Side-Chain Bromination of α-Substituted Toluenes by N-Bromosuccinimide. A Revision and Extension of Previous Observations

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Values for the relative reactivities of α-substituted toluenes with N-bromosuccinimide which have been obtained in previous investigations are not in complete agreement. The reactivities have, therefore, been redetermined through competition experiments using nmr techniques for analysis of the product mixtures. Application of the nmr method has made possible, in most instances, the cross-checking of both the quantities of reactants consumed and the quantities of α-bromotoluene derivatives produced. The logarithms of the relative reactivities of the various α-substituted toluene derivatives ($C_6H_5CH_2X$) show a reasonably good $\rho\sigma$ correlation using the $\sigma_p{}^+$ values of the substituents X; the ρ value is substantially more negative (−2.46) than that observed previously for the reactions of ring-substituted toluenes ($XC_6H_4CH_3$) with N-bromosuccinimide under similar conditions. Thus, appreciable polarization of the benzylic carbon presumably occurs during the activation processes of these reactions.

In 1964, a report was presented from this laboratory concerning the relative rates of reaction of a number of α-substituted toluenes with N-bromosuccinimide in carbon tetrachloride at reflux temperatures.[1] The reactivity series was established by means of experiments in which mixtures of two toluene derivatives competed for a limited amount of halogenating agent. Subsequently, revised values (which differ significantly from the original set) for the reactivities of certain of the compounds were reported from two different laboratories.[2,3] The two sets of revised reactivities are not, however, in particularly good accord even if allowances are made for the fact that the experimental conditions used in the determinations were somewhat different. The discrepancies are believed to be associated primarily with certain difficulties involved with the application of gas–liquid partition chromatographic techniques to the analysis of the product mixtures. However, similar analytical methods have been employed, with no problems of serious consequence, in establishing the relative reactivities of a series of ring-substituted toluenes with N-bromosuccinimide.[4]

In the case of the α-substituted toluenes, in which substituent effects are relayed directly to the reaction center rather than through the aromatic nucleus, there is a much wider variation in reactivity than is observed for ring-substituted toluenes. As a consequence, it is difficult to maintain accuracy in the application of chromatographic analytical techniques to the investigation of α-substituted toluenes at the extreme ends of their reactivity series. An unreactive material such as α-nitrotoluene, for example, is consumed only to a small extent in the typical competition experiment.[3] Thus, a relatively low percentage error in establishing its concentration at the start or termination of reaction can lead to a serious error in the calculation of the amount which has reacted. Other analytical problems encountered in applying the glpc method are related to the fact that some of the α-substituted toluenes cannot be separated satisfactorily from the product mixtures on the columns used.[1-3] Also, cross-check analyses for reaction products cannot be made since many of the α-bromotoluenes are not stable under the glpc conditions.

Suffice it to say, it seemed essential to repeat the earlier work on the reactivities of the α-substituted toluenes with N-bromosuccinimide, this time using an analytical technique which would provide throughout the series for reasonably accurate determinations of both the quantities of unreacted starting materials and the quantities of substituted α-bromotoluenes in the product mixtures. For this purpose, nmr analytical methods have been employed. A reactivity series has now been obtained which is unquestionably far more reliable than those published previously, and which can be accepted, as the earlier figures over-all could not, as reasonable in the light of other observations concerning related reactions.

Experimental Section

Materials.—Commercial samples of benzyl acetate, benzyl methyl ether, α-bromotoluene, *o*-chlorotoluene, cumene, *p*-nitrotoluene, toluene, triphenylmethane (Eastman Organic Chemicals), diphenylmethane, benzyl cyanide (Aldrich Chemical Co. Inc.), α-nitrotoluene (K and K Laboratories Inc.), ethylbenzene, anisole (Matheson Coleman and Bell), benzyl chloride, bromine (Mallinckrodt), and N-bromosuccinimide (Arapahoe Chemicals, Inc.) were used without further purification. Methyl phenylacetate, bp 57.5–58° (0.8 mm), lit.[3] bp 54–55° (1 mm), was prepared by the sulfuric acid catalyzed reaction of phenylacetic acid and methanol. Benzyl phenyl ether, mp 38–40°, lit.[5] mp 39°, and benzyl phenyl sulfide, mp 40.5–42°, lit.[6] mp 40–41° (furnished by Dr. Ian Horman), were prepared from α-chlorotoluene and the sodium salts of phenol and thiophenol, respectively. The procedure of Szmant and Yoncoskie[7] was used in the preparation of 1,1-diphenylethane, bp 93–94° (0.8 mm), lit.[7] bp 126–129° (8 mm). J. T. Baker reagent grade carbon tetrachloride was used as the reaction medium.

The Competition Experiments.—The particular pair of compounds used in an individual competition reaction was chosen so that their nmr proton absorption positions were well separated and so that their rates of reactivity toward N-bromosuccinimide

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were similar. It is essential to compare compounds of similar reactivity in order to obtain reliable results. For each determination the two competing compounds were weighed into a 50-ml flask containing a weighed quantity of N-bromosuccinimide. This mixture was then diluted to approximately 20–25 ml with carbon tetrachloride, treated with 0.1 g of benzoyl peroxide, stirred vigorously, and heated under reflux (measured pot temperature 77°) until the brominating agent had disappeared completely from the bottom of the flask (the reflux time varied from 5 min to over 1 hr depending on the reactivities of the competing compounds toward N-bromosuccinimide).

