was assigned on the basis of its method of preparation and its NMR spectrum ($\mathrm{CCl_4}$): τ 5.50 (s, 2 H), 2.1-2.7 (m, 9 H).

p-Phenylbenzyl bromide was prepared from *p*-biphenylmethanol by using potassium bromide and sulfuric acid;[31] mp 83-84 °C (lit.[25,32] mp 85 °C).

All of the remaining benzyl halides were commercially available (Aldrich Chemical Co.) Their purities were checked by GLC (OV-101) for the liquids or by recrystallization to a constant melting points (ethanol) for the solids. Compounds which contained the corresponding toluenes as impurities or were less than 99% pure were purified by low-temperature fractional crystallization or, as in the case of the solids, by recrystallization from ethanol.

The substituted benzylmercuric iodides were prepared analogously to the method used for the formation of benzylmercuric iodide. In all cases, an equivalent of zinc was allowed to react with the appropriate benzyl iodide in dry tetrahydrofuran. The resulting organozinc was then treated with 1 molar equiv of $\mathrm{HgI_2}$ in THF to form the benzyl mercuric iodide which was then recrystallized from ethanol. The NMR spectra of all of the organomercuriles were consistent with their structures.

m-Cyanobenzylmercuric iodide: colorless crystals; mp 153-154 °C. Anal. Calcd for $\mathrm{C_8H_6NHgI}$: C, 21.66; H, 1.37; N, 3.16. Found: C, 21.55; H, 1.35; N, 3.08.

p-Methylbenzylmercuric iodide: pale yellow crystals; mp 130-131 °C. Anal. Calcd for $\mathrm{C_8H_9HgI}$: C, 22.21; H, 2.10. Found: C, 22.26; H, 2.11.

p-Chlorobenzylmercuric iodide: pale yellow crystals; mp 149.5 °C. Anal. Calcd for $\mathrm{C_7H_6ClHgI}$: C, 18.56; H, 1.34. Found: C, 18.74; H, 1.41.

p-Cyanobenzylmercuric iodide: yellow crystals; mp 169-170 °C. Anal. Calcd for $\mathrm{C_8H_6HgNI}$: C, 21.66; H, 1.37; N, 3.16. Found: C, 21.73; H, 1.41; N, 2.78.

Dibenzylmercury:[33] white crystals; mp 111-111.5 °C. Anal. Calcd for $\mathrm{C_{14}H_{14}Hg}$: C, 43.90; H, 3.69. Found: C, 43.88; H, 3.73.

Procedures. Polarographic measurements were carried out with a Princeton Applied Research (PAR) Model 174A polarograph in a PAR 9300-9302 cell thermostated at 25 °C. Cyclic voltammetry was carried out with a PAR 9323 HMDE and a PAR Model 173-175-176 configuration; the resulting curves were recorded on an X-Y recorder. The cell in all cases used a three-electrode configuration in which the counterelectrode was platinum and the reference electrode was isolated by two glass frits. The reference electrode was AgCl/Ag, AgBr/Ag, or AgI/Ag prepared in each case by anodization of a clean Ag wire in the appropriate supporting electrolyte. The solutions were anhydrous acetonitrile prepared as described above and containing only the benzyl halide (1.0 mmol/L) and the appropriate tetraethylammonium halide supporting electrolyte (10.0 mmol/L).

Cyclic voltammetric curves were obtained by using 0.01 M $\mathrm{(C_2H_5)_4NI}$ as the supporting electrolyte. The supporting electrolyte showed no processes between −0.3 V (mercury oxidation) and −2.3 V (electrolyte discharge). No anodic peaks were observed for any compound within this potential range.

