Effect of Reversible Hydrogen Abstraction on the Mechanism of the Photoinitiated Bromination of Arenes by Bromotrichloromethane. Selectivity of the Trichloromethyl Radical

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Abstract: The anomalously high selectivities observed for the photobrominations of arenes with bromotrichloromethane have been shown to be governed by the reversible abstraction reactions of the bromine atom. During the reaction, a majority of the hydrocarbon radicals formed was found to revert to starting material by transfer with the small amounts of hydrogen bromide found in the reaction. When the bromination is carried out in the presence of added solid potassium carbonate or ethylene oxide, free-radical chain bromination takes place by trichloromethyl radical abstraction, and the selectivity of that radical toward toluene, ethylbenzene, and cumene (1:10:28) could be determined.

The mechanism for the photoinitiated bromination of substituted toluenes with bromotrichloromethane recently has been shown to involve a bromine atom chain (Scheme I).[2]

Scheme I

$$\mathrm{ArCH_3 + Br\cdot \rightleftharpoons ArCH_2\cdot + HBr} \quad (1)$$

$$\mathrm{ArCH_2\cdot + BrCCl_3 \longrightarrow ArCH_2Br + \cdot CCl_3} \quad (2)$$

$$\mathrm{\cdot CCl_3 + HBr \longrightarrow Br\cdot + HCCl_3} \quad (3)$$

This mechanism,[3] considered as an alternative to the pathway suggested originally by Huyser[4] (Scheme II), was rejected by Russell on the basis of the results of a comparison between the relative reactivities obtained for the competitive brominations of a number of aralkyl hydrocarbons with molecular bromine and bromotrichloromethane.[3]

Scheme II

$$\mathrm{ArCH_3 + \cdot CCl_3 \longrightarrow ArCH_2\cdot + HCCl_3}$$

$$\mathrm{ArCH_2\cdot + BrCCl_3 \longrightarrow ArCH_2{-}Br}$$

The relative reactivities/H obtained for the brominations suggested that the bromotrichloromethane brominations were more selective than those carried out with molecular bromine. The results of the brominations using molecular bromine were obtained under conditions designed to minimize the reversal reaction of the benzylic radicals with hydrogen bromide (eq 1), high concentrations of molecular bromine and rapid removal of the hydrogen bromide formed.[3] The reversal reaction was not considered important in the bromotrichloromethane brominations. It should be noted that the values reported for the relative rates of photoinitiated brominations with bromotrichloromethane were average values, whose range was greater than that expected from experimental deviations.[3,5]

In the article on the reinvestigation of the photobromination reactions of toluene and ring-substituted toluenes with bromotrichloromethane,[2] the differences previously reported for the relative rates of bromination of arenes using that reagent or molecular bromine[3] were rationalized by assuming that a significant amount of hydrogen bromide reversal had taken place in the bromotrichloromethane reactions. It was suggested that the usual inequality in the differences of the activation energies of the forward ($E_2 - E_1$) and the reverse reactions ($E_{-2} - E_{-1}$) for two similar exothermic reactions, ($E_{-2} - E_{-1}$) > ($E_2 - E_1$), had allowed the less stable radical to undergo more extensive reversal than the more stable radical in the system, and that an analysis of the disappearance of reactants led to abnormally high selectivities in the bromotrichloromethane bromination. It was reasoned that reversible abstraction would be more important in the bromotrichloromethane brominations than in the substitutions using molecular bromine since, although the hydrogen bromide concentrations in the latter reactions were probably higher, the relative rates of transfer between hydrogen bromide and bromotrichloromethane would be much higher compared with the ratio of transfer rates for hydrogen bromide and molecular bromine.

An investigation of the bromotrichloromethane brominations of toluene, ethylbenzene, and cumene has been carried out to substantiate these proposals. Using conditions previously established[2] to eliminate hydrogen bromide reversal, the selectivity of the trichloromethyl radical could be determined.