When one of the competing compounds was α-nitrotoluene, the mixtures were also irradiated with a 750-W projection lamp. This treatment reduced the reaction times to approximately 1 hr as compared to the much longer reaction times necessary when the mixtures were heated under reflux without irradiation. The heat from the lamp was sufficient to maintain refluxing of the carbon tetrachloride solution during the reaction. Competition experiments using *p*-nitrotoluene and methyl phenylacetate were conducted with and without irradiation. No significant differences were observed in the results obtained by the two procedures.

After the reactions were complete, the cooled mixtures were treated with weighed samples of an appropriate internal standard for nmr analysis. The amounts of the unreacted starting materials and their bromides in the liquid portion of the product mixture were determined, using a Varian Associates Model A-60A instrument, by integration of the appropriate peak areas and the area corresponding to the known amount of internal standard added. All peak areas were corrected for the number of hydrogens responsible for the absorption. At least six integrations were run for every peak. The average deviation of individual integrations from the mean was generally on the order of 1%.[8] It was assumed that the toluenes were attacked only at the side chain and not on the aromatic nucleus. No evidence of the formation of significant quantities of ring bromination products has been obtained.

The chemical shift values (δ in parts per million downfield from TMS) vary slightly in different mixtures. The average individual proton absorptions of the competing compounds, the bromide products, and the internal standards used in the calculation of product compositions are as follows: benzyl methyl ether, δ 3.2 (s, 3 H, CH_3), 4.3 (s, 2 H, CH_2); α-bromobenzyl methyl ether, 3.5 (s, 3 H, CH_3); triphenylmethane, 5.5 (s, 1 H, CH); 1,1-diphenylethane, 1.6 (d, 3 H, $J = 7$ Hz, CH_3), 4.0 (quartet, 1 H, $J = 7$ Hz, CH); benzyl phenyl sulfide, 4.0 (s, 2 H, CH_2); α-bromobenzyl phenyl sulfide, 6.2 (s, 1 H, CHBr); cumene, 1.3 (d, 6 H, $J = 7$ Hz, $(CH_3)_2$); cumyl bromide, 2.2 (s, 6 H, $(CH_3)_2$); benzyl phenyl ether, 4.8 (s, 2 H, CH_2); ethylbenzene, 1.3 (t, 3 H, $J = 7.5$ Hz, CH_3), 2.7 (quartet, 2 H, $J = 7.5$ Hz, CH_2); α-bromoethylbenzene, 2.0 (d, 3 H, $J = 7.5$ Hz, CH_3), 5.3 (quartet, 1 H, $J = 7.5$ Hz, CHBr); diphenylmethane, 3.9 (s, 2 H, CH_2); benzhydryl bromide, 6.1 (s, 1 H, CHBr); benzyl acetate, 2.1 (s, 3 H, COCH_3), 5.2 (s, 2 H, CH_2); α-bromobenzyl acetate, 2.2 (s, 3 H, COCH_3); toluene, 2.3 (s, 3 H, CH_3); benzyl chloride, 4.4 (s, 2 H, CH_2); α-bromobenzyl chloride, 6.5 (s, 1 H, CHClBr); methyl phenylacetate, 3.5 (s, 3 H, COCH_3), 3.6 (s, 2 H, CH_2); α-bromomethyl phenylacetate, 3.7 (s, 3 H, COCH_3), 5.2 (s, 2 H, CHBr); benzyl cyanide, 3.5 (s, 2 H, CH_2); α-bromobenzyl cyanide, 5.3 (s, 2 H, CHBr); benzyl bromide, 4.3 (s, 2 H, CH_2); α-bromobenzyl bromide, 6.4 (s, 1 H, $CH$$Br_2$); α-nitrotoluene, 5.2 (s, 2 H, CH_2); *p*-nitrotoluene, 2.3 (s, 3 H, CH_3); *p*-nitrobenzyl bromide, 4.3 (s, 2 H, CH_2Br); *o*-chlorotoluene, 2.3 (s, 3 H, CH_3); *o*-chlorobenzyl bromide, 4.4 (s, 2 H, CH_2Br); anisole, 3.7 (s, 3 H, CH_3). All absorptions used in calculations were clean and well resolved. For certain starting materials and bromide products more than a single absorption was available on which the quantitative analyses could be based. In such cases calculations based on either absorption gave identical results.

Two experiments were carried out using triphenylmethane and ethylbenzene as the competing compounds and elemental bromine as the brominating agent. A mixture of weighed samples of the reactants was diluted with approximately 25 ml of carbon tetrachloride in a 50-ml three-necked flask equipped with a nitrogen inlet tube, a cold finger condenser containing Dry Ice and carbon tetrachloride, a dropping funnel for bromine, and a magnetic stirrer. The flask was immersed in a refluxing methylene chloride bath (40–41°) and illuminated with a 150-W tungsten lamp while a limited quantity of bromine dissolved in approximately 5 ml of carbon tetrachloride was added dropwise. The rate of addition of bromine was varied in the two experiments, and nitrogen was bubbled into one of the reaction mixtures to remove hydrogen bromide. The product mixtures were again subjected to nmr analysis after treatment with a weighed quantity of an appropriate internal standard. The difference in the procedure did not significantly affect the results obtained (see Table I).