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Registry No. Benzyl chloride, 100-44-7; *p*-chlorobenzyl chloride, 104-83-6; *p*-fluorobenzyl chloride, 352-11-4; *p*-*tert*-butylbenzyl chloride, 19692-45-6; *p*-phenylbenzyl chloride, 1667-11-4; *p*-cyanobenzyl chloride, 874-86-2; *p*-benzoylbenzyl chloride, 42728-62-1; *p*-formylbenzyl chloride, 73291-09-5; *m*-chlorobenzyl chloride, 620-20-2; *m*-methylbenzyl chloride, 620-19-9; *m*-fluorobenzyl chloride, 456-42-8; benzyl bromide, 100-39-0; *p*-phenylbenzyl bromide, 2567-29-5; *p*-cyanobenzyl bromide, 17201-43-3; *p*-benzoylbenzyl bromide, 32752-54-8; *p*-formylbenzyl bromide, 51359-78-5; *p*-carbethoxybenzyl bromide, 26496-94-6; *m*-methylbenzyl bromide, 620-13-3; *m*-fluorobenzyl bromide, 456-41-7; *p*-methylbenzyl bromide, 104-81-4; *m*-cyanobenzyl bromide, 28188-41-2; *m*-bromobenzyl bromide, 823-78-9; *p*-bromobenzyl bromide, 589-15-1; benzyl iodide, 620-05-3; *p*-cyanobenzyl iodide, 874-88-4; *m*-cyanobenzyl iodide, 69113-58-2; *p*-chlorobenzyl iodide, 35424-56-7; *p*-carbethoxybenzyl iodide, 73373-16-7; *p*-methylbenzyl iodide, 4484-74-6; *p*-phenylbenzyl iodide, 73373-17-8; benzylmercuric iodide, 20632-18-2; *p*-cyanobenzylmercuric iodide, 75101-80-3; *m*-cyanobenzylmercuric iodide, 75101-81-4; *p*-chlorobenzylmercuric iodide, 75101-82-5; *p*-methylbenzylmercuric iodide, 75101-83-6; benzylmercuric chloride, 2117-39-7; dibenzylmercury, 780-24-5.

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Polar Radicals. 16.[1] Comments on a Recently Published Mechanistic Study of Photobromination Using Bromotrichloromethane

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The mechanism of the photobromination reactions of a series of 10-substituted 9-methylanthracenes with bromotrichloromethane was reexamined. It was shown, contrary to the previous report, that the reaction proceeded by a mixed chain involving abstraction by both the bromine atom and the trichloromethyl radical. The kinetic results obtained from these reactions were shown to be dominated by reversible hydrogen transfer of the radicals formed in the reaction with the small amounts of hydrogen bromide produced from bromine atom abstraction. When the reactions were carried out in the presence of a hydrogen bromide scavenger, either ethylene oxide or powdered potassium carbonate, the kinetic results of photobromination were found to be almost insensitive to the effects of the changes in substituents. The reactivities of fluorene relative to the 10-substituted 9-methylanthracenes were found to be anomalously high, as was previously reported; however, when the reactions were carried out in the presence of ethylene oxide, the relative reactivities were shown to be predictably almost the same as those obtained when *tert*-butoxy radicals were the abstracting species.

The results of a reinvestigation of the mechanism of the photoinitiated bromotrichloromethane side-chain bromination of arenes has been published a number of years ago.[3-5] The reaction mechanism was found to be more complex than originally proposed[6] (see Scheme I). An

Scheme I

$$\cdot\mathrm{CCl_3} + \mathrm{ArCH_3} \rightarrow \mathrm{ArCH_2}\cdot + \mathrm{HCCl_3} \qquad (1)$$

$$\mathrm{ArCH_2}\cdot + \mathrm{CCl_3Br} \rightarrow \mathrm{BrCH_2Ar} + \cdot\mathrm{CCl_3} \qquad (2)$$

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[1] Part 15: D. D. Tanner, J. A. Plambeck, D. W. Reed, and T. W. Mojelsky, *J. Org. Chem.*, preceding paper in this issue.

[2] University of Alberta, Postdoctoral Fellow, 1980.

