covered by elution with pentane on silica gel prior to distillation or through careful distillation.

tert-**Butylacetylene (1).** Triflate **3** (2.32 g, 0.010 mol) was added to 1.58 g (0.020 mol) of dry pyridine in a 10-ml round-bottom flask and connected to a short-path bulb-to-bulb distillation apparatus. The mixture was heated to 60° and the product was collected over a 15-hr period in a Dry Ice-acetone-cooled receiver, yielding 0.74 g (90%) of **1**, >99% pure by glc: nmr (neat) δ 1.22 (s, 9 H), 2.02 (s, 1 H); ir (CCl_4) 3320 ($C{\equiv}CH$), 2130 cm^{-1} ($C{\equiv}C$).

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Registry No.—**1**, 917-92-0; **2**, 75-97-8; **3**, 27701-32-2; triflic anhydride, 358-23-6.

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Reaction of Bromotrichloromethane with α-Alkyltoluenes and α,α-Dialkyltoluenes[1]

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The relationship between free-radical formation and hydrocarbon structure have usually been based upon consideration of electronic factors. Tertiary radicals are known to be more stable than secondary or primary species. For example, the relative order of reactivity, cumene > ethylbenzene > toluene, for hydrogen abstraction by the trichloromethyl radical has been known for some time.[2] Steric effects, however, may also be of importance. Examples where the relatively small chlorine[3] or bromine[4] atoms show reluctance to attack electronically favored, albeit sterically hindered, positions have been reported. Larger radicals should exhibit even greater steric demands. Minisci and coworkers, utilizing various dialkylammonium radical cations as hydrogen abstracting agents, have observed that the penultimate position of several straight-chain compounds is preferentially attacked.[5] This selectivity is increased as the size of the alkyl groups attached to the nitrogen atom of the abstracting agent becomes larger. It has also been claimed that the selectivity associated with benzylic hydrogen abstractions depends in part on similar steric factors.[6,7] Cases involving benzylic hydrogen abstraction by large radicals from hindered positions seem to show enhanced substituent effects.

Andrews, Keefer, Friedrich, and their coworkers have examined hydrogen abstraction from the benzyl position of α-substituted toluenes.[8,9] In their most recent work they obtained a good correlation of relative rates of hydrogen abstraction by bromine atom with the $\sigma_p{}^+$ parameters of the substituents.[9] The large negative ρ value was taken as evidence for both appreciable charge development in transition state and for the possibility of direct resonance interaction between the substituent and the nascent radical. Although it was stated that steric factors were unimportant in this system, subsequent work indicated that these factors might be involved.[7] Use of the Taft four-parameter equation[10] was required to treat α-substituted toluenes with large substituents.

$$\log \frac{k_x}{k} = \sigma^+\rho + sE_s$$

To examine the importance of steric effects, it was decided to study hydrogen abstraction from α-alkyltoluenes and α,α-dialkyltoluenes by bromotrichloromethane.[11] As relatively small variations in electronic factors should exist among these compounds of a similar structural type, the steric factors operative might become more obvious. In Table I are found the results of the present experiments. All runs were initiated photolytically at 70° and carried out in replicate.

Table I
Relative Rates of Hydrogen Abstraction from α-Alkyltoluenes and α,α-Dialkyltoluenes by Bromotrichloromethane at 70° [a]

Compd	Registry no.	k_X/k_{oumene} Exptl	Calcd
Cumene	98-82-8	1.000	0.701
sec-Butylbenzene	135-98-8	0.48 ± 0.04	0.491
3-Phenylpentane	1196-58-3	0.17 ± 0.02	0.348
Ethylbenzene	100-41-4	0.15 ± 0.01	0.127
n-Propylbenzene	103-65-1	0.12 ± 0.01	0.089
Isobutylbenzene	538-93-2	0.042 ± 0.002	0.034
Toluene	108-88-3	0.017 ± 0.001[b]	0.023
Neopentylbenzene	1007-26-7	0.003 ± 0.0005[c]	0.003

[a] All kinetic results expressed per benzylic hydrogen. [b] Obtained relative to neopentylbenzene. [c] Obtained relative to isobutylbenzene.

