position of reaction in the isomerization might be related to those responsible for the formation of 1,2- or 1,4-polymers in the polymerization of dienes.

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[CONTRIBUTION FROM THE EDGAR C. BRITTON RESEARCH LABORATORY, THE DOW CHEMICAL CO.]

The Photochemically Induced Reactions of Bromotrichloromethane with Alkyl Aromatics

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The photochemically induced reaction of bromotrichloromethane and certain alkyl aromatics yielded the α-bromoalkyl aromatic and an equivalent amount of chloroform through a free radical chain process. Alkyl aromatics having at least one benzylic hydrogen such as toluene, ethylbenzene and cumene, as well as a number of substituted toluenes have been successfully brominated in this manner.

The use of polyhalomethanes as halogenating agents has been known for some time.[2] The reaction presumably involves a free radical chain sequence which results in the halogenated substrate and a haloform.

$$\cdot CX_3 + RH \longrightarrow R\cdot + HCX_3$$

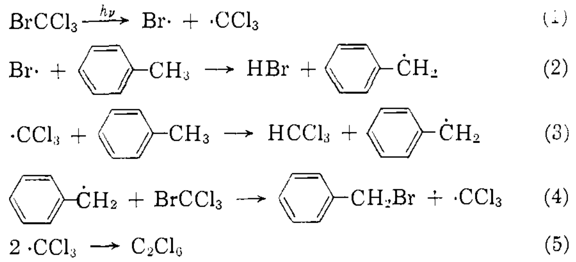
$$R\cdot + CX_4 \longrightarrow RX + \cdot CX_3$$

Carbon tetrachloride and carbon tetrabromide have been reported to halogenate various hydrocarbons,[3] and similar hydrogen–halogen exchange reactions involving alcohols[4] and adehydes[5] with polyhalomethanes have been observed. Kooyman and Farenhorst found that in the free radical reaction of carbon tetrachloride and cyclohexene, allylic chlorination had occurred along with the expected addition reaction.[6] More recently Anderson and Heiba made brief mention of the fact that bromotrichloromethane brominated the benzylic position of alkyl aromatics under the influence of high energy radiation.[7] The present report describes the side chain bromination of various alkylbenzenes and substituted toluenes with bromotrichloromethane under relatively mild photochemical conditions.

Results and Discussion

When bromotrichloromethane and certain alkylated aromatic compounds were exposed to near ultraviolet irradiation, a reaction took place in which the bromine of the polyhalomethane and a benzylic hydrogen were interchanged, the products of the reaction being chloroform and the α-brominated alkylated aromatic. These reactions were carried out in ordinary Pyrex equipment with light from a 275-watt General Electric sunlamp. As can be seen in Table I, the amounts of chloroform and the brominated product were essentially equimolar. Along with those products, small amounts of hydrogen bromide were also found and evidence of small amounts of hexachloroethane was detected in the infrared spectra of the reaction mixtures.

These products and their distribution suggest the following reaction sequence illustrated for the photochemically induced reaction of toluene and bromotrichloromethane. The chain sequence



shown in steps 3 and 4 comprises the major portion of the reaction of bromotrichloromethane and toluene. This is evidenced both by the formation of equimolar amounts of the two products of these steps (chloroform and benzyl bromide), and by their relatively high molar ratio to the hydrogen bromide formed. This ratio is of the order of 20:1 under the conditions used in these reactions. According to the above sequence, hydrogen bromide can be formed only from attack of a bromine atom on toluene (2) and the only source of bromine atoms is the photochemical reaction shown in step 1. The formation of chloroform (3), on the other hand, results not only from the trichloromethyl radical produced in (1) but also from (4) which is part of the chain sequence. Since hydrogen bromide formation is equivalent to the amount of photochemical initiation according to this scheme, this suggests a kinetic chain length for the free radical chain sequence shown in (3) and (4) of about 20 under the conditions of these experiments. The dimerization of two trichloromethyl radicals (5) is a chain-terminating reaction.