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Table I. Relative Rates of Disappearance of a Number of 10-Substituted 9-Methylanthracenes vs. Fluorene during Their Reactions with Bromotrichloromethane at 70 °C

substituent	$k_{rel}{}^{d}$ (this work)	k_{rel} (ref 12)	$k_{rel}{}^{d}$ (this work, ethylene oxide)	$k_{rel}{}^{d}$ (this work, K_2CO_3)
CH_3O	9.30 ± 0.05 (3)	9.00 ± 0.52	3.05 ± 0.35 (4)	3.08 ± 0.26 (2)
CH_3	4.10 ± 0.15 (2)[a]	4.03 ± 0.55[a]	2.71 ± 0.05 (3)[a]	
C_6H_5		1.92 ± 0.11		
H	2.89 ± 0.13 (2)[c]	2.75 ± 0.32[b]	2.93 ± 0.02 (3)[c]	
Cl	2.66 ± 0.05 (3)	1.99 ± 0.29	2.83 ± 0.08 (3)	
Br	2.29 ± 0.08 (3)	1.67 ± 0.12	2.88 ± 0.05 (3)	
CH_3OC	1.04 ± 0.01 (3)	1.17 ± 0.18	2.85 ± 0.15 (3)	
N≡C	0.45 ± 0.01 (3)	0.57 ± 0.03	2.77 ± 0.17 (3)	2.39 ± 0.18 (3)

[a] Statistically corrected. [b] Corrected for ring substitution. [c] Corrected for ring substitution by using the ratio of addition to substitution given in ref 12. [d] Numbers in parentheses represent the number of independent experiments performed.

alternative mechanism, first suggested by Russell[7] (Scheme II), was shown to play a significant role in the overall

Scheme II

$$ArCH_2\cdot + BrCCl_3 \rightarrow ArCH_2Br + CCl_3\cdot \quad (3)$$

$$\cdot CCl_3 + HBr \rightarrow CCl_3H + Br\cdot \quad (4)$$

$$Br\cdot + ArCH_3 \rightarrow HBr + ArCH_2\cdot \quad (5)$$

reaction sequence. Not only was a bromine atom chain as well as a trichloromethyl radical chain involved but also it was pointed out in these papers[3-5] that hydrogen bromide reversibility (eq 6) dominated the kinetics of the re-

$$ArCH_2\cdot + HBr \rightleftarrows ArCH_3 + Br\cdot \quad (6)$$

action. During competitive brominations, it was demonstrated that extensive hydrogen bromide reversibility masked the true distribution of radicals produced during the product-determining abstraction step of the substitution reaction. The radical formed most readily (i.e., the most stable, least reactive radical) underwent the least reversal. The abstracting species, therefore, appeared to be more selective than it in fact was. During the bromotrichloromethane brominations, a majority of the hydrocarbon radicals formed were shown to revert to starting material by transfer with the small amounts of hydrogen bromide formed in the reaction. Since the transfer with hydrogen bromide produced another bromine atom capable of abstraction, small amounts of hydrogen bromide were quite effective in determining the apparent selectivity. When the bromination was carried out in the presence of an added hydrogen bromide scavenger, solid potassium carbonate or ethylene oxide, free-radical chain bromination proceeded by trichloromethyl radical abstraction with a selectivity much lower than is observed in the presence of hydrogen bromide.[3,4]

Since the information concerning the complications inherent in the bromination mechanism first became available, a number[8-12] of mechanistic investigations have appeared which utilized bromotrichloromethane as the halogenating agent in a variety of competitive kinetic studies. The problems pointed out in the reports concerned with the reversible abstraction[3-5] were completely ignored in these publications. The three publications dealing with hydrogen abstraction from substituted benzyl chlorides,[8] phenylacetonitriles,[11] and β-(substituted phenyl)ethyl bromides[10] and a study on long-range substituted effects[9] do not consider the kinetic effects of reversibility nor the duality of the abstracting species. In the most recent publication,[12] a study was made of substituent effects in hydrogen abstractions from 10-substituted 9-methylanthracenes by using bromotrichloromethane. The authors acknowledged one of the papers on the effects of hydrogen bromide reversal in these brominations[3] and dealt with its consequences in the following manner: "The view that benzylic brominations utilizing bromotrichloromethane involve hydrogen abstraction by bromine atom has been advanced.[3] We, however, have chosen to adopt the traditional view that in these reactions, the trichloromethyl radical is the species involved,[6] hence allowing for the desired comparison to be made". Since no consideration was made of a possible competing bromine atom chain nor of the competitive reaction of formed radicals with hydrogen bromide, the bromination of 10-substituted 9-methylanthracenes with bromotrichloromethane has been reinvestigated, and the results are the subject of this paper.