Results and Discussion

The relative rates of photoinitiated bromination of toluene vs. ethylbenzene and ethylbenzene vs. cumene with bromotrichloromethane have been reinvestigated, and the results are in excellent agreement with those originally reported by Russell.[3] The relative rates per α-H calculated for the reactions of toluene, ethylbenzene, and cumene (1.0:50:288) are well within the experimental error of the values (1.0:50:260) reported previously by Russell.[3]

Competitive brominations with bromotrichloromethane were carried out, under the same conditions used to determine the above relative rates, on mixtures of toluene and ethylbenzene-*ethyl-d*$_5$ and on mixtures of ethylbenzene and cumene-α-*d*. The unbrominated substrates were isolated by preparative GLC. The aralkyl hydrocarbons were subjected to mass-spectral analysis (<12 eV), and a comparison of the analysis of the individual substrates before and after reaction with bromotrichloromethane is given in Table I.

The analysis of the parent peaks of the individual unbrominated substrates showed that extensive scrambling of protium and deuterium had accompanied the bromination reactions. In all cases, exchange predominates over halogenation. The amount of exchange observable in these experiments is a minimum value since reactions which exchange hydrogen for hydrogen or deuterium for deuterium cannot be detected. Furthermore, if significant amounts of materials had undergone bromination after exchange had taken place, this exchange could not be determined. A

Table I. Isotopic Compositions of the Parent Ions from Alkylbenzenes before and after the Reaction with Bromotrichloromethane

			M^+ %[a]						
Reaction	C_6H_5R	% conversion	d_0	d_1	d_2	d_3	d_4	d_5	E/C[b]
	$C_6H_5CH_3$		100.0	0.0	0.0	0.0	0.0	0.0	
	$C_6H_5C_2H_5$		100.0	0.0	0.0	0.0	0.0	0.0	
	$C_6H_5C(CH_3)_2H$		100.0	0.0	0.0	0.0	0.0	0.0	
	$C_6H_5CD_2CD_3$		0.0	0.0	0.0	0.0	2.2	96.7	
	$C_6H_5C(CH_3)_2D$		7.5	92.5	0.0	0.0	0.0	0.0	
1	$\{C_6H_5CH_3$	5.4	61.6	33.3	5.1	0.0	0.0	0.0	7.7
	$\{C_6H_5C_2D_5$	95.6	0.0	0.0	0.0	62.8	32.6	4.6	
2	$\{C_6H_5CH_3$	2.9	63.3	29.8	6.2	0.5	0.0	0.0	15.2
	$\{C_6H_5C_2D_5$	95.8	0.0	0.0	0.0	67.1	28.9	4.0	
3	$\{C_6H_5CH_3$	0.1[c]	99.0	1.0	0.0	0.0	0.0	0.0	10.0
	$\{C_5H_5C_2D_5$	2.3[c]	0.0	0.0	0.0	0.0	6.8	93.2	1.5
4	$\{C_6H_5C_2H_5$	9.8	46.3	42.2	11.5	0.0	0.0	0.0	6.0
	$\{C_6H_5C(CH_3)_2D$	31.4	65.0	35.0	0.0	0.0	0.0	0.0	1.3
5	$\{C_6H_5C_2H_5$	15.4	51.0	40.8	8.2	0.0	0.0	0.0	
	$\{C_6H_5C(CH_3)_2D$	43.7	70.5	29.5	0.0	0.0	0.0	0.0	

[a] Values reported are corrected for ^{13}C natural abundance. [b] Lower limits on the number of exchanges (E) to the number of alkylbenzene molecules which have been converted to product (C). [c] Values for these percentage conversions were estimated by determining the amount of $[CCl_3H + CCl_3D]$ and proportioning the reactants consumed using the ratio of the reactants consumed in reaction 1, 5.4/95.6.