The results of the analyses of the various reaction mixtures are summarized in Table I. Included in the tabulation are the initial, $[A]_0$ and $[B]_0$, and final, $[A]_f$ and $[B]_f$, amounts of the compounds competing for the brominating agent. The reported quantities of the α-substituted toluene bromination products, ABr and BBr, usually were determined directly from the appropriate integrated proton peak areas. In some instances, and always when the bromide products did not have any benzylic or other nonaromatic protons, ABr and BBr were calculated as $([A]_0 - [A]_f)$ and $([B]_0 - [B]_f)$, respectively. In such cases, and also in those cases in which $[A]_f$ or $[B]_f$ were calculated as the difference between the amounts of starting materials and the products, the numerical values are reported in parentheses. The agreement between the amounts of α-substituted toluenes consumed and the substituted benzyl bromides produced, as shown in Table I, is generally very good. The relative reactivities, k_A/k_B, of the competing pairs of compounds were calculated using the integrated rate equation (1).

$$k_A/k_B = \log([A]_0/[A]_f)/\log([B]_0/[B]_f) \qquad (1)$$

In most of the experiments summarized in Table I, there was good agreement between the quantities of substituted toluenes consumed and of N-bromosuccinimide initially present in the reaction mixtures. In several cases, however, the mole ratio of toluene derivative consumed to the brominating agent used was significantly less than one. In some instances, as will be mentioned below, this can be traced to a further reaction between N-bromosuccinimide and a product. This in no way affects the accuracy of the k_A/k_B values which are tabulated. Russell and Vinson[3] have indicated that difficulties in obtaining reproducible results were encountered in conducting N-bromosuccinimide competition experiments with phenylacetonitrile as a reactant. In our work with this compound the reproducibility was good. The correlation between the quantities of nitrile consumed and $C_6H_5CH(Br)CN$ produced was also found to be good.

For several of the compounds investigated, including cumene, benzyl acetate, benzyl methyl ether, and benzyl phenyl sulfide, the agreement between total toluene derivative consumed and side-chain bromination product formed (as detected by nmr spectroscopy) was poor. In the case of the cumyl halides, this may be associated with their ready susceptibility to loss of hydrogen halide to form α-methylstyrene.[2,9] The presence of a small amount of α-methylstyrene in the nmr spectra of the cumene reaction products has not, however, been detected. The reaction of benzyl acetate with N-bromosuccinimide yielded α-bromobenzyl acetate, identified on the basis of its nmr absorption at δ 2.18. The poor correlation between the amounts of this substance produced and of phenyl acetate consumed is related to the fact that substantial quantities of benzaldehyde and acetyl bromide (nmr absorption at δ 2.82) were also formed as reaction products. A more extensive discussion of this matter will be presented elsewhere.[10] α-Bromobenzyl methyl ether, which has nmr absorptions (singlets) at δ 3.5 and 6.7 characteristic of the methyl and benzylic hydrogens, respectively, is not produced quantitatively from benzyl methyl ether since it is thermally unstable with respect to decomposition to form benzaldehyde.[11] This will also be dealt with in detail in a separate

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[8] An analytical procedure based on nmr analysis for substituted benzyl bromide products has been used previously in the investigation of side-chain bromination of certain ring-substituted toluenes by R. E. Pearson and J. C. Martin, *J. Amer. Chem. Soc.*, **85**, 354, 3142 (1963).

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TABLE I

COMPETITIVE BROMINATIONS WITH N-BROMOSUCCINIMIDE (CCl_4, 77°)

