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REACTIONS OF ATOMS AND FREE RADICALS IN SOLUTION. XXIX. THE RELATIVE REACTIVITIES OF OLEFINS TOWARD THE FREE TRICHLOROMETHYL RADICAL

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The experimental conditions essential to comparison of the relative reactivities of olefins toward the free trichloromethyl radical have been discussed in previous publications (1), and an ordered series of the relative reactivities of a number of cyclic and acyclic olefins has been compiled. An expansion of this series to include a number of substituted styrenes and butadiene[2] seemed desirable because of the industrial importance of these monomers.

Adducts of bromotrichloromethane and olefins. In the comparison of the relative reactivities of styrene, butadiene, *p*-chlorostyrene, and α-methylstyrene toward the free trichloromethyl radical it was necessary to know the physical constants and properties of the adducts of bromotrichloromethane and the respective olefins. The adducts of bromotrichloromethane with styrene and butadiene[3] have been previously prepared. The adduct formed from bromotrichloromethane and *p*-chlorostyrene was established, by analyses and hydrolysis to *p*-chlorocinnamic acid as 1-chloro-4-(α-bromo-γ,γ,γ-trichloropropyl)benzene (p-ClC_6H_4CHBr-CH_2CCl_3). The formation of the dehydrobrominated one-to-one adduct from α-methylstyrene and bromotrichloromethane may be represented as follows:[4]

$$BrCCl_3 \xrightarrow{h\nu} Cl_3C\cdot + Br\cdot$$

$$1.\quad CH_3(C_6H_5)C{=}CH_2 + Cl_3C\cdot \rightarrow CH_3(C_6H_5)\underset{\bullet}{C}CH_2CCl_3 \quad \mathbf{(A)}$$

$$2.\quad \mathbf{A} + BrCCl_3 \rightarrow CH_3(C_6H_5)CBrCH_2CCl_3 \quad \mathbf{(B)}$$

$$3.\quad \mathbf{B} \xrightarrow{\Delta} CH_2{=}C(C_6H_5)CH_2CCl_3 + HBr$$

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[1] The work reported in this paper was done in connection with the Government Research Program in synthetic rubber under contract with the Office of Synthetic Rubber, Reconstruction Finance Corporation.

[2] Through an unfortunate oversight, the reactivities of styrene and butadiene were estimated [Ref. (1b)] by comparison of their reactivities with that of octene-1. Since both olefins are very much more reactive than octene-1 in competitive experiments employing equimolecular concentrations of octene-1 and olefin (95% of butadiene adduct was obtained; in a similar experiment with octene-1 and styrene about 99% of the styrene adduct was obtained) little or no octene-1 adduct was obtained, and no conclusion regarding the relative reactivities of butadiene and styrene should have been drawn from these data. This oversight has now been corrected by a direct comparison of the reactivities of butadiene and styrene toward free trichloromethyl radicals.

[3] Kharasch and Nudenberg, unpublished work.

[4] An alternative mechanism, whereby the dehydrobrominated one-to-one adduct of α-methylstyrene and bromotrichloromethane could be formed, is to assume that the adduct

The structure of the adduct was established by ozonolysis.

$$H_2C{=}C(C_6H_5)CH_2CCl_3 + O_3 \xrightarrow{HOH} CH_2O + C_6H_5COCH_2CCl_3$$

The formation of an adduct comprising two molecules of α-methylstyrene and one molecule of bromotrichloromethane was also noted (see footnote 4 and the experimental part).

It had been the original intention to include isopropenyl acetate in this series of olefins compared as to relative reactivities. However, because of the complexity of the reaction of this olefin with bromotrichloromethane (see the following equations) it seemed unprofitable to attempt any comparisons.

$$BrCCl_3 \xrightarrow{h\nu} Cl_3C\cdot + Br\cdot$$

1. $CH_2{=}C(CH_3)OCOCH_3 + Cl_3C\cdot \rightarrow CH_3(Cl_3CCH_2)(CH_3OCO)C\cdot$ **(C)**
2. **C** $+ BrCCl_3 \rightarrow Cl_3CCH_2C(Br)(CH_3)(OCOCH_3)$ **(D)** $+ Cl_3C\cdot$
3. **D** $\rightarrow Cl_3CCH_2COCH_3$ **(E)** $+ CH_3COBr$
4. **E** $\rightarrow Cl_2C{=}CCOCH_3 + HCl$

The relative reactivity of olefins toward the free trichloromethyl radical. The reactivities of the double bonds in α-methylstyrene, p-chlorostyrene, and buta-

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is a primary reaction product, formed as indicated below, and not by loss of hydrogen bromide from the one-to-one adduct.

1. $CH_3(C_6H_5)C{=}CH_2 + Cl_3C\cdot \rightarrow CH_3(C_6H_5)\underset{\bullet}{C}CH_2CCl_3$
2. $CH_3(C_6H_5)\underset{\bullet}{C}CH_2CCl_3 + BrCCl_3 \rightarrow CH_2{=}C(C_6H_5)CH_2CCl_3 + HBr + Cl_3C\cdot$

Free radicals (*e.g.*, $Cl_3C\cdot$) may also abstract a hydrogen atom from the free radical indicated in equation 1 to give the compound $CH_2{=}C(C_6H_5)CH_2CCl_3$.

Furthermore, the analytical results do not differentiate between the so-called dehydrobrominated two-to-one adduct of α-methylstyrene and bromotrichloromethane and the compound formed as follows:

$$\begin{tikzcd} CH_3(C_6H_5)C{=}CH_2 + Cl_3C\cdot \arrow[r] & CH_3(C_6H_5)\overset{\bullet}{C}CH_2CCl_3 \arrow[d, "Dimeriz."] \\ {[CH_3(C_6H_5)\underset{|}{C}CH{=}CCl_2]_2} & {[CH_3(C_6H_5)\underset{|}{C}CH_2CCl_3]_2} \arrow[l, "KOH"'] \end{tikzcd}$$

This latter product could have eliminated some additional hydrogen chloride (during the treatment with alcoholic KOH) to account for the low chlorine content (32.0%) of the material. The calculated chlorine content of "dimer" above is 35.5%. The formulations presented above are attractive for the following reasons: (a) they account for the fact that α-methylstyrene does not undergo homopolymerization, whereas styrene polymerizes readily; (b) no active "popcorn seed" [see, Kharasch, Nudenberg, Jensen, Fischer, and Mayfield, *Ind. Eng. Chem.*, **39**, 831 (1947)] will grow in α-methylstyrene, while it grows rapidly in styrene; (c) many other important differences exist between α-methylstyrene and styrene in polymerization reactions.

Note, however, that these speculations do not in any way invalidate the conclusion that α-methylstyrene is a more reactive monomer than styrene insofar as the addition of the free $Cl_3C\cdot$ radical is concerned, except that value 4.2, provisionally assigned by us, is actually somewhat too low since only the amount of dehydrohalogenated adduct of α-methylstyrene with bromotrichloromethane, formed in the reaction, was used in our calculations.

diene with respect to addition of trichloromethyl radicals were compared with the reactivity of the double bond in styrene. The methods and criteria were those outlined previously (1a) and (1b). The results obtained are summarized in Table I.

As indicated in Table I, *p*-chlorostyrene was found to be approximately as reactive as styrene. This estimate is based upon determination of the chlorine content of the mixture of cinnamic and *p*-chlorocinnamic acid formed by hydrolysis of the reaction mixture. Independent experiments indicated that the styrene-bromotrichloromethane adduct, as well as the *p*-chlorostyrene-bromotrichloromethane adduct, were hydrolyzed when heated in acetic acid, in the presence of small amounts of perchloric acid, to give 90% yields of cinnamic and *p*-chlorocinnamic acids, respectively. Furthermore, the chlorine analyses of the mixture of cinnamic and *p*-chlorocinnamic acids obtained by hydrolysis of synthetic mixtures of the bromotrichloromethane adducts of these olefins indicated about a ±10% accuracy of the method here used.

TABLE I

COMPETITIVE REACTIONS OF OLEFINS WITH BROMOTRICHLOROMETHANE

OLEFIN A	A (moles)	STYRENE (B) (moles)	$CBrCl_3$ (moles)	TEMP., °C.	INITIATOR	TIME (hrs.)	REACTION, %	M.R.[a]
$C_6H_5C(CH_3)=CH_2$	(0.226)	(0.226)	1.41	90	Light	24	45	4.2
p-$ClC_6H_4CH=CH_2$	(.107)	(.107)	0.80	80	Light	4	35	1.1
p-$ClC_6H_4CH=CH_2$	(.110)	(.110)	.50	50	Light	6	30	0.9
$CH_2=CHCH=CH_2$	(.125)	(.125)	1.00	80	0.005 mole $(C_6H_5CO_2)_2$	2.5	41	1.9
$CH_2=CHCH=CH_2$	(.125)	(.125)	1.00	80	.005 mole $(C_6H_5CO_2)_2$	1.75	16	1.9

[a] M.R. is the mole ratio of A adduct to styrene adduct.

α-Methylstyrene is much more reactive than styrene towards the free trichloromethyl radical[4] (see experimental part). The boiling range of the reaction mixture obtained when equimolecular amounts of α-methylstyrene and styrene, dissolved in about a threefold excess of bromotrichloromethane (on the basis of the monomers used) are heated, clearly indicated that the α-methylstyrene adduct was present in a preponderant amount. The amount of the sytrene-bromotrichloromethane adduct was estimated from the amount of cinnamic acid formed by hydrolysis of the reaction mixture. Here too, independent experiments showed that 90% of the calculated amount of cinnamic acid was consistently isolated from known mixtures of the adduct of styrene-bromotrichloromethane and α-methylstyrene-bromotrichloromethane. As an additional check on the accuracy of the method, two samples of the reaction adduct from the competition experiment, to one of which had been added a known quantity of styrene-bromotrichloromethane adduct, were hydrolyzed. The results of these experiments showed that α-methylstyrene is 4.2 times as reactive towards the free trichloromethyl radical as styrene.

The competition of butadiene and styrene for the free trichloromethyl radicals was carried out in a sealed tube with benzoyl peroxide as the initiator and a fourfold excess of bromotrichloromethane. The reaction product was a mixture of two adducts. The very small amount of the 1:1:1 adduct of butadiene, styrene and bromotrichloromethane was not sufficient to affect materially the observed ratio of reactivities of the two olefins.

The recovery of the unchanged olefins indicated that about twice as much butadiene as styrene reacted.

The reaction mixture was distilled at reduced pressure, and the fractions collected were submitted to ozonolysis. The butadiene adduct is the only one that reacts with ozone. As a check on the accuracy of the results, a sample of one fraction, which from the amount of ozone it absorbed appeared to contain 86% of the butadiene adduct, was hydrolyzed in a mixture of acetic acid and perchloric acid (5 mole-%). From the amount of cinnamic acid thus obtained, it is estimated that the styrene adduct present in the mixture was about 10%.

An additional check on the qualitative consistency of the results was the determination of the silver equivalent of a fraction which, from ozonolysis experiments, appeared to contain 93% of the butadiene adduct. A good agreement was obtained for the presence of 7% of the styrene-bromotrichloromethane adduct.

The competitive reactions of butadiene and styrene with bromotrichloromethane were carried out at 80°. In one experiment the reaction was interrupted when 16% of the adducts (on the basis of the olefins present) were formed; in the other experiment when 43% of the adducts were formed. However, in both instances butadiene appeared to be twice as reactive as styrene.

The relative order of reactivities of olefins with respect to addition of a free trichloromethyl radical is as follows:

Styrene	1.0
p-Chlorostyrene	1.0
α-Methylstyrene	4.2
Butadiene	2.0

EXPERIMENTAL PART

Bromotrichloromethane (Dow Chemical Co.) was treated with charcoal and distilled through an 8-foot Fenske column at 100 mm. pressure (b.p. 50°/100 mm., n_D^{20} 1.5060).

Styrene (Dow Chemical Co.) was distilled through a 12-inch Vigreux column immediately before use (b.p. 41–42°/18 mm., n_D^{20} 1.5460).

α-Methylstyrene (Dow Chemical Co.) was distilled through a 12-inch Vigreux column immediately before use (b.p. 57°/15 mm., n_D^{20} 1.5368).

Isopropenyl acetate (commercial) was distilled at reduced pressure prior to use (b.p. 46–47°/100 mm., n_D^{20} 1.4001).

Butadiene (Carbide and Carbon Chemical Corp.) was dried and purified by distillation.

1-Octene (Humphrey-Wilkinson Inc.) was distilled through an 8-foot Fenske column (b.p. 121.6°/760 mm., n_D^{20} 1.4089).

p-Chlorobenzaldehyde (Eastman) was dissolved in ether and extracted with 5% sodium carbonate solution. The ether solution was dried over sodium sulfate and used directly.

p-Chlorostyrene (b.p. 64°/4 mm., n_D^{20} 1.5654).

PROCEDURES

The hydrolysis of the trichloromethyl groups in the styrene-bromotrichloromethane adduct and p-chlorostyrene-bromotrichloromethane adduct. The compound to be hydrolyzed (*ca.* 4 g.) is dissolved in 50 ml. of glacial acetic acid, and 3 ml. of 70% perchloric acid is added. The mixture is refluxed until the evolution of hydrogen chloride gas ceases.

Most of the acetic acid is removed by distillation at water aspirator pressure. The residue is diluted with 5–10 volumes of water and extracted with ether. The ether solution is extracted with 5% sodium hydroxide solution. Upon acidification with dilute hydrochloric acid the aqueous solution is extracted with ether. The extraction with alkali, acidification, and ether extraction are repeated, and the ether solution is then dried over sodium sulfate. The ether is removed by distillation *in vacuo* leaving a residue of acidic material. The product is purified by crystallization or sublimation.

When the bromotrichloromethane, styrene and *p*-chlorostyrene adducts are thus hydrolyzed over 90% of the calculated amount of cinnamic acid and *p*-chlorocinnamic acid, respectively, are readily obtained.

The peroxide-induced addition of bromotrichloromethane to α-methylstyrene. α-Methylstyrene (25 g., 0.21 mole) and bromotrichloromethane (104 g., 0.52 mole) were mixed in a 3-necked, 250 ml. flask provided with a reflux condenser, gas inlet tube, and a dropping-funnel. The system was flushed periodically with dry nitrogen. Acetyl peroxide (3.5 g., 0.03 mole) dissolved in 66 g. of bromotrichloromethane (total 0.86 mole) was added dropwise from the dropping-funnel over a period of 5 hours, while the temperature was maintained at 90°. Heating was stopped 2 hours after the addition was complete.

Excess bromotrichloromethane was distilled at 50 mm. The residue (*ca.* 50 g.) was disdissolved in absolute ethanol and treated with 11 g. of potassium hydroxide in absolute ethanol.[5] A precipitate separated at once. The mixture was diluted with water and extracted several times with benzene. The benzene solution was dried over sodium sulfate, and the benzene was removed through a small Vigreux column at 200 mm. The residue was distilled at 0.1 mm. from a Claisen flask. The first fraction (5.6 g.) which distilled at 35–40° was shown to be α-methylstyrene. The dehydrobrominated 1:1 adduct (18 g.) distilled at 70–78°. A high-boiling residue (11.2 g.) remained. On re-distillation the dehydrobrominated 1:1 adduct, a colorless oil which boiled at 67°/0.1 mm., was collected.

Anal. Calc'd for $C_{10}H_9Cl_3$: Cl, 45.22; Mol. wt., 235.5.

Found: Cl, 42.93; Mol. wt., 235.9.

The low chlorine content of this material is undoubtedly due to dehydrochlorination of this adduct by the alkali. The molecular distillate of the high-boiling residue had a chlorine content consistent with its formulation as the dehydrobrominated 2:1 adduct or partially dehydrochlorinated dimer (see footnote 4). It decolorized bromine in carbon tetrachloride very rapidly.

Anal. Calc'd for $C_{19}H_{19}Cl_3$: Cl, 30.01. Found: Cl, 32.0.

The photochemical addition of bromotrichloromethane to α-methylstyrene. A solution of α-methylstyrene (0.21 mole) in bromotrichloromethane (0.86 mole) was maintained at 80–90°, and internally illuminated with a mercury vapor-neon fluorescent coil for 48 hours. The mixture was worked up as described above. The yield of dehydrobrominated 1:1 ad-, duct was 40%. The weight of the high-boiling material, presumably the dehydrobrominated adduct of two molecules of α-methylstyrene and one molecule of bromotrichloromethane, was 13 g.

Ozonolysis of the dehydrobrominated α-methylstyrene-bromotrichloromethane 1:1 adduct. The dehydrobrominated adduct of α-methylstyrene and bromotrichloromethane (1 g.) was dissolved in 300 ml. of reagent-grade carbon tetrachloride and subjected to ozonization. The effluent gases were passed through a water trap. Treatment of the water with a solu-

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[5] The labile tertiary bromine in this adduct is partially removed already during distillation, hence it appeared desirable to isolate the dehydrobrominated product of this adduct.

tion of methone in 30% ethanol gave the methone derivative of formaldehyde (m.p. 186–187°.

The photochemical addition of bromotrichloromethane to p-chlorostyrene with bromotrichloromethane. A solution of *p*-chlorostyrene (17.3 g., 0.125 mole) in bromotrichloromethane (100 g., 0.5 mole) was maintained at 80° and internally illuminated with a mercury vapor-neon fluorescent coil for 48 hours, while a slow stream of dry nitrogen gas was passed through the solution. The unreacted starting materials were removed by distillation at reduced pressure through a small Vigreux column. The residue (42 g.) crystallized upon cooling. When crystallized from methanol, the compound (32 g.) separated in white needles, which melted at 72–73°.

Anal. Calc'd for $C_9H_7BrCl_3$: C, 32.05; H, 2.08; Mol. wt., 337.
Found: C, 32.13; H, 2.26; Mol. wt., 342.

Hydrolysis of the 1:1 adduct of p-chlorostyrene with bromotrichloromethane. The adduct (2 g.) was hydrolyzed by the procedure described previously. A nearly quantitative yield (1.1 g.) of *p*-chlorocinnamic acid was obtained. Upon recrystallization from aqueous ethanol the acid melted at 247–248°.

Anal. Calc'd for $C_9H_7ClO_2$: Cl, 19.40. Found: Cl, 19.10.

The photochemical addition of bromotrichloromethane to isopropenyl acetate. A solution of isopropenyl acetate (25 g., 0.25 mole) in bromotrichloromethane (200 g., 1 mole) was maintained at 80° and internally illuminated with a mercury vapor-neon fluorescent coil for 24 hours, while a slow stream of nitrogen gas was passed through the solution. A small amount (2 g.) of *tert*-butylcatechol was then added and the unreacted bromotrichloromethane and isopropenyl acetate were removed at reduced pressure. The residue was distilled in a Claisen flask and a colorless fraction boiling at 38°/0.1 mm. was collected (21 g.). The material fumed strongly in air and turned dark upon standing.

Anal. Calc'd for $C_4H_5Cl_3O$: C, 27.40; H, 2.86.
Found: C, 29.14; H, 3.18.

The material was then shaken with water, extracted with ether, and the ether solution was washed with potassium carbonate solution (three times) and with water. After drying over sodium sulfate the mixture was distilled at reduced pressure to remove the ether. The residue was distilled from a Claisen flask. A very stable, pale yellow oil (b.p. 75–76°/40 mm., n_D^{20} 1.4904) was thus obtained which was shown to be 4,4-dichloro-3-buten-2-one.

Anal. Calc'd for $C_4H_4Cl_2O$: C, 34.9; H, 2.9; Cl, 51.0.
Found: C, 35.3; H, 3.21; Cl, 50.98.

The product gave a *hydrazone* when treated with 2,4-dinitrophenylhydrazine (m.p. 194–195°).

Anal. Calc'd for $C_5H_8Cl_2N_3O$: Cl, 36.1; N, 21.4.
Found: Cl, 36.27; N, 21.05.

The *semicarbazone* of the compound melted at 162–163°.

Peroxide-induced addition of bromotrichloromethane to isopropenyl acetate. Isopropenyl acetate (25 g., 0.25 mole) and bromotrichloromethane (200 g., 1 mole) were mixed in a three-necked, 250 ml. flask provided with a reflux condenser and a gas inlet tube through which the system was flushed with nitrogen. Through the third neck 1 g. of benzoyl peroxide and two additional quantities of this material were added at one-hour intervals (total, 3 g. of benzoyl peroxide). The mixture was heated to 90° with an oil-bath. Heating was stopped two hours after the addition of the last batch of peroxide. The mixture was worked up exactly as the photochemical reaction mixture. The product and the yield were the same as in the photochemical reaction.

Ozonolysis of 4,4-dichloro-3-buten-2-one. A sample of the ketone (2.2 g., 0.016 mole) was dissolved in 300 ml. of reagent-grade ethyl acetate. The solution was cooled to −80° in a Dry Ice-acetone cooling bath. Ozone was passed through the mixture of 1 hour. The compound took up ozone relatively slowly. Excess ozone was removed by flushing with oxygen. The reaction vessel was then removed from the bath at −80°, and allowed to come to room temperature. The phosgene formed in the reaction mixture was removed in a stream of nitrogen gas and collected in a solution of aniline in benzene. About 1 g. of diphenylurea (m.p. 233–234°) was thus obtained.

Oxidation of 4,4-dichloro-3-3-buten-2-one with hypobromite. The ketone (5 g.) was added to 100 ml. of distilled water. Freshly prepared potassium hypobromite (15 g. of potassium hydroxide, 13 g. of bromine, 125 ml. of water) was added. The mixture was agitated vigorously for 4 hours. The reaction was stopped by the addition of sodium bisulfite.

The reaction mixture was acidified with dilute hydrochloric acid and extracted with ether. The ether solution was extracted with 5% sodium carbonate solution and the ether solution was rejected. The aqueous phase was acidified and again extracted with ether. The ether solution was dried over sodium sulfate and the ether was removed at reduced pressure. A brown oil remained which crystallized on standing. Upon crystallization from alcohol the compound melted at 75–76°.

This material did not depress the melting point of an authentic sample of β,β-dichloroacrylic acid, prepared by the method of Wallach (2).

The competitive reactions of styrene and α-methylstyrene with bromotrichloromethane. A mixture of α-methylstyrene (26.65 g., 0.226 mole), styrene (23.50 g., 0.226 mole), and bromotrichloromethane (280 g., 1.41 moles) was internally illuminated by a mercury vapor-neon fluorescent coil. The mixture was heated to 90°, while a slow stream of nitrogen gas was passed through the solution. At the end of 24 hours the unreacted bromotrichloromethane and olefins were distilled through a 12-inch Vigreux column at reduced pressure. The residue (52 g. *ca.* 45% reaction) was distilled at 0.1 mm. through a Claisen set-up. After the passage of a small forerun (5 g.) the main portion (30 g.) distilled at 75–93°. A high-boiling residue (10 g.) remained.

Analysis of products. An attempt to effect separation of the adducts by careful distillation led to the qualitative result that the α-methylstyrene adduct was present in considerable excess over the styrene adduct, since only the last fraction had a boiling range high enough for the styrene adduct and only part of this fraction crystallized (m.p. 55–56°). It was not known how much styrene adduct was dissolved in the α-methylstyrene adduct.

Known mixtures of the α-methylstyrene and the styrene adducts were hydrolyzed in the manner described earlier and 90% of the calculated amount of cinnamic acid was consistently isolated. Two samples of the competition reaction product were hydrolyzed in this manner. To one of them was added a known quantity of styrene-bromotrichloromethane adduct. The results were in good agreement. They indicated that the α-methylstyrene and styrene adducts were present in a ratio of 4.2:1.

Inhibition of 1-octene-carbon tetrachloride reaction by α-methylstyrene. 1-Octene (37 g., 0.33 mole), carbon tetrachloride (154 g., 1 mole), α-methylstyrene (5.9 g., 0.05 mole), and benzoyl peroxide (5 g., 0.02 mole) were mixed in a 3-necked, 250-ml. flask provided with a condenser, gas inlet tube, and thermometer. After the air in the system had been replaced by nitrogen gas the inlet tube was replaced by a glass stopper. A tube from the top of the condenser was led through a Dry Ice-trap into a tube containing a 150-mm. column of mercury. The mixture was heated with an oil-bath. The temperature did not rise above 90°. After 4 hours the excess reactants were removed by distillation *in vacuo*. A black residue (9 g.), presumably α-methylstyrene polymer and benzoic acid, remained. No octene-carbon tetrachloride adduct was formed.

The competitive reaction of butadiene and styrene with bromotrichloromethane. Styrene (13 g., 0.125 mole), benzoyl peroxide (1.2 g., 0.005 mole), and bromotrichloromethane (200 g., 1 mole) were mixed in a bomb tube connected to a standard-taper joint with a short piece of thick-walled capillary tubing. The mixture was degassed on the high-vacuum line and butadiene (7 g., 0.125 mole) was distilled into the reaction vessel. The butadiene was measured by distilling it into a calibrated tube and adjusting its volume to the mark at −6°, using the value 0.65 g./ml. for the density of butadiene. The bomb tube was sealed and heated at 80°. In one experiment the reaction was stopped after 2½ hours (41% reaction), and in the second experiment after 1¾ hours (16% reaction).

The tube was cooled to −80° and opened. The tube was then attached to the high vacuum line and the unreacted butadiene was removed by distillation from the reaction vessel, immersed in an ice-salt mixture (−5°), and collected in a receiver cooled to −190°. After vigorous bubbling had ceased the distillation was allowed to proceed for another hour. The remaining solution was distilled at reduced pressure (90 mm.) through a 12-inch Vigreux column to remove the unreacted bromotrichloromethane. The unreacted styrene was removed at a somewhat low pressure (20 mm.). The residue was subjected to distillation at reduced pressure (0.1 mm.) and three fractions were collected. These are given in Table II. The residue was distilled in a molecular still. The molecular weight (356) of this material suggests that it is 1:1:1 adduct of butadiene, styrene and bromotrichloromethane.

Determination of butadiene bromotrichloromethane adduct and of styrene bromotrichloromethane adduct in fractions 1, 2, 3 from the competitive reaction. The butadiene-bromotrichloromethane adduct in fractions 1, 2, 3 (Table II) was estimated from the amount of ozone consumed by the sample. Before and after each ozonolysis the rate of flow of ozone through the solution was calibrated.

Weighed samples of each fraction were dissolved in 300 ml. of ethyl acetate (reagent grade) and cooled to −80°. Ozone was passed through the solution until the first visible appearance of free iodine (yellow color) in the effluent potassium iodide trap. The time of ozone uptake was recorded. A blank using pure ethyl acetate showed a time lag of 0.8 minute before coloration became visible in the iodide solution. This value was subtracted from the observed times.

TABLE II

COMPETITIVE REACTION OF BUTADIENE AND STYRENE WITH BROMOTRICHLOROMETHANE

EXPERIMENT	FRACTION	WEIGHT (g.) OF FRACTION	B.P., °C. 0.1 MM.	BUTADIENE[a] ADDUCT, %	MOLES OF B[b] / MOLES OF S
1	1	16.5	58–65	93.0	2.0
	2	6.0	66–85	29.5	
	3	5.0	85–100	0.0	
2	1	6.6	58–65	86.0	2.0
	2	2.6	66–85	18.6	
	3	0.8	85–100	0.0	

[a] Calculated from ozone absorption.

[b] B is the butadiene adduct. S is the styrene adduct.

The number of moles of ozone absorbed is a direct measure of the number of moles of butadiene adduct present in the sample.

Recovery of olefins. The olefin recovery was low, particularly for butadiene. However, the results are of interest since they supported the conclusions reached from examination of the ozonization and hydrolyses experiments.

Experiment 1: Moles of butadiene reacted: 0.093
Moles of styrene reacted: 0.040
Experiment 2: Moles of butadiene reacted: 0.050
Moles of styrene reacted: 0.022

Hydrolysis of mixture of bromotrichloromethane, butadiene, and styrene bromotrichloromethane adducts. A quantity (3.6 g.) of Fraction 1 (Experiment 2, Table II), which contained 86% of the butadiene adduct calculated from the ozonolysis data, was hydrolyzed with acetic and perchloric acids. The cinnamic acid isolated (0.13 g.) is in fair agreement with the calculated amount of cinnamic acid (0.17 g.) which one would expect to be formed from the styrene-bromotrichloromethane adduct (14%) present in this fraction.

Silver equivalent. The silver equivalent of Fraction 1 (Experiment 1) was determined by means of a Parr bomb halogen analysis. Calculated for a mixture of 93% butadiene adduct and 7% styrene adduct: Ag equiv., 64.1. Found: Ag equiv., 63.9.

The competitive reaction of styrene and p-chlorostyrene with bromotrichloromethane. A mixture of *p*-chlorostyrene (14.8 g., 0.107 mole), styrene (11.2 g., 0.107 mole) and bromotrichloromethane (160 g., 0.80 mole) was internally illuminated by a mercury vapor-neon fluorescent coil. The temperature of the mixture was maintained at 80°, while a slow stream of nitrogen gas was passed through the solution.[6] Samples (1 ml.) were withdrawn from time to time and titrated for unsaturation using bromate-bromide reagent (1b). After 4 hours (35% reaction) illumination was stopped, and the unreacted materials were removed at reduced pressure (1 mm.) at room temperature. To remove the last traces of the olefins used, the temperature was finally raised to 70°. A residue (23 g.) remained. Titration of the residue for unsaturation showed the presence of about 5 mole-% of olefinic material. The product was a pale yellow liquid which did not crystallize. Duplicate reactions were carried out.

A sample of the reaction mixture (3.85 g.) was hydrolyzed with acetic and perchloric acids in the manner described previously. A 75% yield (1.6 g.) of a mixture of cinnamic and *p*-chlorocinnamic acid was obtained. The *chlorine content* of the mixture of these acids was determined. Experiment 1: Cl, 11.1%. Experiment 2: Cl, 9.08%.

Mole ratio of *p*-chlorostyrene adduct to styrene adduct: Experiment 1: 1.1:1. Experiment 2: 0.9:1.

SUMMARY

1. A semiquantitative method for the hydrolysis of the bromotrichloromethane adducts of styrene and ring-substituted styrenes to the corresponding cinnamic acids was developed.

2. Bromotrichloromethane was added to α-methylstyrene, *p*-chlorostyrene, and isopropenyl acetate to give α-methylene-γ,γ,γ-trichloropropylbenzene, 1-chloro-4-(α-bromo-γ,γ,γ-trichloropropyl)benzene, and 4,4-dichloro-3-buten-2-one, respectively. The structures of these adducts were established by conventional methods.

3. The relative reactivities of a number of olefins with respect to addition of a free trichloromethyl radical were determined: α-methylstyrene 4.2; butadiene 2.0; *p*-chlorostyrene 1.0; and styrene 1.0.

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[6] For the design of the apparatus, see reference (1a).