knowledge of the initial concentrations of reactants, percentage conversion, and the percentage of incorporation for each substrate, in the cases where conversion was minimal, allowed the calculation, to a reasonable approximation, of the ratio of exchange (E) to bromination (C). The E/C ratios obtained for the competitive bromination of toluene and ethylbenzene-*ethyl*-d_5 showed that the more reactive benzyl radical reacts with deuterium bromide prior to transfer with bromotrichloromethane 89–94% of the time (reactions 1 and 2, Table I). This value must be even higher if one corrects for the deuterium isotope effect which is present during the transfer of benzyl radicals with hydrogen or deuterium bromide.[6] The E/C values obtained at a very low conversion (reaction 3, Table I) demonstrate that the more reactive benzyl radical underwent exchange (relative to transfer) more extensively than the α radical generated from ethylbenzene, and that at least 90% of the toluyl radicals and 60% of the radicals from ethylbenzene underwent exchange prior to reaction.

The reactions of ethylbenzene and cumene-α-d (reactions 4 and 5, Table I), likewise, demonstrated that the less stable α radical from ethylbenzene underwent more exchange (76–86%) than did the cumyl radical (45–56%).

In the bromotrichloromethane brominations of toluene and toluene-α-d_3, the exchange reaction was shown to arise from a reversible radical-transfer reaction between hydrogen bromide and the benzyl radical.[2] Other modes of exchange, in that system, were ruled out by a number of control experiments. The exchange between a benzyl radical and perdeuteriochloroform was shown not to take place during bromotrichloromethane brominations, and it is safe to assume that, in the even more endothermic reactions of chloroform with the α radical of ethylbenzene or with the cumyl radical, this reaction is, likewise, unimportant. The ionic exchange reaction, ring substitution, equally unimportant for ethylbenzene and cumene as it is for toluene,[7] was likewise ruled out. The absence of this reaction is further substantiated by the observation that, in the mass-spectral analysis of the reisolated arenes, no evidence of hexadeuterated ethylbenzene or dideuterated cumene was detected. The occurrence of an aralkyl radical substrate exchange reaction could be ruled out since, under conditions which would not interfere with this reaction, the exchange reaction could be eliminated (see reaction run with added potassium carbonate and ethylene oxide).

It was found that, as in the case of toluene,[2] the hydrogen bromide produced in the reactions could be scavenged by carrying out the reaction with added powdered potassium carbonate or ethylene oxide. Qualitatively the reactions run in the presence of either additive were five to ten times slower than the photolysis without additives. When these reactions were completed, no detectable amounts of hydrogen bromide could be found. The reduction in the rate of the reaction with added ethylene oxide indicates that the reactions with and without hydrogen bromide were not proceeding by the same mechanism.

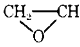
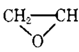
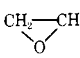
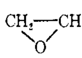
When 1:1 mixtures of toluene and ethylbenzene-*ethyl*-d_5 or mixtures of ethylbenzene and cumene-α-d were subjected to the photoinitiated bromination reaction with bromotrichloromethane, in the presence of added solid potassium carbonate, the scrambling reaction of deuterium and protium was almost completely eliminated while, with added ethylene oxide (20 mol %), the reisolated substrates were found to be completely free of scrambling, see Table II. GLC analyses of the reaction mixtures containing additives were identical with those without additives, with the exception that after reaction, the reactions with added ethylene oxide contained unreacted ethylene oxide and β-bromoethanol, the reaction product of the oxide with hydrogen bromide.

The relative rates of bromination with bromotrichloromethane of ethylbenzene compared with toluene and cumene compared with ethylbenzene were determined with added potassium carbonate and added ethylene oxide. A comparison of the values obtained with these additives is given in Table III.

The 1°:2°:3° selectivities for photobromination with bromotrichloromethane in the presence of added potassium carbonate and with added ethylene oxide are, within experimental error, the same (see Table III). A comparison of these values with those obtained without additives (1.0:50:288) shows that the values obtained in the absence of hydrogen bromide denote abstraction by a much less selective radical. The lower selectivity, 1:10:28, can be assigned to the selectivity for trichloromethyl radical abstraction and appears to be a more reasonable value for abstraction by a carbon-centered radical.

