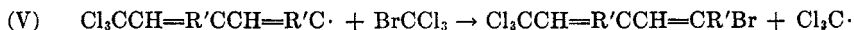
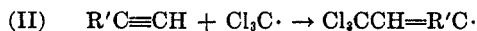
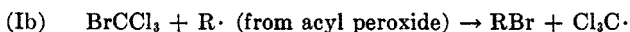
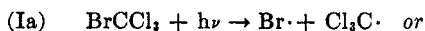


REACTIONS OF ATOMS AND FREE RADICALS IN SOLUTION. XXII.
THE ADDITION OF POLYHALOMETHANES TO ALKYNES

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Under visible illumination, or in the presence of thermally-decomposing acyl peroxides, bromotrichloromethane reacts additively with 1-octyne to form the one-to-one adduct exclusively. With phenylacetylene or 2-octyne, however, bromotrichloromethane forms, not only the one-to-one adducts, but products that result from the condensation of one molecule of the halide with two molecules of the respective alkynes. Under the experimental conditions imposed in this study these one-to-two adducts comprise, respectively, 20 and 16 per cent of the total products. The reaction scheme proposed to account for the observed products may be outlined as follows:



When carbon tetrachloride is substituted for bromotrichloromethane in analogous reactions of 1-octyne and 2-nonyne the yields of one-to-one adducts are extremely small.¹ The reaction products consist chiefly of high-boiling materials that decompose even under very low-pressure distillation. From the apparent molecular weights and the chlorine contents of admittedly impure fractions it is possible to surmise that these products consist of: (a) some material of the composition $\text{R}'\text{CCl}=\text{CHCl}$, or perhaps more probably, $\text{R}'\text{CH}=\text{C}=\text{CCl}_2$,² (b) a small amount of the one-to-one adduct, and (c) a mixture of higher condensates containing many molecules of alkyne and many chlorine atoms.

Under similar conditions phenylacetylene yields a short-chain "polymer" containing chlorine.

Whereas the alkenes (except styrene) corresponding to the alkynes used in this study produce good yields of one-to-one carbon tetrachloride adducts (1), it is evident that with respect to the over-all addition reaction the alkynes constitute the less reactive class. It is of interest to determine whether the relative unreactivity of the alkynes must be referred to the first step of the addition

¹ It should be noted that in photochemical reactions involving carbon tetrachloride ultraviolet irradiation is necessary.

² The product here suggested might result from the loss of a chlorine atom (perhaps through disproportionation) from the product of the first additional step [$\text{Cl}_3\text{CCH}=(n\text{-C}_6\text{H}_{13})\text{C}\cdot$], accompanied by a hydrogen-atom shift. Evidence for such processes has been obtained in other work in this laboratory (Kharasch and Büchi, unpublished work).

(corresponding to equation II), to the second step (corresponding to equation III), to or both.

Because both bromotrichloromethane and carbon tetrachloride generate the same primary free radical ($\text{Cl}_3\text{C}\cdot$), and because the alkenes concerned in this study produce good yields of one-to-one adducts with both bromotrichloromethane (2) and carbon tetrachloride, whereas alkynes produce comparable yields of one-to-one adducts only with the former, it may be concluded that in the second step of the carbon tetrachloride addition the alkyne intermediate is less reactive than the corresponding alkene intermediate. Specifically, the free radical derived by the addition of a trichloromethyl radical to an alkyne is less reactive with respect to its ability to attack carbon tetrachloride (equation IIIa) than is the free radical derived by the addition of a trichloromethyl radical to the corresponding alkene (equation IIIb).



In order to establish a basis for comparison of reactivities in the first step of the carbon tetrachloride addition (corresponding to equation II), carbon tetrachloride, 1-octene, 1-octyne, and acetyl peroxide, in the molecular proportions 110:20:5:1, were caused to react in the usual way. In such experiments the yield of one-to-one halide-1-octene adduct (64-69 per cent) is only a little lower than in similar experiments in which 1-octyne is omitted (72-74 per cent). It may therefore be inferred that the addition of a trichloromethyl radical to 1-octene takes place more readily than does the similar addition to the corresponding alkyne, 1-octyne.