Results and Discussion

Mixtures of bromobenzene and bromotrichloromethane in approximate 2:3 molar ratios were used as solvents for reaction mixtures of the appropriate 10-substituted 9-methylanthracene and fluorene. The mixtures, with added *p*-di-*tert*-butylbenzene as an internal standard, were placed in NMR tubes, degassed, and photolyzed (275-W General Electric sunlamp, 70 °C) until the least reactive substrate had reacted from 10 to 90%. The values of the relative rates of disappearance of the 9-methylanthracene relative to fluorene were calculated from an analysis of an integrated NMR spectra of the reaction mixture before and after photolysis. A comparison of the relative rates for the two substrates, k_{an}/k_{fl}, obtained in this study with those reported by Gleicher et al.[12] is listed in Table I. The two sets of relative rates are quite similar, although a number of relative reactivities have differences outside of the given experimental errors. Both sets of data show satisfactory Hammett linear free-energy correlations having ρ (σ^+) values that are almost the same (this work, $\rho = -0.84$, r

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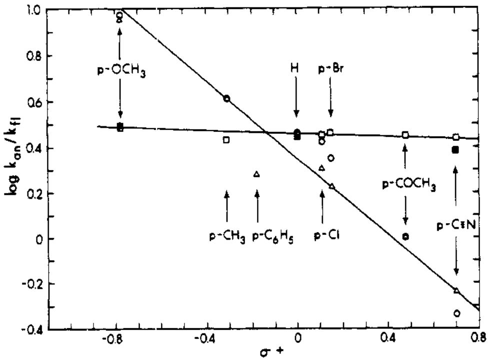

Figure 1. Logarithms of the rates of hydrogen abstraction for a series of 10-substituted 9-methylanthracenes relative to fluorene [values for log k_{an}/k_{fl} obtained from the photobromination of the substrates using bromotrichloromethane: △, taken from ref 12; ○, this work; □, this work with added ethylene oxide; ■, this work with added solid potassium carbonate] vs. σ^+ constants [values of σ^+ constants were taken from the recommended best values: O. Exner, "Correlation Analysis in Chemistry", N. B. Chapman and J. Shorter, Eds., Plenum Press, London, 1978].

= 0.97; ref 12, $\rho = -0.75$, $r = 0.97$; see Figure 1).

The reactions run with an added hydrogen bromide scavenger, ethylene oxide or powdered potassium carbonate, showed uniform selectivities, where all the 10-substituted 9-methylanthracenes showed the same relative reactivity toward abstraction by trichloromethyl radicals ($k_{an}/k_{fl} = 2.86 \pm 0.08$, $\rho \simeq 0.0$; see Table I and Figure 1).

A plot of log k_{rel} vs. σ^+ for the kinetic data given in Table I (see Figure 1) clearly demonstrates the similarity between the bromination reactions carried out in the presence of the small amounts of hydrogen bromide formed in the reaction (ref 12 and this work) and the dramatic effect on the kinetics obtained by carrying out the reaction in the presence of a hydrogen bromide scavenger.