The sensitivity of the bromotrichloromethane brominations toward polar effects has been studied for a series of ring-substituted toluenes,[8] ethylbenzenes,[9] and cumenes.[10] In the absence of hydrogen bromide, the ρ value obtained from a Hammett correlation of the photobrominations of the substituted toluenes was found to be lower, -0.69^2 compared with -1.46,[8] than the value reported for the bromina-

Table II. Isotopic Compositions of the Parent Ions from Alkylbenzenes before and after the Reaction with Bromotrichloromethane with Added Potassium Carbonate or Ethylene Oxide

				M+ %[b]						
Reaction	Additive[a]	C_6H_5R	% conversion	d_0	d_1	d_2	d_3	d_4	d_5	E/C[c]
		$C_6H_5CH_3$		100.0	0.0	0.0	0.0	0.0	0.0	
		$C_6H_5C_2H_5$		100.0	0.0	0.0	0.0	0.0	0.0	
		$C_6H_5C(CH_3)_2H_5$		100.0	0.0	0.0	0.0	0.0	0.0	
		$C_6H_5CD_2CD_3$		0.0	0.0	0.0	0.0	2.2	96.7	
		$C_6H_5C(CH_3)_2D$		7.5	92.5	0.0	0.0	0.0	0.0	
6	K_2CO_3	$C_6H_5CH_3$	10.3	99.1	0.9	0.0	0.0	0.0	0.0	0.08
		$C_6H_5CD_2CD_3$	21.2	0.0	0.0	0.0	0.0	4.0	96.0	0.03
7	K_2CO_3	$C_6H_5CH_3$	7.8	99.7	0.3	0.0	0.0	0.0	0.9	0.04
		$C_6H_5CD_2CD_3$	12.2	0.0	0.0	0.0	0.0	5.0	95.0	0.12
8		$C_6H_5CH_3$	2.2	100.0	0.0	0.0	0.0	0.0	0.0	0.00
		$C_6H_5CD_2CD_3$	3.9	0.0	0.0	0.0	0.0	3.2	96.8	0.00
9		$C_6H_5CH_3$	12.5	100.0	0.0	0.0	0.0	0.0	0.0	0.00
		$C_6H_5CD_2CD_3$	15.2	0.0	0.0	0.0	0.0	2.9	97.1	0.00
10	K_2CO_3	$C_6H_5CH_2CH_3$	11.2	99.3	0.7	0.0	0.0	0.0	0.0	0.06
		$C_6H_5C(CH_3)_2D$	7.1	6.8	93.2	0.0	0.0	0.0	0.0	0.00
11	K_2CO_3	$C_6H_5CH_2CH_3$	18.1	99.0	1.0	0.0	0.0	0.0	0.0	0.05
		$C_6H_5C(CH_3)_2D$	3.7	5.7	94.3	0.0	0.0	0.0	0.0	0.00
12		$C_6H_5CH_2CH_3$	16.4	100.0	0.0	0.0	0.0	0.0	0.0	0.00
		$C_6H_5C(CH_3)_2D$	3.5	6.6	93.4	0.0	0.0	0.0	0.0	0.00
13		$C_6H_5CH_2CH_3$	19.4	100.0	0.0	0.0	0.0	0.0	0.0	0.00
		$C_6H_5C(CH_3)_2D$	4.8	3.9	96.1	0.0	0.0	0.0	0.0	0.00

[a] Additives were solid potassium carbonate (10 mol % of bromotrichloromethane) and ethylene oxide (20 mol % of bromotrichloromethane). [b] Values reported are corrected for ^{13}C natural abundance. [c] Lower limits on the number of exchanges (*E*) to the number of alkylbenzenes which have been converted to product (*C*).

tions carried out in the presence of small amounts of hydrogen bromide. The ρ values reported for the bromotrichloromethane brominations of ethylbenzenes[9] and substituted cumenes[10] must, likewise, be influenced by reversible bromine atom abstraction. A reinvestigation of these studies, with added ethylene oxide, is now in progress.

