redistilled, this material gave a product which was shown to be 1,1,1-trichlorononane, 13 g. (22%); b. p. 65-70° (0.5 mm.);  $n_{D}^{20}$  1.4620.

*Anal.* Calcd. for  $C_9H_{17}Cl_3$ : Cl, 46.0; mol. wt., 231.5. Found: Cl, 43.7; mol. wt., 225.

The residual portion of the reaction mixture (12 g.) was distilled in a molecular still. The main fraction of this distillate contained 28.2% chlorine. The compound consisting of two moles of octene and one mole of chloroform contains 31.0% chlorine.

**Identification of the Chloroform-Octene-1 Addition Product (1,1,1-Trichlorononane).**—The product obtained from chloroform and octene-1 was shown to be 1,1,1-trichlorononane by converting it to pelargonic acid by the method of Prins.<sup>9</sup> A mixture of 1.0 g. of the product and 5 ml. of concentrated sulfuric acid was vigorously stirred and heated to 80-90° for three hours. At the end of that time, no more hydrogen chloride was evolved. The mixture was poured into ice water and the solution was extracted with ether. The ether solution was extracted with aqueous sodium bicarbonate; the bicarbonate solution was acidified and extracted with ether. Evaporation of the ether from the final extract yielded 0.2 g. of an oily acid. The *p*-toluidide of this acid melted at 81.8-82.5° and did not depress the melting point of an authentic sample of the *p*-toluidide of pelargonic acid.

**Reaction of Chloroform with Biallyl.**—Biallyl (21 g., 0.25 mole), chloroform (119 g., 1 mole) and acetyl peroxide (1.9 g., 0.016 mole) were heated together under 37 cm. excess pressure. Carbon dioxide (1.7 g., 0.039 mole) and 485 ml. of gas (presumably methane) were evolved. The chloroform was distilled from the reaction mixture and the residue was distilled *in vacuo*. The fraction (2.7 g., 5%) boiling at 38-40° (0.2 mm.) was collected. Upon distillation, this material gave a compound which presumably is trichloroheptene; b. p. 78° (10 mm.),  $n_{D}^{20}$  1.4719.

*Anal.* Calcd. for  $C_7H_{11}Cl_3$ : Cl, 52.8. Found: Cl, 52.5.

The residue (9 g.) was distilled in a molecular still. The main fraction of the distillate showed a chlorine content of 38.7%.

**Reaction of Bromoform with Octene-1.**—A mixture of bromoform (284 g., 1.12 moles), and octene-1 (43.3 g.) was heated to 80°, and a solution of acetyl peroxide (3.2 g., 0.027 mole) in octene (18.0 g., total octene 0.55 mole) was added slowly during a period of one hour. Heating was continued for four hours longer. During the reaction, carbon dioxide (1.32 g., 0.03 mole) was evolved and a liquid (0.4 g.) was condensed in the cold trap. This liquid was shown to be methyl bromide.

*Anal.* Calcd. for  $CH_3Br$ : mol. wt., 95. Found: mol. wt., 90.

The unchanged octene-1 and bromoform were removed from the reaction mixture at reduced pressure. Distillation of the residue yielded a product (63 g.) which was shown to be 1,1,3-tribromononane; b. p. 99-102° (0.3 mm.);  $n_{D}^{20}$  1.5178.

*Anal.* Calcd. for  $C_9H_{17}Br_3$ : Br, 65.8; mol. wt., 365. Found: Br, 65.1; mol. wt., 361.

**Identification of the Bromoform-Octene-1 Addition Product (1,1,3-Tribromononane).**—The product obtained from the reaction of bromoform and octene-1 was shown to be 1,1,3-tribromononane by converting it to 2-nonenal by the following procedure.

The addition product (40.0 g.) was slowly dropped into a solution of sodium (15.2 g.) in absolute ethanol (400 ml.). After the addition was complete, potassium iodide (1 g.) was added to the reaction mixture, and it was heated under reflux for fifteen hours, and allowed to cool. Acetic acid

(9) Prins, *J. prakt. Chem.*, **89**, 414 (1914).