The brominated products formed in these reactions (Table I) of the various alkylbenzenes are

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TABLE I

PHOTOCHEMICAL BROMINATIONS WITH BROMOTRICHLOROMETHANE AT 60°

			Recovd. starting materials		Products		
Substrate (mole)	$BrCCl_3$, mole	Time, hr.	Substrate, mole	$BrCCl_3$, mole	$HCCl_3$, mole	Bromide, mole	Conv., %
Toluene (0.50)	0.50	6	0.34	0.34	0.17	Benzyl bromide (0.17)	34
Ethylbenzene (0.50)	.50	6	.13	.10	.36	α-Bromoethylbenzene (0.36)	72
Cumene (0.50)	.50	5.5	.29	.29	.17	Cumyl bromide (0.20)[a]	34
t-Butylbenzene (0.25)	.50	6	.25	.50	.00	No reaction (0.00)	0
p-Chlorotoluene (0.50)	.50	6[b]	.21	.18	.30	*p*-Chlorobenzyl bromide (0.29)	58
p-Bromotoluene (0.33)	.50	7	.19	.36	.14	*p*-Bromobenzyl bromide (0.14)	42
Methyl *p*-toluate (0.50)	.50	6	.38	.39	.10	Methyl α-bromo-*p*-toluate (0.09)	18
p-Methylanisole (0.25)	.25	3	.17	.17	.07	*p*-Bromomethylanisole (0.06)	24
p-Xylene (0.50)	.50	4	.21	.18	.27	α-Bromo-*p*-xylene (0.24)[c]	48
α-Bromo-*p*-xylene (0.30)	.30	6	.19	.18	.09	α,α'-Dibromo-*p*-xylene (0.10)[d]	30
p-Cresol (0.50)	.50	6	..	..	.00	No reaction (0.00)	0
p-Tolunitrile (0.20)	.50	23[b]	.13	..	..	α-Bromotolunitrile (0.06)	30

[a] Cumyl bromide not isolated; see Experimental. [b] Reaction run at 70°. [c] 0.03 mole of dibromo-*p*-xylenes also isolated. [d] Product largely α,α'-dibromo-*p*-xylene.

the α-bromo compounds, the trichloromethyl radical apparently being capable of abstracting only benzylic hydrogens. *t*-Butylbenzene, having no benzylic hydrogens, does not react with bromotrichloromethane under these conditions. In the cases of ethylbenzene and cumene, however, the reaction does take place with relatively good conversions. The brominated products of these reactions appear to be exclusively the α-bromo compounds although no brominated product was actually isolated in the cumene case, since the α-bromocumene is unstable at the temperature required to isolate it from the reaction mixture.[8]

Substituted toluenes were converted to the corresponding benzyl bromides when illuminated with bromotrichloromethane. No isolable amounts of benzal bromides were found in the reaction products. The close correlation in the number of moles of chloroform and benzyl bromides found in these reactions indicates little if any disubstitution. This suggests a low reactivity of the hydrogens of the bromomethyl group toward attack by a trichloromethyl radical. In the reaction of α-bromo-*p*-xylene, however, the infrared spectrum of the crude reaction product did show traces of α,α-dibromo-*p*-xylene indicating some attack of a trichloromethyl radical on the hydrogens of a bromomethyl group.

p-Cresol did not react with bromotrichloromethane in the same manner as other substituted toluenes under these conditions, presumably because of the free radical chain-inhibiting properties of phenolic aromatics.