Experimental Section

Reagents. Freon 113 (Matheson of Canada, Ltd.) and Freon 112 (PCR Incorporated) were distilled from phosphorus pentoxide. Purification of toluene, ethylbenzene, and cumene was accomplished by washing with concentrated sulfuric acid, then water, and drying over magnesium sulfate, followed by fractional distillation. Bromotrichloromethane (Aldrich) water white material was used without further purification. Ethylene oxide (Matheson of Canada, Ltd.) was distilled before use.

Ethylbenzene-*ethyl*-d_5, kindly supplied by Dr. A. Kalantar, Department of Chemistry, The University of Alberta, was purified by preparative GLC. Mass spectrometric analyses showed the reagent to be 96.7% ethylbenzene-*ethyl*-d_5 and 3.3% ethylbenzene-*ethyl*-d_4.

Cumene-α-*d* was prepared according to Hart[11] from α-phenylisopropyl potassium[12] and deuterium oxide (Merck Sharp and Dohme of Canada Ltd.). Purification was accomplished by preparative GLC. Mass spectrometric analyses showed 92.5% d_1, 7.5% d_0.

The purity of all of the reagents was checked by GLC.

GLC Analysis. Analytical determinations were carried out using an Aerograph Model 202 gas chromatograph equipped with a thermal conductivity detector and fitted with a 20 ft × ⅛ in. stainless steel column packed with 5% DEGS on acid-washed Chromosorb W. Standard calibration curves were constructed to correct for the molar sensitivity of Freon 112, chloroform, and bromotrichloromethane in order to determine the percentage reaction or the percentage formation of the products.

An Aerograph Model 1520 gas chromatograph equipped with a thermal conductivity detector and fitted with a 10 ft × 0.25 in. glass column packed with 10% DEGS on acid-washed Chromosorb W was employed for collection and purification of the alkylbenzenes.

Mass Spectrometric Analysis. A.E.I. Models MS9 and MS12 mass spectrometers were used throughout the study. All the spectra of deuterated and nondeuterated toluene, ethylbenzene, and cumene were obtained at an electron-beam energy of 4.0–11.5 eV to avoid the fragmentation of the alkylbenzenes into their corresponding tropylium cation radicals. Using this range of electron-beam energy, it was found that the peaks P − 1 and P − 2 were negligibly small and allowed quantitative analyses in scrambling studies of the alkylbenzenes.

Competitive Brominations. Aliquot solutions of toluene (2.0 *M*), ethylbenzene (1.0 *M*), the standard Freon 112 (1.3 *M*), bromotrichloromethane (1.7 *M*), and Freon 113 (5.1 *M*) were degassed by the freeze-pump-thaw method and sealed in Pyrex ampoules. The reaction tubes were placed in a merry-go-round apparatus, thermostated at 40.0 ± 0.1° in a Pyrex water bath, and irradiated using a Hanovia 140-W utility lamp. The ampoules were removed after various lengths of time (24–48 hr), frozen in liquid nitrogen, and opened, and the contents were analyzed by GLC (20 ft × ⅛ in. 5% DEGS, 55–75°). The conversion of toluene or ethylbenzene was always more than 10% in each reaction analyzed.

The relative reactivity was calculated in the usual manner[13] from a determination of the relative amounts of the two substrates that had undergone reaction.

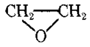
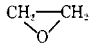
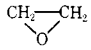
The competitive reactions carried out with added ethylene oxide (20%) were irradiated under conditions comparable to those used for the reactions without additives and gave a negligible (<5%) reaction. Direct irradiation (lamp distance fixed 5 in. from the thermostated sample) gave sufficient reaction in 100–150 hr.

The competitive reactions were also carried out with added solid potassium carbonate (10 mol % of bromotrichloromethane). Dried (130°) anhydrous potassium carbonate was ground in air prior to use. The irradiation of the sealed tubes continued for 100–150 hr under constant shaking by a Burrell Wrist Action Shaker. The shaking kept the carbonate in a fine suspension throughout the irradiation.