In consideration of the range of reactivities (with respect to the reaction represented by equation II) displayed by variously substituted ethenes (3), there is a reasonable supposition that variously substituted ethynes might also vary widely in reactivity. It by no means follows from the observations already recorded that *any* alkyne is less reactive than *any* alkene.

Evidence that this is not the case is supplied by an experiment similar to the one just described in which phenylacetylene is substituted for 1-octyne. It was found that phenylacetylene completely inhibits the formation of the halide-1-octene adduct, although the one-to-one halide-phenylacetylene adduct is not formed either. This observation is interpreted as indicating that phenylacetylene undergoes the first step of the addition reaction (corresponding to equation II) much more readily than does 1-octene. Phenylacetylene therefore captures virtually all the trichloromethyl radicals liberated, thus blocking 1-octene out of the reaction. The intermediate free radical formed by the addition of a trichloromethyl radical to a phenylacetylene molecule is, however, incapable of undergoing the second step of the addition reaction (equation IIIa) at a rate competitive with that of the condensation reaction ("polymerization," equation IV). The net effect is the preponderant formation of chlorine-containing phenylacetylene "polymers."

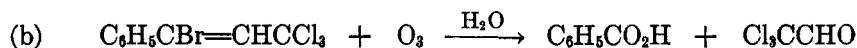
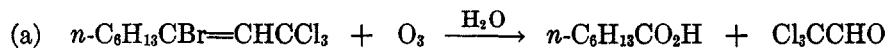
To facilitate further comparisons of relative reactivities of alkynes and alkenes

with respect to the first step of the addition reaction bromotrichloromethane was chosen as the addendum for the reason that it readily undergoes the second step of the addition reaction (corresponding to equation III) with all the intermediates formed in the first step.

When a competitive reaction is conducted in this way with styrene and phenylacetylene, the one-to-one adduct of the former was formed to the total exclusion of that of the latter. It would thus seem a safe conclusion that, although some alkynes react with trichloromethyl radicals more readily than do some alkenes, any given alkene is more reactive in this respect than is the *corresponding* alkyne.

Several other competitions which do not bear so directly on this point, but which are, nevertheless, of incidental interest were studied. 1-Octyne and allyl chloride were found to react with bromotrichloromethane at comparable rates. Phenylacetylene reacts much more rapidly than either allyl or methallyl chloride.

Identification of one-to-one addition products. The expected one-to-one addition products were tentatively identified by their apparent molecular weights (cryoscopic, benzene) and halogen contents (silver equivalents).³ Confirmations of tentative identifications were obtained by ozonolytic degradations:



Details of the procedures are described in the experimental part.

EXPERIMENTAL

Apparatus and procedure. The apparatus and the general method of operation employed have been described previously (3). Any significant deviations from the general method are noted at the appropriate points hereafter.

Photochemical reaction of 1-octyne with bromotrichloromethane. A solution of 31.9 g. (0.29 mole) of 1-octyne (n_D^{20} 1.4182) in 360.0 g. (1.79 mole) of bromotrichloromethane (n_D^{20} 1.5062), maintained at 65° by an oil-bath, was internally illuminated with a neon-type glass coil containing mercury vapor for a period of 4½ hours. Residual starting materials were removed from the reaction mixture under reduced pressure, and the crude product (28.0 g.) was subjected to "molecular" distillation. The following fractions were collected: fraction 1 (8.4 g.), n_D^{20} 1.5093, mol. wt., 281, Ag equiv. 82.7; fraction 2 (8.4 g.), n_D^{20} 1.5117, mol. wt., 288, Ag equiv. 89.0; fraction 3 (9.3 g.), n_D^{20} 1.5136, mol. wt., 309, Ag equiv. 79.4; fraction 4 (0.8 g.), mol. wt., 362, Ag equiv. 83.3.

Fraction 3 consisted essentially of the one-to-one adduct, 1,1,1-trichloro-3-bromo-2-nonenone (calc'd mol. wt., 308.5; calc'd Ag equiv., 77.1).