Experimental

Materials.—Bromotrichloromethane (The Dow Chemical Co.) containing less than 1% carbon tetrachloride by vapor phase chromatographic analysis was used without further purification, $n^{25}D$ 1.5029; toluene, solvent grade redistilled, b.p. 110° (740 mm.), $n^{25}D$ 1.4930; ethylbenzene (Dow) redistilled, b.p. 135° (745 mm.), $n^{25}D$ 1.4928; cumene (Dow) redistilled, b.p. 98° (158 mm.), $n^{25}D$ 1.4897; *t*-butylbenzene (Eastman Kodak Co.) used without further purification, $n^{25}D$ 1.4905; *p*-chlorotoluene (Heyden Newport Chemical Corp.) used without further purification, $n^{25}D$ 1.5183; *p*-bromotoluene (Eastman Kodak Co.) used without further purification, m.p. 27°; methyl *p*-toluate, prepared by oxidation of *p*-xylene followed by esterification, m.p. after recrystallization from petroleum ether, 33.5–34°; *p*-methylanisole (Eastman Kodak Co.) used without further purification, $n^{25}D$ 1.5098; *p*-xylene (Humble Oil Co.) redistilled, b.p. 138–139° (740 mm.), $n^{25}D$ 1.4930; α-bromo-*p*-xylene, prepared by photobromination of *p*-xylene, recrystallized from petroleum ether, m.p. 34–35°; *p*-cresol (Eastman Kodak Co.) redistilled immediately before using; *p*-tolunitrile (Eastman Kodak Co.) used without further purification, m.p. 29°.

All reactions were initiated by illumination from a General Electric 275 watt sunlamp. Vapor phase chromatographic analyses were performed on a column packed with Dow Corning 550 Silicone fluid on Celite with helium used as the carrier gas.[9] All melting points are uncorrected.

Benzyl Bromide.—A reaction mixture consisting of 46.0 g. (0.50 mole) of toluene and 99 g. (0.50 mole) of bromotrichloromethane was placed in a Pyrex 250-ml. round-bottomed flask equipped with an 18" spiral reflux condenser. The flask was illuminated by the sunlamp 6" from the bottom of the flask. Temperature was maintained at 60 ± 5° by means of an air stream directed at the bottom of the flask. After 6 hr. of illumination, the contents of the flask were distilled. Vapor phase chromatographic analysis of the fraction boiling from 60 to 109° showed 20.5 g. (0.17 mole) of chloroform, 31.3 g. (0.34 mole) of toluene and 67.3 g. (0.34 mole) of bromotrichloromethane. Benzyl bromide (29.0 g., 0.17 mole) distilled at 80–85° (22 mm.). The thiouronium picrate of this material melted at 186.5–187°, reported[10] m.p. 188°.

α-Bromoethylbenzene.—Ethylbenzene (53 g., 0.50 mole) and bromotrichloromethane (99 g., 0.50 mole) were illuminated in the same manner for 6 hr. at 60 ± 5°. The reaction mixture was distilled. A fraction, boiling from 50° (745 mm.) to 80° (50 mm.), was collected; vapor phase chromatographic analysis indicated that this consisted of 43 g. (0.36 mole) of chloroform, 20 g. (0.10 mole) of bromotrichloromethane, and 14 g. (0.13 mole) of ethylbenzene. α-Bromoethylbenzene (67 g., 0.36 mole) distilled at 77° (12 mm.).

The infrared spectrum of this material was identical with that of an authentic sample of α-bromoethylbenzene. A small portion of the material was treated with an equivalent amount of magnesium in anhydrous ether. An equivalent amount of phenyl isocyanate was added to the reaction mixture. On hydrolysis, however, no isolable methylphenyl acetanilide was found (reported[11] m.p. 133°). The only material isolated was the *meso*-2,3-diphenylbutane, a known reaction product of magnesium and α-bromoethylbenzene,[12a] m.p. 126–127° from ethyl alcohol, reported[12b] m.p. 126–127°. *Anal.* Calcd. for $C_{16}H_{18}$: C, 91.44; H, 8.56. Found: C, 90.87; H, 8.39.

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[8] G. A. Russell and H. C. Brown, THIS JOURNAL, **77**, 4025 (1955).

[9] Vapor phase chromatography instrument designed and built by the Spectroscopy Laboratory, The Dow Chemical Co.

[10] E. L. Brown and N. Campbell, *J. Chem. Soc.*, 1699 (1937).

[11] H. Staudinger and L. Ruzicka, *Ann.*, **380**, 299 (1911).

[12a] See V. Grignard and K. Ono, *Bull. soc. chim.*, **39**, 159 (1926).

[12b] E. Ott, *Ber.*, **61**, 2137 (1928).