The sensitivity of the rate of abstraction of an abstracting radical to small changes in substrate structure will be related to the selectivity of the radical and its sensitivity to polar interactions. An indication of the relative magnitude of these effects for a particular radical can be obtained by an examination of the primary/secondary/tertiary selectivity of the radical and the ρ value obtained when the reaction is carried out with a series of substituted toluenes as substrates. For isoentropic reactions which are exothermic, the larger the negative enthalpy of the reaction the smaller will be the ρ value observed. It should be predictable, a priori, that a series of 10-substituted 9-methylanthracenes which is much more reactive than the corresponding series of toluenes should show a ρ value, toward abstraction by trichloromethyl, very much smaller than the value, -0.69, previously reported for that radical.[3] An estimate of the magnitude expected for the ρ value for α substitution of a 10-substituted 9-methylanthracene can be obtained by comparing its relative rate of reaction to that of toluene. The rate of bromination of toluene relative to fluorene was determined indirectly for the photoinitiated bromotrichloromethane-promoted halogenation reactions (70 °C, added ethylene oxide). The results are listed in Table II. Since changes in ρ for differences ($10-20 \times k_{rel}$) in relative reactivity of the parents of two series typically appear to lower the ρ value by about 50% and for higher differences in relative rate by even a greater amount,[13] the observation is not unreasonable that the bromotrichloromethane bromination of 10-substituted 9-methylanthracenes was insensitive to substituent effects, $\rho \simeq 0$.

Table II. Relative Rates of Abstraction of α-H

substrate	rel reactv/molecule[a]	
	$\cdot CCl_3$	$(CH_3)_3CO\cdot$
toluene	1	1
ethylbenzene	4.7 ± 0.04	2.9 ± 0.17
cumene	5.0 ± 0.05	4.7 ± 0.18
fluorene	8.8 ± 0.05	7.7 ± 0.20
9,10-dimethylanthracene	47.5 ± 0.07	43.4 ± 0.31
10-methoxy-9-methylanthracene	27.3 ± 0.35	25.6 ± 0.31

[a] At 70 °C.

The relative reactivity of two substrates which are relatively insensitive to substituent effects, i.e., alkanes or highly reactive arylalkanes, show similar selectivity toward radicals with high or low electronegativities. This selectivity is governed primarily by the primary/secondary/tertiary selectivity of the radical. The reactivity of a 10-substituted 9-methylanthracene relative to fluorene, 2.86 ± 0.08, observed for the bromotrichloromethane brominations should be, therefore, comparable to the relative reactivity of other radicals that have similar selectivities. A comparison of the relative rates of reaction of another radical with fluorene and 9,10-dimethylanthracene or 10-methoxy-9-methylanthracene is given in Table II. The reaction of *tert*-butoxy radicals ($\rho = -0.4$, 40 °C)[14] shows relative rates very similar to those found for the bromotrichloromethane photobrominations of those substrates carried out in the presence of ethylene oxide. The anomalously high values recently reported[12] for the relative rates of bromination of these substrates (see Table I), carried out without a hydrogen bromide scavenger, are clearly an artifact of the reversible kinetics, since the *tert*-butoxy radical, a radical of relatively low response to the effect of substituents, shows almost the same relative rates of abstraction as does the trichloromethyl radical.

Experimental Section

Quantitative analyses of the kinetic trials involving the substituted anthracenes were performed by NMR spectroscopy using either a Perkin-Elmer R32 (90 MHz), a Varian HA-100, or a Bruker WH-200 spectrometer. When higher resolution was necessary (i.e., for the reactions with added ethylene oxide) a Bruker WH 400-MHz spectrometer was employed.

GLC analytical determinations of the kinetic runs involving toluene, ethylbenzene, and cumene were carried out by using a Hewlett-Packard 5840A chromatograph equipped with a thermal-conductivity detector and fitted with a 20 ft × $^1/_8$ in. stainless-steel column packed with 10% DEGS on Chromosorb W/AW (60–80 mesh).

Materials. Bromotrichloromethane (Aldrich Chemical Co.) was purified by the method of Stock;[15] bp 104 °C (lit. bp 104 °C). Bromobenzene (Aldrich Chemical Co.) was distilled by using a 28-in. spinning-band column [bp 155–156 °C (710 mm), lit.[16] bp 155–156 °C (760 mm)], and its purity was checked by GLC (Carbowax 20M on Chromosorb W/AW 80/100). *p*-Di-*tert*-butylbenzene (Aldrich Chemical Co.) was used as supplied; mp 77–78 °C (lit.[17] mp 77–78 °C). Fluorene (Matheson Coleman and Bell) was recrystallized from ethanol; mp 116–117 °C (lit.[18] mp 116–117 °C). 9,10-Dimethylanthracene was prepared by the method of Kreevoy and Brown; mp 183–185 °C (lit.[19] mp 184–185 °C) or, alternatively, by the reduction of commercially available 9-