A	B	$[A]_0$, mmol	$[A]_f$, mmol	$[B]_0$, mmol	$[B]_f$, mmol	ABr, mmol	BBr, mmol	NBS,^{a} mmol	k_A/k_B per molecule	k_A/k_{toluene} per H
$C_6H_5CH_2C_6H_5$	$C_6H_5CH_3$	8.21	4.59	36.65	(34.86)	3.62	1.79	5.62	11.6	17.4^b
$C_6H_5CH_2C_6H_5$	$C_6H_5CH_3$	8.56	4.66	30.22	(28.74)	3.90	1.48	5.62	12.0	18.0^b
$C_6H_5CH_2C_6H_5$	$C_6H_5CH_3$	6.19	3.10	21.59	(20.35)	3.09	1.24	4.40	11.6	17.4^b
$C_6H_5CH_2CH_3$	$C_6H_5CH_2C_6H_5$	11.13	6.26	14.80	9.85	(4.87)	4.95	9.82	1.42	25.0^b
$C_6H_5CH_2CH_3$	$C_6H_5CH_2C_6H_5$	10.70	3.57	8.12	3.80	(7.13)	4.31	11.75	1.44	25.4^b
$C_6H_5CH_2OC_6H_5$	$C_6H_5CH_2C_6H_5$	5.68	2.12	8.34	5.66	(3.56)	2.56	6.04	2.55	44.9^c
$C_6H_5CH_2OC_6H_5$	$C_6H_5CH_2C_6H_5$	6.16	3.01	9.54	7.20	(3.15)	2.34	6.70	2.56	45.1^c
$C_6H_5CH_2OC_6H_5$	$C_6H_5CH(CH_3)_2$	5.86	2.18	5.80	3.21	(3.68)	2.46	6.56	1.67	48.0^d
$C_6H_5CH(CH_3)_2$	$C_6H_5CH_2C_6H_5$	7.45	3.86	13.50	9.02	3.19	(4.48)	8.42	1.63	57.4^c
$C_6H_5CH(CH_3)_2$	$C_6H_5CH_2C_6H_5$	11.21	6.84	23.20	17.15	3.70	(6.05)	11.0	1.63	57.4^c
$C_6H_5CH(CH_3)_2$	$C_6H_5CH_2C_6H_5$	10.70	6.57	15.20	11.30	3.56	(3.90)	9.26	1.64	57.7^c
$C_6H_5CH_2SC_6H_5$	$C_6H_5CH_2CH_3$	6.24	2.82	6.91	4.90	2.16^e	2.14	5.92	2.30	58.0^d
$C_6H_5CH_2SC_6H_5$	$C_6H_5CH_2CH_3$	5.87	2.80	5.06	3.60	1.82^e	(1.46)	5.25	2.18	55.0^d.
$C_6H_5CH_2SC_6H_5$	$(C_6H_5)_3CH$	5.98	3.16	7.70	4.56	1.95^e	(3.14)	5.60	1.21	61.6^c
$(C_6H_5)_2CHCH_3$	$C_6H_5CH(CH_3)_2$	10.71	6.12	7.50	4.66	(4.59)	2.52	9.72	1.16	66.6^f
$(C_6H_5)_2CHCH_3$	$C_6H_5CH(CH_3)_2$	8.11	5.09	6.56	4.32	(3.02)	2.24	7.39	1.12	64.4^f
$(C_6H_5)_2CHCH_3$	$(C_6H_5)_3CH$	7.25	4.84	8.00	4.33	(2.41)	(3.67)	7.94	0.659	67.1^f
$(C_6H_5)_3CH$	$C_6H_5CH_2C_6H_5$	12.90	4.59	9.09	6.38	(8.31)	(2.71)	11.0	2.91	103^c
$(C_6H_5)_3CH$	$C_6H_5CH_2C_6H_5$	9.81	4.79	8.31	6.49	(5.02)	(1.82)	7.01	2.92	103^c
$(C_6H_5)_3CH$	$C_6H_5CH_2CH_3$	10.19	1.41	10.30	3.75	(8.78)	6.68	15.42	1.96	98.8^d
$(C_6H_5)_3CH$	$C_6H_5CH(CH_3)_2$	10.04	4.39	8.39	5.26	(5.65)	3.18	8.84	1.78	102^d
$(C_6H_5)_3CH$	$C_6H_5CH_2CH_3$	9.14	3.34	6.43	3.98	(5.80)	2.52	*g, h*	2.08	105^b
$(C_6H_5)_3CH$	$C_6H_5CH_2CH_3$	11.98	7.95	10.11	8.34	(4.03)	1.93	*g*	2.12	107^d
$C_6H_5CH_2OCH_3$	$C_6H_5CH_2C_6H_5$	5.25	1.12	9.46	8.00	2.54^e	1.51	5.60	9.07	160^c
$C_6H_5CH_2OCH_3$	$C_6H_5CH_2C_6H_5$	9.21	2.52	14.00	12.10	4.09^e	(1.90)	9.85	8.79	155^c
$C_6H_5CH_2OCH_3$	$C_6H_5CH_2CH_3$	5.21	1.31	8.44	6.80	2.95^e	1.76	5.21	6.39	161^d
$C_6H_5CH_2OCH_3$	$C_6H_5CH_2CH_3$	6.44	1.56	11.25	9.04	3.78^e	(2.21)	6.60	6.42	162^d
$C_6H_5CH_2OCH_3$	$C_6H_5CH_2CH_3$	8.24	2.38	13.99	11.42	(5.86)	(2.57)	8.49	6.21	157^d
$C_6H_5CH_2OCH_3$	$(C_6H_5)_3CH$	4.50	1.39	5.20	3.54	2.04^e	(1.66)	4.68	3.04	155^d
$C_6H_5CH_2OCH_3$	$(C_6H_5)_3CH$	4.85	2.01	6.55	4.98	1.75^e	1.57	4.63	3.18	162^c