Photochemical Reaction of Cumene with Bromotrichloromethane.—A reaction mixture consisting of 60 g. (0.50 mole) of cumene and 99 g. (0.50 mole) of bromotrichloromethane was illuminated for 6 hr. at 60 ± 5°. On vacuum distillation, volatile materials amounting to 90 g. were collected in a Dry Ice trap and a fraction boiling up to 35° (10 mm.) amounting to 23 g. was collected as the pot temperature was increased to 80° (10 mm.). Above this temperature, decomposition took place. The materials collected in the trap and receiver were analyzed by vapor phase chromatography as chloroform (0.17 mole), bromotrichloromethane (0.29 mole) and cumene (0.29 mole). A residue amounting to 41 g. remained. This material when treated with 80% ethanol gave a positive halogen test with silver nitrate but failed to crystallize even at Dry Ice temperature.

***p*-Chlorobenzyl Bromide.**—In the manner described above, 63.3 g. (0.50 mole) of *p*-chlorotoluene and 99 g. (0.50 mole) of bromotrichloromethane were illuminated at 70 ± 5° for 6 hr. The reaction mixture was distilled, and vapor phase chromatographic analysis of the lower boiling material (50° (748 mm.)–80° (45 mm.)) showed it to consist of 36 g. (0.30 mole) of chloroform, 36 g. (0.18 mole) of bromotrichloromethane and 27 g. (0.21 mole) of *p*-chlorotoluene. The residue, *p*-chlorobenzylbromide, amounted to 58 g. (0.29 mole). On cooling, this material solidified and after recrystallization from ethyl alcohol melted at 49.5–50.5°, reported[13] m.p. 50°.

***p*-Bromobenzyl Bromide.**—A reaction mixture consisting of 63 g. (0.33 mole) of *p*-bromotoluene and 99 g. (0.50 mole) of bromotrichloromethane was illuminated for 7 hr. at 60 ± 5°. Vapor phase chromatographic analysis of the lower boiling material showed 16.5 g. (0.14 mole) of chloroform and 71 g. (0.36 mole) of bromotrichloromethane. Unreacted *p*-bromotoluene (33.5 g., 0.19 mole) distilled at 75–80° (25 mm.). The residue was *p*-bromobenzyl bromide and amounted to 34 g. (0.14 mole), m.p. 60.5–61° (from ethyl alcohol), reported[14] 61°.

Methyl α-Bromo-*p*-toluate.—A reaction mixture consisting of 75 g. (0.50 mole) of methyl *p*-toluate and 99 g. (0.50 mole) of bromotrichloromethane was illuminated for 6 hr. at 60 ± 5°. The reaction mixture was distilled, and the lower boiling fractions (50–105° (atm.)) were analyzed by vapor phase chromatography. These fractions consisted of 11.9 g. (0.10 mole) of chloroform and 77.2 g. (0.39 mole) of bromotrichloromethane. Fifty-seven grams (0.38 mole) of unreacted methyl *p*-toluate was recovered by further distillation. The residue, 21 g. (0.09 mole) of methyl α-bromo-*p*-toluate, solidified on cooling. After recrystallization from ethyl alcohol, the material melted at 55–56°, reported[15] 53–53.5°.

***p*-Bromomethylanisole.**—Thirty-one grams (0.25 mole) of *p*-methylanisole and 49 g. (0.25 mole) of bromotrichloromethane were illuminated for 3 hr. at 60 ± 5°. The lower boiling fractions (50° (atm.)–100° (8 mm.)) amounting to 63 g. were analyzed by vapor phase chromatography as chloroform (0.07 mole), bromotrichloromethane (0.17 mole) and unreacted *p*-methylanisole (0.17 mole). The *p*-bromomethylanisole (11.5 g., 0.06 mole) distilled at 105–110° (8 mm.). The thiouronium picrate of this material melted at 164–165.5°. *Anal.* Calcd. for $C_{15}H_{15}N_5O_8S$: C, 42.3; H, 3.55. Found: C, 42.20; H, 3.59. No detectable amounts of any other materials were found after distillation of the *p*-bromomethylanisole.