The above data could be treated in several ways. Qualitatively the standard electronic dependence is noted with all tertiary and most secondary systems being more reactive than toluene. Several linear free energy treatments were utilized in attempts to correlate the data. The best least-squares correlation was obtained using the relationship

$$\log \frac{k}{k_{\text{cumene}}} = -5.78(\Sigma\sigma^+) + 0.85(\Sigma E_s) - 3.75$$

The calculated values of the relative rates are also shown in Table I. The average deviation between these calculated values and their experimental counterparts is less than 25%. It is felt that this is creditable considering the range of nearly three powers of ten between the extreme relative rates shown by members of this series. Figure 1 illustrates the correlation between experimental and calculated logarithms of relative rates. The correlation shows a slope nearly equal to unity and a correlation coefficient of 0.980.

Experimental Section

Materials. Bromotrichloromethane, chlorobenzene, toluene, ethylbenzene, propylbenzene, cumene, isobutylbenzene, *sec*-butylbenzene, and neopentylbenzene were obtained from commercial sources. The remaining compound, 3-phenylpentane, was prepared from the reaction of 3-pentanone with phenylmagnesium bromide to yield 3-phenyl-3-pentanol followed by dehydration and catalytic hydrogenation. All materials were distilled before use. Physical properties corresponded with values in the literature. Purities greater than 99% were determined by glc.

Product Studies. Prior work has shown that exclusive benzylic bromination occurs for toluene, ethylbenzene, cumene,[6] propylbenzene,[13] and neopentylbenzene.[7] It was assumed that the remaining compounds studied would proceed in identical manner.

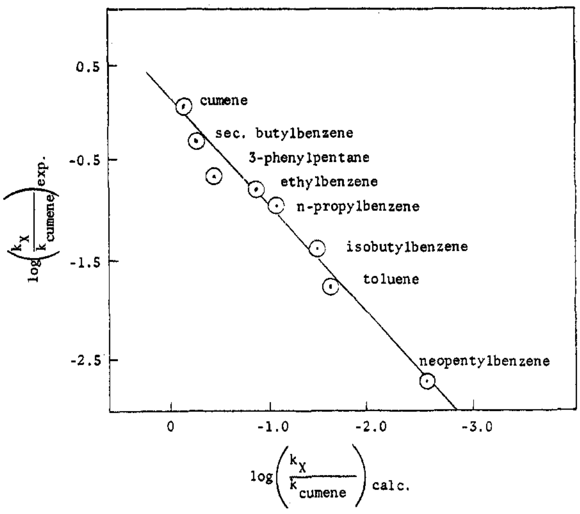

Figure 1. Relative rates of hydrogen atom abstraction from alkyl-substituted toluenes.

Kinetic Studies. Solutions of two alkylbenzenes, bromotrichloromethane, and chlorobenzene were prepared in the approximate molar ratio of 1:1:20:1. Approximately 0.75 ml of the solution was placed in each of the several ampoules. The ampoules were cooled to Dry Ice-isopropyl alcohol temperature until the solutions solidified. The ampoules were evacuated at 0.5-1.0 mm and flushed with nitrogen several times with three intermediate thawings. The ampoules were sealed under vacuum and one was reserved for the analysis of the unreacted starting materials. The remainder were placed horizontally just below the surface of a mineral oil constant-temperature bath maintained at 70.0 ± 0.5°. The solution was irradiated with ultraviolet light provided by a Sylvania 275-W sun lamp placed 20 cm above the surface of the oil. Reaction times varied from 3 to 7 hr, by which time 15-95% of the total hydrocarbons had reacted. The ampoules were then cooled and opened. Analysis of the mixtures, both before and after the reaction, was carried out *via* glc on either a 5% SE-30 on Chromosorb W column or a 5% Fluorolube GR 362 on Chromosorb W column.

Registry No.—Bromotrichloromethane, 75-62-7.

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