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methylanthracene-10-carboxaldehyde.[20]

9-Methyl-10-methoxyanthracene. Anthracene, excess aqueous potassium hydroxide, and methyl iodide were reacted together by using the method of Barnett and Cook.[21] Recrystallization from petroleum ether gave the title compound, mp 139–142 °C (lit.[21] mp 141–143 °C).

9-Methyl-10-cyanoanthracene. 9-Methylanthracene-10-carboxaldehyde was converted to the oxime, which was in turn converted by the action of acetic anhydride to the desired product,[22] mp 140–142 °C (lit.[22] mp 141–143 °C).

9-Methyl-10-acetylanthracene. Commercial 9-methylanthracene, acetyl chloride, and AlCl$_3$ were reacted in benzene (-5 °C) to give the ketone,[23] mp 133–134 °C (lit.[23] mp 133–135 °C).

9-Methyl-10-haloanthracenes. Both chloro- and bromoanthracenes were prepared by reaction of the appropriate anhydrous cupric halide with 9-methylanthracene[24] in CCl$_4$. The 9-methyl-10-chloroanthracene was obtained [mp 178–180 °C (lit.[24] mp 180–181 °C)] along with the bromo analogue, mp 170–171 °C (lit.[24] mp 170–172 °C).

Toluene, ethylbenzene, and cumene (Phillips reagent grade) were used without further purification. Freon 112 (Matheson) was distilled before use. *tert*-Butyl hypochlorite was made according to the literature procedure.[25]

Kinetic Procedure. Bromotrichloromethane. Bromination of the appropriate 10-substituted 9-methylanthracene (0.15 M) vs. fluorene (0.07 M) was carried out as described by Gleicher,[12] or the reactions were run in a similar manner but with 20 mol % (0.05 M) of added ethylene oxide. Upon the completion of these reactions, it was found that the ethylene bromohydrin formed in the reaction interfered with NMR analyses, since the methylene absorption was almost coincident with the fluorene resonance. The analysis of the mixture could be obtained, however, by using the 400-MHz spectrometer. The reactions carried out with powdered potassium carbonate, under analogous reaction conditions, were run in Pyrex ampules containing excess potassium carbonate (see ref 3 and 4). During irradiation the reaction mixtures were shaken continuously. The bromination reactions of toluene, ethylbenzene, cumene, and fluorene with bromotrichloromethane (added ethylene oxide) were carried out at 70 °C and analyzed by using the method previously reported.[4]

***tert*-Butyl Hypochlorite.** To mixtures of the appropriate substituted anthracene (0.15 M) and fluorene (0.07 M) in bromobenzene as solvent containing tetramethylsilane (0.015 M) as standard was added *tert*-butyl hypochlorite (0.19 M). The mixtures were placed in NMR tubes and degassed, and the tubes were sealed. The thermostated solutions (70 °C) were irradiated until the reaction was complete (3–4 min).

The halogenation of arenes with *tert*-butyl hypohlorite was carried out at 70 °C by using Freon 112 as an internal standard.[26] The reactions relative to fluorene also contained bromobenzene as solvent.

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Registry No. Bromotrichloromethane, 75-62-7; 10-methoxy-9-methylanthracene, 21992-33-6; 9,10-dimethylanthracene, 781-43-1; 10-phenyl-9-methylanthracene, 13425-08-6; 9-methylanthracene, 779-02-2; 10-chloro-9-methylanthracene, 19096-07-2; 10-bromo-9-methylanthracene, 23674-17-1; 10-acetyl-9-methylanthracene, 36778-18-4; 10-cyano-9-methylanthracene, 1467-01-2; toluene, 108-88-3; ethylbenzene, 100-41-4; cumene, 98-82-8; fluorene, 86-73-7.

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