α-Bromo-*p*-xylene.—*p*-Xylene (53 g., 0.50 mole) and 99 g. (0.50 mole) of bromotrichloromethane were illuminated for 4 hr. at 60 ± 5°. The lower boiling fractions (50° (atm.)–55° (50 mm.)) were analyzed by vapor phase chromatography as chloroform (31.2 g., 0.27 mole), bromotrichloromethane (35.7 g., 0.18 mole) and *p*-xylene (22.2 g., 0.21 mole). α-Bromo-*p*-xylene (44.0 g., 0.24 mole) distilled at 60–65° (7 mm.) and solidified on cooling, m.p. 35°, reported[16] m.p. 35.5°. A high boiling residue consisting of dibromo-*p*-xylene, amounting to 8.7 g. (0.03 mole), remained. After one recrystallization from chlorobenzene, this material melted at 143°; reported[16] m.p. for α,α′-dibromo-*p*-xylene 144°. Infrared analysis of the crude residue showed only trace amounts of α,α-dibromo-*p*-xylene. An infrared absorption band at 12.83 μ was attributed to hexachloroethane.

α,α′-Dibromo-*p*-xylene.—α-Bromo-*p*-xylene (55.5 g., 0.30 mole) and bromotrichloromethane (59.4 g., 0.30 mole) were illuminated for 6 hr. at 60 ± 5°. The reaction mixture was heated under reduced pressure and the lower boiling materials, collected in a Dry Ice trap, were analyzed by vapor phase chromatography as chloroform (10.5 g., 0.09 mole) and unreacted bromotrichloromethane (36 g., 0.18 mole). Unreacted α-bromo-*p*-xylene was removed by distillation (b.p. 65–75° (8 mm.)) and amounted to 35 g. (0.19 mole). On cooling, the residual dibromo-*p*-xylene (27.5 g., 0.10 mole) solidified. On recrystallization from chlorobenzene, this material melted at 144°. Infrared analysis of the crude material showed only traces of α,α-dibromo-*p*-xylene, the rest of the material being α,α′-dibromo-*p*-xylene.

α-Bromo-*p*-tolunitrile.—A reaction mixture consisting of 23.4 g. (0.20 mole) of *p*-tolunitrile and 99 g. (0.50 mole) of bromotrichloromethane was illuminated at 70° for 23 hr. After removal of the chloroform and unreacted bromotrichloromethane under reduced repressure, 15 g. (0.13 mole) of unreacted *p*-tolunitrile distilled at 105–110° at 15 mm. The residue, α-bromo-*p*-tolunitrile (12.5 g., 0.06 mole) melted at 114° after one recrystallization from benzene; reported[17] m.p. 115–116°.

Determination of Chain Length.—A charge of 92 g. (1.0 mole) of toluene and 198 g. (1.0 mole) of bromotrichloromethane was illuminated for 5.5 hr. at 60 ± 2° in a 250-ml. round-bottomed flask equipped with an 18″ spiral condenser. During the illumination, nitrogen was sparged through the reaction mixture at a rate of 5–10 liters per hour. After passing through the condenser, the gas was bubbled through a liquid bubbler containing 250 ml. of 0.10 *N* sodium hydroxide. The nitrogen flow was continued for 5.5 hr. after illumination was terminated. On working up the reaction mixture, 32 g. (0.19 mole) of benzyl bromide (b.p. 95–100° (35 mm.)) was obtained. A 25-ml. aliquot of the standard sodium hydroxide in the liquid bubbler required 10.72 ml. of 0.10 *N* hydrochloric acid for neutralization. Calculation indicates a ratio of 19.3 moles of product per mole of hydrogen bromide formed in the reaction.

Attempted Photochemical Reactions of *p*-Cresol and *t*-Butylbenzene with Bromotrichloromethane.—Attempts to brominate these materials with bromotrichloromethane in the manner described previously resulted in no detectable amounts of either chloroform or brominated products. Although the reaction mixtures became dark during the illumination, the recovery of the starting materials was nearly quantitative.

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