The relative reactivity of cumene vs. ethylbenzene was determined under the conditions employed above.

Bromotrichloromethane Brominations of Toluene and Ethylbenzene-*ethyl*-d_5. Mixtures of toluene (9.35 × 10^{-4} mol), ethylbenzene-*ethyl*-d_5 (2.86 × 10^{-4} mol), bromotrichloromethane (7.73 × 10^{-4} mol), Freon 112 (5.37 × 10^{-4} mol), and Freon 113 (1.9 × 10^{-3} mol) placed in sealed, degassed ampoules were allowed to react under the same conditions as those used for the competitive bromination (~1–10 days). The ampoules were frozen in liquid nitrogen and broken open under 30–50 ml of water in stoppered

Table III. Relative Reactivities of Toluene, Ethylbenzene, and Cumene toward Bromotrichloromethane in the Presence of Potassium Carbonate or Ethylene Oxide at 40.0°

Substrate	Additives	Relative reactivity/molecule[a]			Relative reactivity/α-H
Toluene	K_2CO_3	1.00		1.00	1.00
Ethylbenzene	K_2CO_3	6.78 ± 0.49[b]	1.00	6.78 ± 0.49	10.2 ± 0.7[e]
Cumene	K_2CO_3		1.47 ± 0.07[e]	9.97 ± 1.23[d]	29.9 ± 3.7[e]
Toluene		1.00		1.00	1.00
Ethylbenzene		6.96 ± 0.57[b]	1.00	6.96 ± 0.57	10.4 ± 0.9[e]
Cumene			1.33 ± 0.22[c]	9.26 ± 2.41[d]	28.1 ± 6.6[e]

[a] Errors reported are average deviations from the mean for three independent experiments. [b] Relative to toluene. [c] Relative to ethylbenzene. [d] $k_{\text{ethylbenzene}}/k_{\text{toluene}} \times k_{\text{cumene}}/k_{\text{ethylbenzene}}$. [e] (Rel reactivity of the substrate/rel reactivity of toluene) × 3/α-hydrogen in substrate.

flasks. A small amount (2–3%) of hydrogen bromide was quantitatively determined by the iodometric titration of the iodine liberated after addition of excess potassium iodide and potassium iodate.[14] The organic layer was separated and dried over anhydrous sodium sulfate, and aliquots of the solutions were analyzed by GLC (DEGS, 55–175°). The percentage conversion of toluene and ethylbenzene-*ethyl-d_5* was determined by GLC analysis. Chloroform, benzyl bromide, β-bromoethanol, hexachloroethane, and α-phenylethyl bromide were formed as products, and their identities were confirmed by a comparison of their GLC retention with those of authentic materials. The unreacted toluene and ethylbenzene were reisolated by preparative GLC. The results of the mass spectrometric analyses of these materials are shown in Table I.

Reactions carried out with added ethylene oxide (20 mol % of the bromotrichloromethane) gave no detectable amount of hydrogen bromide after 48–72 hr of direct irradiation. The percentage conversion of toluene and ethylbenzene-*ethyl-d_5* was determined by GLC analysis to be ~2.2–12.5% and ~3.9–15.2%, respectively. Mass spectrometric analyses of these alkylbenzenes showed that no detectable extent of protium-deuterium scrambling had taken place during the reactions. Results are shown in Table II.

Bromotrichloromethane Brominations of Ethylbenzene and Cumene-*α-d*. Mixtures of ethylbenzene (8.07×10^{-4} mol), cumene-*α-d* (7.30×10^{-4} mol), bromotrichloromethane (8.71×10^{-4} mol), Freon 112 (7.65×10^{-4} mol), and Freon 113 (1.9×10^{-3} mol) were placed in Pyrex ampoules and degassed, and the ampoules were sealed. The tubes were irradiated for 19.5–39.5 hr at 40.0 ± 0.1° using a Hanovia 140-W utility lamp. A small amount (5.4–5.9×10^{-5} mol) of hydrogen bromide was detected by iodometric titration. GLC analyses showed that the conversion of ethylbenzene and cumene was 9.8–15.4% and 31.4–43.7%, respectively. Chloroform (42.9–65.3%), α-phenylethyl bromide, cumyl bromide, β-bromoethanol, and hexachloroethane were found as the products. Ethylbenzene and cumene were isolated by preparative GLC (DEGS, 100°) and examined by mass spectrometry. The results are shown in Table I.