$C_6H_5CH_2OCOCH_3$	$C_6H_5CH_3$	9.90	6.23	9.14	5.56	2.23^i	3.58	9.01	0.935	1.40^d
$C_6H_5CH_2OCOCH_3$	$C_6H_5CH_3$	10.00	6.95	16.14	10.67		5.47	9.41	0.878	1.32^d
$C_6H_5CH_2OCOCH_3$	$C_6H_5CH_2Cl$	8.41	4.69	11.89	9.79	1.73^i	2.56	8.67	3.02	1.39^d
$C_6H_5CH_2OCOCH_3$	$C_6H_5CH_2Cl$	10.21	3.94	11.05	8.10	4.31^i	3.15	12.50	3.06	1.41^d
$C_6H_5CH_2OCOCH_3$	$C_6H_5CH_2Cl$	9.65	4.56	11.70	9.00	2.94^i	2.62	11.40	2.86	1.32^d
o-$ClC_6H_4CH_3$	$C_6H_5CH_3$	9.44	(7.69)	6.51	(2.89)	1.75	3.62	5.86	0.252	0.252^d
o-$ClC_6H_4CH_3$	$C_6H_5CH_3$	11.19	(9.26)	5.08	(2.32)	1.93	2.76	5.11	0.242	0.242^d
o-$ClC_6H_4CH_3$	$C_6H_5CH_3$	12.05	(10.19)	5.60	(2.86)	1.86	2.74	5.01	0.250	0.250^d
o-$ClC_6H_4CH_3$	$C_6H_5CH_3$	9.95	(8.18)	5.12	(2.31)	1.77	2.81	5.00	0.248	0.248^d
$C_6H_5CH_2Cl$	$C_6H_5CH_3$	15.71	12.31	10.81	4.94	(3.40)	5.57	9.44	0.311	0.468^d
$C_6H_5CH_2Cl$	$C_6H_5CH_3$	12.60	9.79	6.84	2.96	(2.81)	3.91	7.56	0.302	0.453^d
$C_6H_5CH_2Br$	$C_6H_5CH_2Cl$	10.31	7.06	10.21	3.77	3.23	(6.44)	10.14	0.380	0.18^d
$C_6H_5CH_2Br$	o-$ClC_6H_4CH_3$	10.55	7.58	9.11	4.48	2.80	(4.63)	8.29	0.466	0.18^d
$C_6H_5CH_2Br$	o-$ClC_6H_4CH_3$	12.36	8.80	7.75	3.79	3.49	4.00	8.24	0.472	0.18^d
$C_6H_5CH_2COOCH_3$	$C_6H_5CH_3$	14.81	(12.07)	7.46	2.20	2.74	5.11	8.42	0.170	0.26^d
$C_6H_5CH_2COOCH_3$	$C_6H_5CH_2Cl$	10.42	(6.69)	7.81	3.44	3.73	4.42	8.35	0.545	0.25^d
$C_6H_5CH_2COOCH_3{}^j$	$C_6H_5CH_2Br$	8.66	(4.14)	8.39	5.21	4.52	3.22	8.24	1.56	0.28^d
$C_6H_5CH_2COOCH_3$	$C_6H_5CH_2Br$	6.71	3.36	8.27	5.27	3.26	2.88	6.75	1.54	0.28^d
$C_6H_5CH_2COOCH_3$	o-$ClC_6H_4CH_3$	10.61	(6.68)	8.10	4.30	3.93	(3.80)	8.03	0.716	0.27^d
$C_6H_5CH_2CN$	o-$ClC_6H_4CH_3$	8.80	5.48	7.89	3.50	2.98	4.33	8.12	0.585	0.22^d
$C_6H_5CH_2CN$	o-$ClC_6H_4CH_3$	10.25	7.60	7.77	4.23	2.69	(3.54)	6.85	0.492	0.18^d
$C_6H_5CH_2CN$	o-$ClC_6H_4CH_3$	10.22	7.31	7.29	3.76	2.86	(3.53)	6.94	0.506	0.19^d
$C_6H_5CH_2CN$	o-$ClC_6H_4CH_3$	10.20	7.65	7.96	5.13	2.40	(2.83)	5.56	0.651	0.24^d
$C_6H_5CH_2CN$	$C_6H_5CH_2Cl$	10.25	6.80	7.11	2.96	3.16	4.19	7.95	0.467	0.22^d
$C_6H_5CH_2CN$	$C_6H_5CH_2Br$	9.42	5.07	8.69	5.51	4.44	3.38	8.90	1.37	0.25^d
p-$NO_2C_6H_4CH_3$	o-$ClC_6H_4CH_3$	10.43	(8.05)	8.54	(3.30)	2.38	5.24	8.14	0.274	0.068^d
p-$NO_2C_6H_4CH_3$	o-$ClC_6H_4CH_3$	12.59	(9.84)	8.11	(3.72)	2.75	4.39	7.75	0.304	0.075^d
p-$NO_2C_6H_4CH_3{}^j$	o-$ClC_6H_4CH_3$	11.01	(8.41)	8.16	(3.52)	2.60	4.64	7.78	0.320	0.080^d
$C_6H_5CH_2NO_2{}^j$	p-$NO_2C_6H_4CH_3$	9.65	8.49	7.09	2.35	(1.16)	4.07	6.81	0.117	0.013^d
$C_6H_5CH_2NO_2{}^j$	p-$NO_2C_6H_4CH_3$	10.01	8.76	8.21	3.07	(1.25)	4.55	7.20	0.134	0.015^d
$C_6H_5CH_2NO_2{}^j$	p-$NO_2C_6H_4CH_3$	11.48	10.12	6.56	1.21	(1.36)	4.36	7.95	0.0736	0.008^d
$C_6H_5CH_2NO_2{}^j$	$C_6H_5CH_2Br$	8.34	7.40	6.34	1.43	(0.94)	4.40	6.65	0.0804	0.014^d

[a] Initial N-bromosuccinimide. [b] Internal standard is $C_6H_5CH_2Cl$. [c] Internal standard is $C_6H_5CH_2CH_3$. [d] Internal standard is $C_6H_5CH_2C_6H_5$. [e] The value is low probably because of reaction of ABr with N-bromosuccinimide. [f] Internal standard is $C_6H_5OCH_3$. [g] Br_2 was used as the brominating agent and the reactions were conducted at 40° under irradiation with a 150-W tungsten lamp (*cf.* ref 12). [h] N_2 was bubbled into the solution during the competition reaction (*cf.* ref 12). [i] The value is low since CH_3COBr is also a product of the reaction. [j] The competition reaction was conducted under irradiation with a 750-W projection lamp.

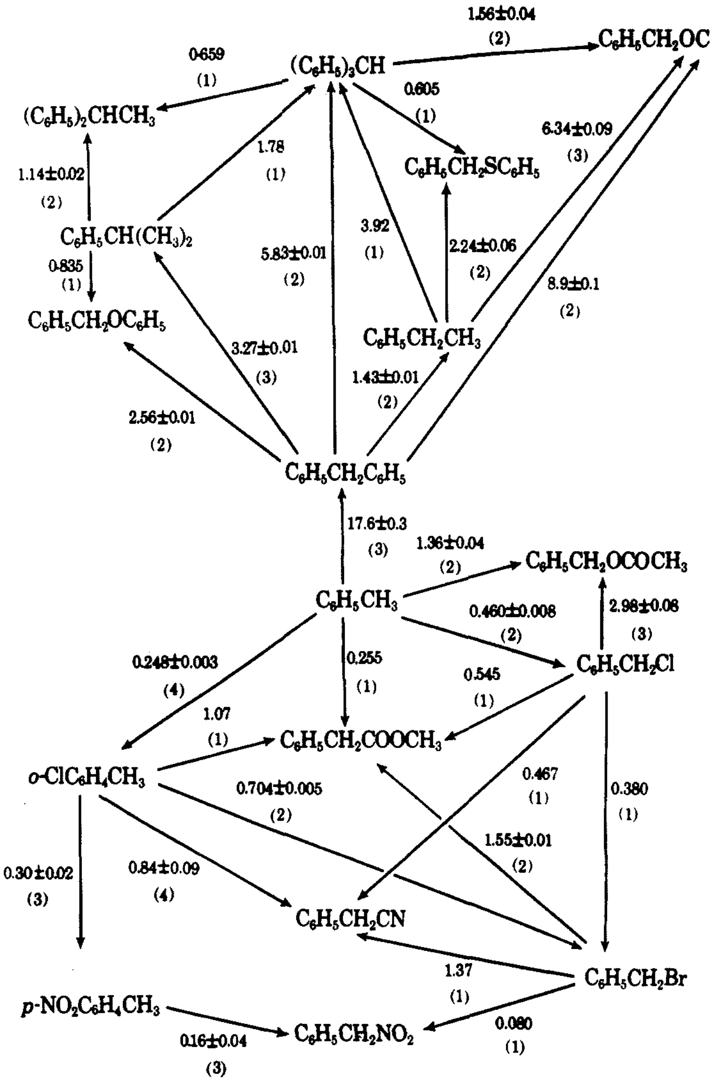

Figure 1.—Summary of competitive NBS brominations. Arrows indicate direct competitions. Numbers are relative reactivities per hydrogen of the compound at the head of an arrow to that at the tail. Numbers in parentheses are the number of determinations.

report.[10] The fact that the amount of bromo compound detected was much less than the amount of starting material consumed in the reaction of the benzyl phenyl sulfide is thought to reflect the partial conversion of the initial reaction product to a succinimide derivative $[C_6H_5CH(SC_6H_5)N(COCH_2)_2]$ through reaction with N-bromosuccinimide. An nmr absorption presumed to be characteristic of this substance was found in the product mixtures at δ 2.40 and is ascribed to succinimidyl hydrogens. In the case of benzyl phenyl ether, a comparison between ether consumed and bromo derivative formed has not been made because the nmr absorption for the benzyl proton of the bromide is obscured by the ring-proton absorptions. Again, however, the nmr spectrum of the reaction mixture involving this ether and N-bromosuccinimide shows evidence of the formation of a succinimidyl derivative with an absorption at δ 2.25, characteristic of succinimidyl protons.

Results and Discussion

A summary of all the competition experiments of Table I is shown in Figure 1. The average reactivities of the "k_A/k_B per molecule" column of Table I have been corrected to account for the differences in the number of benzylic hydrogens in the various toluene derivatives. Average deviations, when available, are included. The excellent cross-checks on the relative rate values obtained for the compounds investigated is clearly indicated by Figure 1. For example, the rate for methyl phenylacetate relative to toluene can be calculated *via* a variety of pathways involving different reference compounds, each route resulting in almost exactly the same relative rate value.

The averages of the "$k_A/k_{toluene}$ per α-hydrogen" values listed in Table I are summarized in Table II along with the corresponding values obtained in earlier investigations.[1-4,12,13] The agreement between the values for reaction in carbon tetrachloride at 77° which were previously determined using gas chromatographic methods of analysis and those obtained in the present investigation is fair, except for those figures at the extreme ends of the reactivity series. With certain exceptions the order of reactivity of the various α-substituted toluenes, as established by the current study, is like that reported previously for reaction at 40° (see the first and third columns of Table II). In both sequences, the alkylbenzenes fall in the order cumene > ethylbenzene > toluene, and diphenylmethane is intermediate in reactivity between toluene and ethylbenzene. However, triphenylmethane has been found to be about twice as reactive as cumene, and also more reactive than

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(12) G. A. Russell and C. Deboer, *J. Amer. Chem. Soc.*, **85**, 3136 (1963).

(13) G. A. Russell and K. M. Desmond, *ibid.*, **85**, 3139 (1963).

TABLE II

RATES RELATIVE TO TOLUENE FOR REACTIONS OF α-SUBSTITUTED TOLUENES WITH N-BROMOSUCCINIMIDE

Toluene deriv	Current results per α-H (CCl_4, 77°)	Previous results[a] per α-H (CCl_4, 77°)[b]	(CH_2Cl_2, 40°)[c]
$C_6H_5CH_2OCH_3$	159	59	
$(C_6H_5)_3CH$	102 (106)[d]		17.8[e]
$(C_6H_5)_2CHCH_3$	66.0		42.0[e]
$C_6H_5CH_2SC_6H_5$	58.2	24	
$C_6H_5CH(CH_3)_2$	57.5	36 (50)[f]	45[g]
$C_6H_5CH_2OC_6H_5$	46.0	22	
$C_6H_5CH_2CH_3$	25.2	14 (23.6)[f]	21
$C_6H_5CH_2C_6H_5$	17.6	10	10
$C_6H_5CH_2OCOCH_3$	1.37	2.4	1.08
$C_6H_5CH_3$	1.00	1.00	1.00
$C_6H_5CH_2Cl$	0.46	0.47	0.24
$C_6H_5CH_2COOCH_3$	0.27	0.35	0.042
$C_6H_5CH_2CN$	0.22	0.13	0.56
$C_6H_5CH_2Br$	0.18		
$C_6H_5CH_2NO_2$	0.013	2.8 (0.104)[c]	0.052

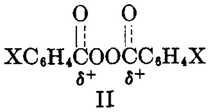
[a] Based on glpc analysis of product mixtures obtained in competition experiments. [b] From ref 1 and 2. Where values are listed for a compound in both references, that tabulated here is from ref 2. [c] From ref 3. [d] Same experimental conditions as in *e*. [e] From ref 12. For reaction with Br_2 in carbon tetrachloride at 40°. [f] From ref 4. [g] From ref 13.

1,1-diphenylethane. This is in contrast to the previous report[12] that at 40° triphenylmethane is photobrominated less rapidly than either cumene or 1,1-diphenylethane. Also, on the basis of certain semiquantitative observations concerning the reactivities of the tertiary and secondary hydrogens of $(C_6H_5)_2CHC_6H_4CH_2OCH_3$-*p* with respect to attack by bromine atoms generated from N-bromosuccinimide, it has been suggested that triphenylmethane may fall between toluene and ethylbenzene in reactivity.[14] However, in so placing it an assumption has been made that, when the N-bromosuccinimide bromination product of *p*-benzhydrylbenzyl methyl ether is hydrolyzed, the tertiary bromide should hydrolyze much faster than the α-bromo ether. Recent work indicates that this is not a safe assumption.[10,11] The accuracy of the present figures for N-bromosuccinimide bromination is supported by the results of a large number of cross-check experiments using different reference compounds as indicated in Table I and Figure 1. A reevaluation in the present study of the reactivity of triphenylmethane relative to toluene with respect to photobromination with molecular bromine at 40° (see Table I) has given a new figure of 106 for k_{Ph_3CH}/k_{PhCH_3} (per α-hydrogen). This value is in good agreement with that (102) observed for reaction at 77° with N-bromosuccinimide as the halogen source, and is in accord with the well-established theory that the bromine atom is the chain-carrying species in reactions of either brominating agent.[8,13,15] Thus, our findings result in a revised reactivity sequence in the order triphenylmethane > 1,1-diphenylethane > cumene > ethylbenzene.