Peroxide-induced reaction of 1-octyne with bromotrichloromethane. A solution of 0.94 g. (0.008 mole) of acetyl peroxide in a small portion of a total of 27.5 g. (0.25 mole) of 1-octyne was added slowly over a two-hour period to a solution of the greater part of the 1-octyne in 198.5 g. (1.0 mole) of bromotrichloromethane, maintained at a temperature of 100°. One hour after completion of the addition heating was discontinued and residual reactants

³ The term silver equivalent is defined as the number of grams of the halogen-containing compound which react with one mole of silver nitrate in accordance with the equation: $\text{Ag}^+ + \text{X}^- \rightarrow \text{AgX}$.

were removed under reduced pressure. "Molecular" distillation of the product effected the separation of 61.2 g. (80%) of material identical in properties with that of fraction 3 of the photochemical reaction product. Less than a gram of material of higher molecular weight was present.

Identification of the bromotrichloromethane-1-octyne addition product (1,1,1-trichloro-3-bromo-2-nonene). The oily and aqueous layers resulting from ozonolysis of the addition product and hydrolytic cleavage of the ozonide were separated.

The aqueous layer was extracted with ether, and solvent was evaporated from the extract. Sulfuric acid was added to the residue, and the mixture was subjected to distillation. The distillate yielded a 2,4-dinitrophenylhydrazone which melted at 125–127° in agreement with the melting point reported for the derivative of chloral (4). There was no depression of melting point upon mixture with a sample prepared from chloral hydrate.

The oily layer was taken up in aqueous sodium hydroxide, and the alkaline solution was extracted with ether to remove neutral impurities. Acidification of the extracted aqueous solution yielded an acid which was converted to the *p*-bromophenacyl ester by the method of Reid and Judefind (5). The melting point of this derivative (70–71°) was not depressed by mixture with a sample of ester similarly prepared from authentic heptanoic acid (6).

The identity of the one-to-one bromotrichloromethane-1-octyne adduct as 1,1,1-trichloro-3-bromo-2-nonene is thus established.

Photochemical reaction of 2-octyne with bromotrichloromethane. A solution of 16.7 g. (0.15 mole) of 2-octyne (n_D^{20} 1.4278) in 366.4 g. (1.85 mole) of bromotrichloromethane was internally illuminated for a period of 26 hours. Removal of unchanged reactants under reduced pressure yielded 19.0 g. of crude product, which was separated by "molecular" distillation into distillate (15.6 g.) and relatively non-volatile residue (3.1 g.). By the cryoscopic method in benzene, the distillate had an apparent molecular weight of 308.0, consistent with that calculated for the one-to-one halide-2-octyne adduct, $C_9H_{11}BrCl_3$ (308.5).

Peroxide-induced reaction of 2-octyne with bromotrichloromethane. A solution of 0.59 g. (0.005 mole) of acetyl peroxide in 27.5 g. (0.25 mole) of 2-octyne and 198.5 g. (1.0 mole) of bromotrichloromethane was allowed to react at 100° for 2½ hours. After removal of the solvents the product was distilled with the aid of a short Vigreux column, yielding 6.3 g. of relatively low-boiling fractions and 15.2 g. of material (n_D^{20} 1.5185) boiling at 92–95° under 2 mm. The principal distillate had a halogen content (Ag equiv., 80.1) consistent with that calculated for the one-to-one halide-2-octyne adduct, $C_9H_{11}BrCl_3$ (Ag equiv., 77.1).

Photochemical reaction of phenylacetylene with bromotrichloromethane. A solution of 50.0 g. (0.49 mole) of phenylacetylene (n_D^{20} 1.5482) in 500.0 g. (2.52 moles) of bromotrichloromethane, maintained at 60° by means of an oil-bath, was internally illuminated for a period of 19 hours. Unchanged reactants were removed under reduced pressure, and the product was subjected to "molecular" distillation. The following fractions were collected: fraction 1 (14.5 g.), n_D^{20} 1.5961, mol. wt., 275, Ag equiv. 78.3; fraction 2 (15.4 g.), n_D^{20} 1.5968, mol. wt., 279, Ag equiv. 75.9; fraction 3 (15.1 g.), n_D^{20} 1.5983, mol. wt., 270, Ag equiv. 74.3; fraction 4 (7.6 g.), n_D^{20} 1.6014, mol. wt., 293, Ag equiv. 75.1; fraction 5 (9.2 g.), n_D^{20} 1.6100, mol. wt., 299, Ag equiv. 77.8; fraction 6 (16.0 g.), mol. wt., 376, Ag equiv. 95.2.