(25 g.) was then added, and the mixture was subjected to steam distillation. The oil which distilled was taken up in low-boiling ligroin, the ligroin solution washed with water, and sodium carbonate solution (10%), and dried over anhydrous sodium sulfate. On distillation, there was obtained an oil (9 g.), b. p. 90–110° (12 mm.);  $n_D^{20}$  1.4520. This material formed a 2,4-dinitrophenylhydrazone which melted at 125–126°, and did not depress the melting point of an authentic sample of the 2,4-dinitrophenylhydrazone of 2-nonenal.<sup>10</sup>

**Reaction of Bromoform with Styrene.**—A mixture of bromoform (156 g., 0.62 mole), redistilled styrene (15.6 g., 0.15 mole), and benzoyl peroxide (1.0 g.) was heated at 100° for four hours. Then an additional amount of benzoyl peroxide (0.8 g., total benzoyl peroxide 0.008 mole) was added and heating was continued for two hours longer. The excess bromoform was removed by distillation at reduced pressure, and a small amount of benzoic acid was removed by sublimation *in vacuo*. The residue (26.6 g.) was a thick black sirup which appeared to consist chiefly of a product containing two moles of styrene to one mole of bromoform with smaller amounts of products containing one, three and perhaps four moles of styrene per mole of bromoform.

*Anal.* Calcd. for  $C_{17}H_{17}Br_3$ : Br, 52.2; mol. wt., 460. Found: Br, 44.6; mol. wt., 507.

The sirupy reaction product (26 g.) was transferred to a small distilling flask and distilled *in vacuo*. The distillate (2.6 g.) appeared to be slightly impure phenyltribromopropane, b. p. 110–115° (0.1 mm.),  $n_D^{20}$  1.6110.

*Anal.* Calcd. for  $C_9H_9Br_3$ : Br, 67.2. Found: Br, 65.4.

**The Reaction of Carbon Tetrachloride with Octene-1 in Ultraviolet Light.**—Carbon tetrachloride (182.1 g., 1.18 mole) and octene-1 (39.9 g., 0.36 mole) were mixed in a quartz reflux apparatus. The mixture was held at its boiling point and irradiated with a 500-watt Hanovia ultraviolet lamp for a period of four hours.

(10) Scanlan and Swern, *THIS JOURNAL*, **62**, 2309 (1940).

After the unchanged carbon tetrachloride and octene-1 had been removed by distillation, 1,1,1,3-tetrachlorononane (b. p. 72–75° (0.1 mm.);  $n_D^{20}$  1.4768; 20.3 g.) distilled. A residue (3.9 g.) remained in the distilling flask.

Because yields obviously depend on intensity and duration of irradiation no percentage yield is recorded in Table I.

### Summary

In photochemical or peroxide-induced reactions with olefins containing terminal double bonds, carbon tetrachloride, carbon tetrabromide, chloroform and bromoform yield addition and polymerization-addition products.

Reactions of carbon tetrachloride with octene-1, styrene, ethyl acrylate, allyl, propylene and ethylene; of carbon tetrabromide with octene-1, styrene and ethylene; of chloroform with octene-1 and allyl; and of bromoform with octene-1 and styrene are described.

For all the halides mentioned, chain reactions may be induced by the free radicals generated in the thermal decomposition of diacyl peroxides.

Carbon tetrabromide participates in chemical reactions under the influence of visible light; carbon tetrachloride requires ultraviolet light.

Reaction mechanisms have been proposed, and the determined structures of one-to-one halide-olefin addition products are consistent therewith.

Approximately equivalent ratios of halide to olefin in polymerization-addition products have been estimated.

CHICAGO, ILLINOIS

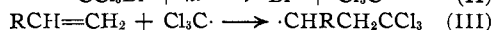
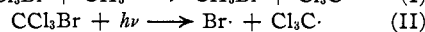
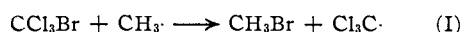
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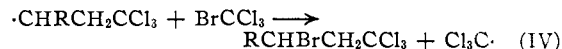
## Reactions of Atoms and Free Radicals in Solution. XI. The Addition of Bromotrichloromethane to Olefins

BY M. S. KHARASCH, OTTO REINMUTH AND W. H. URRY

The considerations outlined in our previous paper on the addition of carbon tetrachloride, carbon tetrabromide, chloroform and bromoform to olefins,<sup>1</sup> suggested an investigation of the reactions of heteropolyhalides with olefins. The addition reactions of bromotrichloromethane with a number of olefins are described in the present paper. These reactions, both with regard to ease of initiation and propagation, and the nature of the products formed, resemble those of carbon tetrabromide rather than those of carbon tetrachloride. It is, therefore, a reasonable supposition that the reactions of bromotrichloromethane with olefins are initiated by reactions I and II, and are propagated by reactions III and IV.



(1) Kharasch, Jensen and Urry, *THIS JOURNAL*, **69**, 1100 (1947).



The following additions have been effected:

