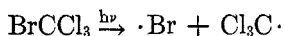


REACTIONS OF ATOMS AND FREE RADICALS IN SOLUTION. XXI.
THE RELATIVE REACTIVITY OF OLEFINS TOWARDS
A FREE TRICHLOROMETHYL RADICAL

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It has been postulated in previous articles from this Laboratory that the addition to olefins of polyhalomethanes (1), α -bromo esters, etc. (2), proceeds in two steps. Specifically, the addition of bromotrichloromethane to olefins in the presence of light is assumed to proceed as follows:



1. $\text{RCH}=\text{CH}_2 + \text{Cl}_3\text{C}\cdot \rightarrow \cdot\text{CHRCH}_2\text{CCl}_3$
2. $\cdot\text{CHRCH}_2\text{CCl}_3 + \text{Cl}_3\text{CBr} \rightarrow \text{RCHBrCH}_2\text{CCl}_3 + \text{Cl}_3\text{C}\cdot$

The energetics of the two steps are different for the same olefin, and, furthermore, the energetics for the same step differ from olefin to olefin. In the present paper the relative reactivities of a number of olefins, as regards their respective abilities to react with free trichloromethyl radicals (Step 1) have been evaluated.

It is obvious that in order to compare olefins with regard to Step 1 the experimental conditions must be carefully adjusted to insure that Step 2 takes place readily. In the present study this has been accomplished by using bromotrichloromethane as the reagent, since at 50–60° it reacts with all the olefins used in this study to give excellent yields of the one-to-one adducts.

RESULTS

Before a comparison of the reactivities of the olefins was undertaken, the one-to-one adducts of bromotrichloromethane and the olefins were prepared and carefully characterized (Table II). Whenever possible, pairs of olefins which gave adducts with bromotrichloromethane markedly different in boiling points and indices of refraction, were selected for comparison. Furthermore, whenever a mixture of two adducts was obtained, the composition of the reaction mixture was determined by: (a) analyses, (b) index of refraction. Since, in most cases the index of refraction is not a linear function of composition, it was necessary to construct index of refraction–molar composition curves from mixtures of the one-to-one adducts of known composition. In all cases, the compositions of the unknown mixtures determined from the index of refraction agreed very well with the values calculated from analyses for one or more elements.

In most of the experiments equimolecular mixtures of the two olefins were dissolved in four molecular equivalents of bromotrichloromethane, and the reaction mixture was irradiated by a mercury vapor-argon fluorescent coil (3). The progress of the reaction was followed by withdrawal of small samples and titration for unsaturates by a standard procedure. Ordinarily, the reaction was allowed to proceed until about 25–50% of the total olefins had reacted. In the case of

styrene and butadiene, which are tremendously more reactive than the ordinary olefins the reaction was carried to the point at which these olefins reacted almost completely.

The relative reactivity of a number of olefins toward the free trichloromethyl radical is indicated in Table I.

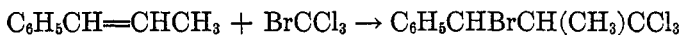
The structural characteristics of the olefins which increase or decrease the ability of the olefin to combine with a free trichloromethyl radical (Step 1) are, for the most part, self evident; what is of considerable interest is the very low reactivity of cyclohexene, β -methylstyrene, and ethyl cinnamate.

TABLE I
THE RELATIVE REACTIVITIES OF OLEFINS TOWARDS A FREE TRICHLOROMETHYL RADICAL

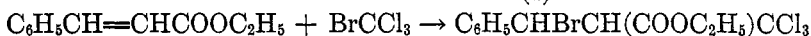
Styrene.....	>100.
Butadiene.....	18.0 ^a
Methallyl chloride.....	1.6
2-Ethyl-1-butene.....	1.4
β -Methylstyrene.....	1.1
1-Octene.....	1.0
2-Methyl-2-butene.....	0.9
Ethyl cinnamate.....	.8
Vinyl acetate.....	.8
Ethyl vinylacetate.....	.7
Allylbenzene.....	.7
Allyl chloride.....	.5
Allyl cyanide.....	.3
4,4,4-Trichloro-1-butene.....	.3
Cyclohexene.....	.2

^a Bromotrichloromethane adds to butadiene to give about $75 \pm 10\%$ of the 1,4 adduct and about $25 \pm 10\%$ of the 1,2 adduct (unpublished work of Kharasch and Nudenberg).

Structure of adducts of bromotrichloromethane with β -methylstyrene and with ethyl cinnamate. Only one of two possible structural isomers is formed by the addition of bromotrichloromethane to β -methylstyrene and to ethyl cinnamate.



(I)



(II)

The structure of Compound I was established by hydrolysis (in glacial acetic acid containing hydrogen bromide) to α -methylcinnamic acid. Compound II when hydrolyzed in a similar way gave some cinnamic acid, and a large quantity of benzaldehyde. The formation of these products is to be expected if Compound II is first hydrolyzed to benzylidenemalonic acid (4).

EXPERIMENTAL

All of the experiments described in this paper were carried out in an atmosphere of nitrogen gas.

METHODS OF INITIATING THE REACTION OF BROMOTRICHLOROMETHANE WITH OLEFINS

(a) *Diacyl peroxide induced reactions.* The reactions, when initiated by the thermal decomposition of diacyl peroxides, were carried out in a three-necked flask of suitable capacity equipped with an all-glass stirrer, a dropping-funnel, and a suitable condenser. Ground-glass connections were used throughout. When low-boiling solvents were used a Dry Ice condenser was used to prevent loss of material. The condenser was attached to a long tube filled with calcium chloride.

(b) *Photochemically induced reactions.* Whenever the reactions were initiated photochemically, the reaction mixture was illuminated internally by a mercury vapor-argon fluorescent coil. Stirring was accomplished by passing a slow stream of nitrogen gas through a fine sintered disc in the bottom of the tube. The outlet and condenser system were arranged in the manner described in (a). Some reactions were carried out in containers from which the air was removed by the usual vacuum technique, and illuminated by a Mazda lamp.

ISOLATION OF REACTION PRODUCTS

In all of the experiments, the reaction mixture was worked up by removal of the unreacted bromotrichloromethane and olefin through a Vigreux column at about 50–100 mm., with the temperature of the heating bath below 70°. A very slow stream of nitrogen gas was admitted through a fine capillary tube to prevent superheating of the material.

The residue was usually fractionally distilled through a Vigreux column at 0.5 to 0.02 mm. pressure. A slow stream of nitrogen gas was admitted through a fine capillary tube. Any volatile materials were caught in a trap cooled with Dry Ice or in liquid nitrogen.

The preparation of 1-bromo-2-trichloromethylcyclohexane. The preparation of the adducts of bromotrichloromethane with the olefin given in Table II resembles in all of the essential details the preparation of 1-bromo-2-trichloromethylcyclohexane. Because this substance is thermally unstable, it was necessary to distill it at a low pressure and to avoid the use of a column.

A solution of 51.4 g. (0.63 mole) of peroxide free cyclohexene and 250 cc. (2.50 moles) of freshly distilled bromotrichloromethane was internally illuminated for 36 hours by a mercury vapor-argon fluorescent coil. The temperature of the mixture was maintained at 25° by external cooling. The unreacted materials were stripped through a Vigreux column at 30°/30 mm., and the temperature of the oil bath gradually raised to 55°, while a slow stream of nitrogen gas was admitted through a fine capillary tube. The residue (133 g.) was distilled through a short Claissen head and the following fractions were collected: Fraction I: 24 g., b.p. 35–83°/0.2 mm. This material fumed strongly in air and turned dark brown upon exposure to air. Fraction II: 53 g., b.p. 83–85°/0.3 mm. Very light yellow color; n_D^{20} 1.5470.

Anal. Fraction II. Calc'd for $C_7H_{10}Cl_3Br$: Ag equiv., 70.1; Mol. wt., 280.

Found: Ag equiv., 70.8; Mol. wt., 288.

The competitive addition of bromotrichloromethane to olefins. The apparatus used in the photochemical competition experiments was the same as that used in the initial preparations of the adducts of bromotrichloromethane to olefins, except that a graduated one-cc. pipet was sealed to the apparatus which enabled us to remove a definite amount of the reaction mixture. For details of the design of the apparatus the paper by Kharasch and Friedlander (3) should be consulted.

The two unsaturates in equimolar quantities were dissolved in a four-fold excess of bromotrichloromethane and duplicate one-cc. samples analyzed for unsaturation by the following procedure:

The sample (containing about 4 milliequiv. of the olefins) was added to 15 ml. of reagent grade carbon tetrachloride contained in a 100-ml. ground-glass stoppered container. A solution of 25 ml. of bromate-bromide (5 milliequiv. Br), and 3 ml. of concentrated HCl were then added, the vessel stoppered and shaken vigorously for about 30 seconds, and set

TABLE II
THE ADDITION OF BROMOTRICHLOROMETHANE TO OLEFINS^a

OLEFIN	(MOLE)	MOLES BrCCl ₂	TIME (HRS)	TEMP. (°C.)	PRODUCT	YIELD (%)	B.P./MM. (°C.)	n _D ²⁰	AG EQUIV.		MOL. WT.	
									Calc'd	Found	Calc'd	Found
H ₂ C=CClCH ₂ Cl	(0.1)	0.8	312	55	Cl ₃ CCH ₂ CClBrCH ₂ Cl ^b	8	52/0.03	1.5443	51.6	52.0	310	311
H ₂ C=CHCH ₂ CN	(.2)	0.8	14	30	Cl ₃ CCH ₂ CHBrCH ₂ CN ^c	65	77-78/0.03	1.5276	—	—	266	267
H ₂ C=C(CH ₃)CH ₂ Cl	(.2)	1.0	4	40	Cl ₃ CCH ₂ CBBr(CH ₃)CH ₂ Cl	45	65/0.10	1.5341	57.6	57.3	—	—
H ₂ C=CHCH ₂ CO ₂ C ₂ H ₅	(.2)	0.8	20	25	Cl ₃ CCH ₂ CHBrCH ₂ CO ₂ C ₂ H ₅	92	73/0.06	1.4996	78.1	77.5	312	313
H ₂ C=CHC ₆ H ₅ -2,4-Cl ₂	(.3)	1.0	6	50	Cl ₃ CCH ₂ CHBrC ₆ H ₃ -2,4-Cl ₂	20	108/1.00	1.5973	61.9	62.1	371	344
H ₂ C=CHCH ₂ C ₆ H ₅	(.2)	0.8	26	35	Cl ₃ CCH ₂ CHBrCH ₂ C ₆ H ₅	49	79/0.05	1.5650	79.1	79.1	316	316
H ₂ C=C(C ₂ H ₅) ₂	(.2)	0.7	15	25	Cl ₃ CCH ₂ CBBr(C ₂ H ₅) ₂	91	68/0.70	1.5156	70.5	70.2	283	288
H ₂ CCH=C(CH ₃) ₂	(.2)	0.8	34	50	Cl ₃ CCH(CH ₃)CBBr(CH ₃) ₂	77	32/0.07	1.5234	67.1	67.2	269	271
Cyclohexene	(.6)	2.5	36	25	1-Bromo-2-trichloromethyl cyclohexane	30	83-85/0.20	1.5470	70.1	70.8	281	285
C ₆ H ₅ CH=CHCOOC ₂ H ₅	(.3)	1.0	3 days	75	C ₆ H ₅ CHBrCH(COOC ₂ H ₅)- CCl ₃ ^d	60	M.P. 64.5	e	93.6	93.9	374	370

^a Unless otherwise specified the reaction mixture was illuminated internally by a mercury vapor-argon fluorescent coil.

^b Besides this product an equal quantity of an adduct of two molecules of the olefin and one molecule of bromotrichloromethane is formed. The addition of the reagent to the olefin takes place very slowly.

^c Anal. Calc'd for C₆H₅BrCl₃N: N, 5.27%. Found: N, 5.26%.

^d About four grams of diacetyl peroxide was added in 0.1 g. portions every four hours.

^e Calc'd for C₁₂H₁₂BrCl₃O₂: C, 38.45; H, 3.20. Found: C, 38.53; H, 3.27.