Although obviously impure, or modified by secondary reactions, fractions 1 to 4 inclusive must be derived principally from the one-to-one halide-octyne adduct.

The apparent molecular weight (299) and the halogen content (Ag equiv., 77.8) of fraction 5 agree fairly well with those calculated (mol. wt., 300.5; Ag equiv., 75.1) for the one-to-one halide-alkyne adduct, 1-bromo-1-phenyl-3,3,3-trichloropropene.

Anal. Calc'd for $C_9H_8BrCl_3$: C, 36.0; H, 2.0.

Found: C, 35.8; H, 2.2.

The apparent molecular weight (376) and the halogen content (Ag equiv., 95.2) of fraction 6 correspond roughly to these calculated for a product derived from one molecule of halide and two molecules of octyne (mol. wt., 402.5; Ag. equiv., 100.6). Assuming that fraction 6 consists essentially of the two-to-one adduct, contaminated with one-to-one

adduct, the halogen analysis and the molecular weight determination would indicate a 78-74% content of the former to 22-26% of the latter.

Peroxide-induced reaction of phenylacetylene with bromotrichloromethane. A solution of 0.94 g. (0.008 mole) of acetyl peroxide in a small portion of a total of 198.5 g. (1.0 mole) of bromotrichloromethane was added gradually over a two-hour period to a solution of 25.5 g. (0.25 mole) of phenylacetylene in the greater part of the halide, maintained at a temperature of 105°. One hour after completion of the addition heating was discontinued and residual reactants were removed under reduced pressure. "Molecular" distillation of the product yielded the following fractions: fraction 1 (7.0 g.), n_D^{20} 1.6110, mol. wt., 278; fraction 2 (6.4 g.), n_D^{20} 1.6150, mol. wt., 287; fraction 3 (14.9 g.), n_D^{20} 1.6114, mol. wt., 280; residue (28.2 g.).

From the residue were isolated small amounts of white crystals (m.p., 176-177°; Ag equiv., 80) and of orange crystals (m.p., 203-205°).

Identification of the bromotrichloromethane-phenylacetylene addition product (1-bromo-1-phenyl-3,3,3-trichloropropene). Ozonolysis of the supposed one-to-one adduct and hydrolytic cleavage of the ozonide yielded benzoic acid (m.p. and mixture m.p., 122-123°) and chloral, identified through its 2,4-dinitrophenylhydrazone (m.p. and mixture m.p., 123.5-124.0°). In a second ozonolytic experiment trichloroacetic acid, identified through its *p*-nitrobenzyl ester (m.p. and mixture m.p., 82°), rather than chloral, was obtained.

The identity of the one-to-one bromotrichloromethane-phenylacetylene adduct as 1-bromo-1-phenyl-3,3,3-trichloropropene is thus established.

Peroxide-induced reaction of 1-octyne with carbon tetrachloride. By the usual experimental procedure, already described, a total of 8.26 g. (0.07 mole) of acetyl peroxide was gradually (over a period of 16 hours) added to and decomposed in a total of 73.8 g. (0.67 mole) of 1-octyne and 838.3 g. (5.4 moles) of carbon tetrachloride, maintained at the reflux temperature of the reaction mixture. Unchanged reactants were removed under reduced pressure and the product was distilled, yielding the following fractions: fraction 1, 48-56°/4 mm., 4.3 g.; fraction 2, 55-60°/3 mm., 3.0 g.; fraction 3, 91-92°/4 mm., 8.6 g.; residue.

The residue from the original distillation, subjected to "molecular" distillation, yielded the following fractions: fraction 4, 5.0 g.; fraction 5, 4.5 g.; residue 18.4 g., apparent mol. wt., 982, Cl, 34.6%.

Anal. Calc'd for $C_8H_{14}Cl_2$ ($n-C_8H_{13}CCl=CHCl$): Cl, 39.2; mol. wt., 181.0.

Calc'd for $C_8H_{14}Cl_2$ ($n-C_8H_{13}CH=C=CCl_2$): Cl, 36.8; mol. wt., 193.0.