Reactions carried out with added ethylene oxide (20 mol % of bromotrichloromethane) gave after 69–141 hr direct irradiation 16.4–19.4% and 3.5–4.8% conversion of ethylbenzene and cumene, respectively; no detectable amount of hydrogen bromide was found. Mass-spectral analyses of the recovered ethylbenzene and cumene-*α-d* showed that no protium-deuterium exchange had taken place during the reaction (see Table II).

Material Balance. A material balance for the reaction of bromotrichloromethane with ethylbenzene and cumene in the presence and absence of added ethylene oxide was determined by the following method.

A degassed mixture of bromotrichloromethane (1.94×10^{-3} mol), ethylbenzene (2.76×10^{-3} mol), Freon 112 (3.19×10^{-3} mol), and Freon 113 (9.3×10^{-3} mol) in a Pyrex ampoule was irradiated at 40.0° for 6 days. Products were analyzed in the same way as mentioned earlier. Hydrogen bromide (0.03×10^{-3} mol), chloroform (1.66×10^{-3} mol), α-phenylethyl bromide (1.82×10^{-3} mol), and hexachloroethane (trace) were found as the products. Ethylbenzene (1.22×10^{-3} mol) and bromotrichloromethane (0.04×10^{-3} mol) were found as unreacted starting materials. The material balances for the trichloromethyl group, phenylethyl group, and bromine were 88, 110 and 97%, respectively.

The same reaction mixture as above with added ethylene oxide (0.40×10^{-3} mol) was subjected to direct irradiation at 40.0° for 6 days. Chloroform (1.13×10^{-3} mol), α-phenylethyl bromide (1.21×10^{-3} mol), β-bromoethanol (0.27×10^{-3} mol), and hexachloroethane (0.07×10^{-3} mol) were found as products. Ethylbenzene (1.75×10^{-3} mol), ethylene oxide, and bromotrichloromethane (0.24×10^{-3} mol) were found as remaining starting materials. No hydrogen bromide was detected. The material balances for the trichloromethyl group, phenylethyl group, and bromine were 78, 107, and 89%, respectively.

A degassed mixture of bromotrichloromethane (1.95×10^{-3} mol), Freon 112 (3.19×10^{-3} mol), cumene (2.67×10^{-3} mol), and Freon 113 (9.3×10^{-3} mol) in a Pyrex ampoule was irradiated at 40.0° for 60 hr using a merry-go-round apparatus. Hydrogen bromide (0.10×10^{-3} mol), chloroform (1.32×10^{-3} mol), cumyl bromide[15] (0.91×10^{-3} mol), and hexachloroethane (trace) were found as products. Cumene (1.22×10^{-3} mol) and bromotrichloromethane (0.21×10^{-3} mol) were found as remaining starting materials. The material balances for the trichloromethyl group, cumyl group, and bromine were 78, 87, and 63%, respectively.

The same mixture as in the above reaction but with added ethylene oxide (0.40×10^{-3} mol) was subjected to direct irradiation at 40.0° for 6 days. Chloroform (0.46×10^{-3} mol), cumyl bromide (0.46×10^{-3} mol), β-bromoethanol (small amount), and hexachloroethane (0.14×10^{-3} mol) were found as products. Cumene (2.26×10^{-3} mol), ethylene oxide, and bromotrichloromethane (0.81×10^{-3} mol) were found as remaining starting materials. No hydrogen bromide was detected. The material balances for the trichloromethyl group, cumyl group, and bromide were calculated to be 79, 102, and 65%, respectively.

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References and Notes

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