TABLE III
COMPETITIVE PHOTOCHEMICAL REACTIONS OF OLEFINS WITH BROMOTRICHLOROMETHANE

REACTION NO.	OLEFIN A	(MOLE)	OLEFIN B	(MOLE)	MOLES BRCCl ₃	TEMP. (°C)	TIME (MIN.)	PER CENT REACTION ^c	PER CENT A ADDUCT ^b
1	H ₂ C=CH- <i>n</i> -C ₆ H ₁₃	(.25)	H ₂ C=CHCH ₂ Cl	(.25)	2.0	30	290	45	64.7 (I, Ag)
2 ^e , e	H ₂ C=CH- <i>n</i> -C ₈ H ₁₇	(.25)	H ₂ C=CHC ₆ H ₅	(.25)	2.0	70	150	27	<1.0
3	H ₂ C=CH- <i>n</i> -C ₈ H ₁₇	(.25)	H ₂ C=C(CH ₃)CH ₂ Cl	(.25)	2.0	30	270	26	36.3 (I, Ag)
4	H ₂ C=CH- <i>n</i> -C ₆ H ₁₃	(.25)	H ₂ C=C(C ₂ H ₅) ₂	(.25)	2.0	35	600	45	41.3 (I, Ag)
5	H ₂ C=CH- <i>n</i> -C ₆ H ₁₃	(.25)	H ₂ C=CHCH ₂ CN	(.25)	2.0	35	1130	29	76.9 (I, N)
6 ^d , e	H ₂ C=CH- <i>n</i> -C ₈ H ₁₇	(.20)	H ₂ C=CHCH=CH ₂	(.20)	0.2	68	840	—	5.6 (C, H)
7	H ₂ C=CH- <i>n</i> -C ₆ H ₁₃	(.25)	H ₃ CCH=C(CH ₃) ₂	(.25)	2.0	30	180	39	53.0 (I, Ag)
8	H ₂ C=CH- <i>n</i> -C ₆ H ₁₃	(.25)	H ₂ C=CHCH ₂ CO ₂ C ₂ H ₅	(.25)	2.0	30	180	25	58.6 (C, H)
9	H ₂ C=CH- <i>n</i> -C ₆ H ₁₃	(.25)	H ₂ C=CHO ₂ CCH ₃	(.25)	2.0	30	180	49	55.5 (C, H)
10	H ₂ C=CH- <i>n</i> -C ₆ H ₁₃	(.06)	H ₂ C=CHCH ₂ CCl ₃	(.06)	0.24	45	100	45	66.0 (I)
11 ^d	H ₂ C=CHCH ₂ Cl	(.25)	Cyclohexene	(.25)	0.25	25	1.6×10 ⁴	—	73.7 (I, Ag)
12 ^e , e	H ₂ C=CHCH ₂ Cl	(.19)	H ₂ C=CHC ₆ H ₅	(.19)	2.0	70	180	28	<1.0
13	H ₂ C=CH- <i>n</i> -C ₆ H ₁₃	(.10)	H ₂ C=CH-CHC ₆ H ₅	(.10)	0.10	60	1680	37	60.0 (I)
14	H ₂ C=CH- <i>n</i> -C ₆ H ₁₃	(.10)	H ₃ CCH=CHC ₆ H ₅	(.10)	0.15	60	3600	—	47.0 (I)
15	H ₂ C=CH- <i>n</i> -C ₆ H ₁₃	(.10)	C ₆ H ₅ CH=CHCO ₂ C ₂ H ₅	(.10)	0.80	75	390	40	55.1 (I, Ag)

^a In all cases in which bromotrichloromethane was present in material excess of the amount necessary to react with all the olefin present the total reaction percentage was regarded as equal to the percentage decrease in unsaturation as estimated by bromate-bromide titration.

^b The percentage of one-to-one addition product that resulted from addition to olefin A was estimated in various ways: by determination of the index of refraction (I); by determination of the silver equivalent (Ag); by analyses for carbon (C), hydrogen (H), and nitrogen (N). The nature of the data on which the estimate is based is indicated by the appropriate symbol or symbols. When more than one symbol appears the figure reported is the average of closely concordant estimates.

^c In reactions 2 and 12 the residue which remained after distillation solidified. The crude solid melted at 45-50°, indicating that it consisted substantially of the styrene (B) adduct (m.p., 54.5-55.0°).

^d Reactions 6 and 11 were carried out in sealed containers.

^e Reactions 2, 6, 12, and 15 were peroxide-induced, rather than photochemical; hence the relatively high temperatures at which they were conducted. Essentially the same results were obtained when reaction 1 was peroxide induced rather than photochemical.

aside in the dark place. After 15 minutes 1.0 g. of solid potassium iodide was quickly added and the bottle immediately restoppered and shaken vigorously. The iodine was then titrated with 0.1 *N* thiosulfate. To achieve greater accuracy in the titrations, it is desirable to replace the air in the flask by either carbon dioxide or nitrogen, and to allow the reaction mixture to stand four hours, instead of 30 seconds before adding the potassium iodide.

After the initial unsaturation per ml. had been determined, the reaction was allowed to proceed until 25-50% of the olefins had reacted. This usually required about 1-2 hours. At the end of that time, the reaction mixture was worked up in the manner previously described.

SUMMARY

1. The one-to-one adducts of the following olefins with bromotrichloromethane have been prepared: 2,3-dichloropropene-1, allyl cyanide, methallyl chloride, ethyl vinylacetate, allylbenzene, 2-ethyl-1-butene, 2-methyl-2-butene, ethyl cinnamate, and cyclohexene.

2. The relative reactivities of fifteen olefins towards a free trichloromethyl radical have been established.

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REFERENCES

- (1) KHARASCH, REINMUTH, AND URRY, *J. Am. Chem. Soc.*, **69**, 1105 (1947); KHARASCH, JENSEN, AND URRY, *J. Am. Chem. Soc.*, **69**, 1100 (1947).
- (2) KHARASCH, SKELL, AND FISHER, *J. Am. Chem. Soc.*, **70**, 1055 (1948).
- (3) KHARASCH AND FRIEDLANDER, *J. Org. Chem.*, **14**, 239 (1949).
- (4) STUART, *J. Chem. Soc.*, **49**, 357 (1886).