Found (fraction 1): Cl, 37.0; mol. wt., 187; (fraction 2): Cl, 38.3; mol. wt., 196.

Calc'd for $C_8H_{14}Cl_4$ (1:1 adduct): Cl, 53.7; mol. wt., 264.0.

Found (fraction 3): Cl, 46.3; mol. wt., 228; (fraction 4): Cl, 49.3; mol. wt., 283; (fraction 5): Cl, 47.3; mol. wt., 321.

In the final residue there are, on the average, at least nine chlorine atoms and six molecules of octyne per "polymer" molecule.

Peroxide-induced reaction of phenylacetylene with carbon tetrachloride. By the usual experimental procedure, already described, a total of 13.1 g. (0.11 mole) of acetyl peroxide was decomposed, over a period of four hours, in 23.2 g. (0.23 mole) of phenylacetylene and 154.0 g. (1.0 mole) of carbon tetrachloride, maintained at the reflux temperature of the reaction mixture. Removal under reduced pressure of the unchanged reactants left a black, tarry residue which had an apparent molecular weight of 436 and a chlorine content of 16.0%.

The reaction product was dissolved in ether. The addition of methanol to the ethereal solution precipitated a yellow curd-like material. Attempts to crystallize this precipitate from ligroin and other solvents did not affect its color, physical appearance, or melting point range (155-160°). The apparent molecular weight was 2037, and the chlorine content 12.0%.

The material recovered from the carbon-decolorized ether-methanol solution had an apparent molecular weight of 450 and a chlorine content of 12.5%.

Peroxide-induced reaction of 2-nonyne with carbon tetrachloride. In the usual manner,

2.0 g. (0.016 mole) of acetyl peroxide was decomposed in 38.3 g. (0.29 mole) of 2-nonyne (n_D^{20} 1.4325) and 320 g. (2.1 moles) of carbon tetrachloride. After separation from residual reactants the product was distilled at reduced pressure: fraction 1, 44–60°/0.2 mm., Cl, 36.5%; 0.6 g.; fraction 2, 60–90°/0.2 mm., 2.1 g. During the distillation of fraction 2 gas evolution, indicative of decomposition, was noted.

Anal. Calc'd for $C_{10}H_{16}Cl_4$ (1:1 adduct): Cl, 49.0; mol. wt., 288.

Found (fraction 2): Cl, 38.2; mol. wt., 232.

1-Octyne-inhibition of the peroxide-induced reaction of 1-octene with carbon tetrachloride.

In duplicate experiments, conducted in the usual way, acetyl peroxide, 1-octyne, 1-octene, and carbon tetrachloride, in the relative molecular proportions 1:5:20:110, were allowed to interact for periods of 21 and 24 hours, respectively. The yields of the known (1) one-to-one carbon tetrachloride-1-octene adduct, identified by its boiling point (67–74°/1 mm.) and refractive index (n_D^{20} 1.4770), were 64.0% and 69.0%, respectively.

Otherwise comparable experiments with reaction mixtures from which the 1-octyne had been omitted yielded 74.0% and 71.5%, respectively, of the one-to-one adduct (1,1,1,3-tetrachlorononane).

Phenylacetylene-inhibition of the peroxide-induced reaction of 1-octene with carbon tetrachloride. In duplicate experiments similar to those just described, but in which phenylacetylene was substituted for 1-octyne, the mixtures were allowed to interact for 21½ and 24½ hours, respectively. The yields of one-to-one halide-1-octene adduct obtained were only 3.8% and 4.1%, respectively. Quantities of "polymeric" material (ca. 10 g.) approximated those obtained in uninhibited reactions in which the yields of addition product were much larger.

Competition of styrene with phenylacetylene in the photochemical reaction with bromotrichloromethane. A solution of 11.0 g. (0.11 mole) of styrene, 10.0 g. (0.10 mole) of phenylacetylene, and 324.6 g. (1.64 mole) of bromotrichloromethane was internally illuminated by a neon-type mercury-vapor coil for a half-hour. Unchanged reactants were removed under reduced pressure and the residue was subjected to "molecular" distillation. Virtually the whole of the product was thus converted into a crystalline sublimate. Recrystallized from methanol, the material melted at 53–55° and did not depress the melting point of an authentic sample of the known (2) styrenebromo-trichloromethane adduct (1,1,1-trichloro-3-bromo-3-phenylpropane).

Competition of phenylacetylene with allyl chloride in the photochemical reaction with bromotrichloromethane. A solution of 30.0 g. (0.25 mole) of phenylacetylene, 19.1 g. (0.25 mole) of allyl chloride, and 397.0 g. (2.0 moles) of bromotrichloromethane was internally illuminated by a neon-type mercury-vapor coil for two hours. Removal of unchanged reactants under reduced pressure yielded 2.9 g. of residue.

Anal. Calc'd for $C_4H_5BrCl_3$: Ag equiv., 55.0.

Calc'd for $C_9H_7BrCl_3$: Ag equiv., 75.1. Found: Ag equiv., 80.0.

It is concluded the product consists principally of the one-to-one phenylacetylene-bromotrichloromethane adduct (1-bromo-1-phenyl-3,3,3-trichloropropene).

Competition of phenylacetylene with methallyl chloride in the photochemical reaction with bromotrichloromethane. A solution of 30.0 g. (0.25 mole) of phenylacetylene, 24.5 g. (0.25 mole) of methallyl chloride, and 401.0 g. (2.0 moles) of bromotrichloromethane was internally illuminated by a neon-type mercury-vapor coil for two hours. Removal of unchanged reactants under reduced pressure yielded 10.4 g. of residue.

Anal. Calc'd for $C_8H_7BrCl_3$: Ag equiv., 57.8.

Calc'd for $C_9H_7BrCl_3$: Ag equiv., 75.1. Found: Ag equiv., 83.1.

It is concluded that the product consists principally of the one-to-one phenylacetylene-bromotrichloromethane adduct (1-bromo-1-phenyl-3,3,3-trichloropropene).

Competition of 1-octyne with allyl chloride in the photochemical bromotrichloromethane reaction. A solution of 27.5 g. (0.25 mole) of 1-octyne, 19.1 g. (0.25 mole) of allyl chloride, and 397.0 g. (2.0 moles) of bromotrichloromethane was internally illuminated by a neon-type mercury-vapor coil for three hours, at which time approximately 25% of the hydro-

carbons had reacted. After removal of unchanged reactants at reduced pressure, the residue (28.2 g.) was subjected to "molecular" distillation: fraction 1 (5.6 g.), n_D^{20} 1.5254, mol. wt., 275, Ag equiv., 58.0, Cl/Br 3.4; fraction 2, (8.0 g.), n_D^{20} 1.5232, mol. wt., 285, Ag equiv., 59.7, Cl/Br 2.8; fraction 3 (8.5 g.), n_D^{20} 1.5208, mol. wt., 287, Ag equiv., 62.4, Cl/Br 3.2; fraction 4 (3.6 g.), n_D^{20} 1.5151, mol. wt., 301, Ag equiv. 78.2, Cl/Br 1.4; residue (1.2 g.), mol. wt., 339, Ag equiv., 71.3, Cl/Br 1.8.

The calculated and observed constants for the respective one-to-one adducts are: Allyl chloride adduct ($C_4H_5BrCl_4$): n_D^{20} 1.5337, mol. wt., 275.0, Ag equiv., 55.0, Cl/Br 4; 1-Octyne adduct ($C_8H_{14}BrCl_3$): n_D^{20} 1.5180, mol. wt., 308.1, Ag equiv., 77.1, Cl/Br 3.

In view of the known tendency of such adducts to undergo decomposition upon distillation it may be inferred from the data recorded only that very little "polymeric" material was formed in the course of the experiment, and that both adducts were present in quantities sufficient to justify the conclusion that the over-all rates of the two addition reactions are comparable.

SUMMARY

1. In photochemical or peroxide-induced reactions with 1-alkynes bromotrichloromethane yields one-to-one adducts and polymerization-addition products.

2. Any 1-alkyne is less reactive than the corresponding 1-alkene, both in ability to add free trichloromethyl radicals and in the ability of the free radical thus formed to react with bromotrichloromethane.

3. Phenylacetylene is less reactive than styrene in so far as the ability to add a free trichloromethyl radical is concerned but more reactive than 1-octene.

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