A number of processes in which radicals abstract hydrogen from systems of the type XC_6H_4YH are amenable to treatment by the Hammett $\rho\sigma$ correlation and, in fact, many such reactions are better correlated if σ^+ [16] rather than σ values are used.[17] Among the processes for which good linear relationships between the logarithms of the relative rates and the σ^+ values of the substituents X are found are the reactions of ring-substituted toluenes with bromine atoms[4] and with trichloromethyl radicals.[18] This is regarded as evidence that at the transition state (Ia–c), as shown for a reaction in which Br· is the abstracting species, there is a substantial contribution from structure Ib.[19] It is

$$[\underset{\text{Ia}}{XC_6H_4CH_2\text{–}H\ Br\cdot} \leftrightarrow \underset{\text{Ib}}{XC_6H_4\overset{+}{C}H_2\ \dot{H}\ Br:^-} \leftrightarrow \underset{\text{Ic}}{XC_6H_4\dot{C}H_2\ H\text{–}Br}]$$

interesting in this connection that good linear correlations of σ^+ with the logarithms of the relative rates of thermal dissociation of symmetrically substituted benzoyl peroxides $(XC_6H_4COO)_2$[20] can also be demonstrated to exist. Thus, in the latter reaction, the capacity of X to disperse positive charge at the exocyclic carbonyl carbon (II) is clearly a critical factor in determining reactivity.



$$XC_6H_4\underset{\delta+}{\overset{\overset{\delta-}{O}}{\overset{\Vert}{C}}}OO\underset{\delta+}{\overset{\overset{\delta-}{O}}{\overset{\Vert}{C}}}C_6H_4X$$

II

The variations in reactivity of α-substituted toluenes with changes in substituents X which have been observed in the present study are directionally similar to those which have been found for the reactions of ring-substituted toluenes with N-bromosuccinimide. To facilitate comparison of the intensity of the substituent effects in the present study with intensities observed in other radical reactions in which the substituents are on the toluene ring, a plot of the logarithms of the relative rates of reaction of the α-monosubstituted toluenes with N-bromosuccinimide (first numerical column, Table II) *vs.* σ_p^+ is presented in Figure 2. Considering that by definition, σ^+ values relate to systems in which substituent effects are transmitted through an aromatic ring, the correlation is surprisingly satisfactory, much more so than if σ_m values are used and somewhat better than if σ_p values are used.[21] The line of Figure 2 is based on a least-squares treatment of the data and has a slope (ρ) of -2.46 (correlation coefficient $r = 0.95$ and standard deviation $s = 0.30$). The ρ value is substantially larger than that[4] (-1.38) reported for reactions of ring-substituted toluenes with N-bromosuccinimide under much the same conditions. This could have been predicted since the extent of polarization at the transition state should be substantially greater when the substituents in question are on the α carbon rather than the ring. Forms of the type III are presumed to make important contributions

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(21) All values of σ_p^+ are taken from ref 16.

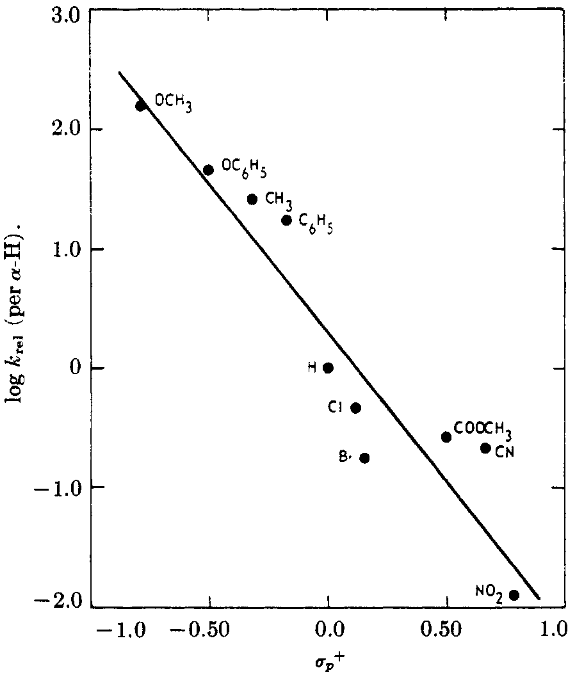

Figure 2.—Logarithms of rates, relative to that for toluene, for the reactions of $C_6H_5CH_2X$ with N-bromosuccinimide (CCl_4, 77°) *vs.* σ_p^+ values for the substituents X.

$$[C_6H_5CH{=}\overset{+}{O}CH_3\ \dot{H}\ Br{:}^-]$$

III

to structure at the transition state when the α substituent, *e.g.*, methoxyl, is electron releasing through resonance. Inasmuch as the points of Figure 2 conform to the least-squares line as well as they do, it appears that the changes in reactivity with changes in X are not to a significant degree associated with corresponding changes in steric barrier to attainment of the transition state. Since the medium in this case (CCl_4) cannot contribute significantly to the polarization process accompanying activation, this is not entirely surprising.

The relative reactivities of α-substituted toluenes with peroxy radicals fall into a pattern which is neither that to be expected of a reaction in which the structure at the transition state is radicallike nor of a reaction in which that structure is significantly polar in nature.[19a] Substituent effects characteristic of both types of reactions have been observed (*e.g.*, the reactivities of α-substituted toluenes, $C_6H_5CH_2X$, change with X in the order $CH_3 > Cl > H > CN$). In their reactions with peroxy radicals the ring-substituted toluenes respond to changes in X more or less as predicted by σ^+ values, but the ρ value for the reaction[17] is significantly less than that observed when bromine is the attacking radical. Presumably the difference in substituent effects on the course of the reactions involving the two radicals Br· and RO_2· can be traced to differences in electronegativities of the radicals[22] and in the extent of bond breaking at the transition states. An extended discussion of the matter must await a further elaboration of the influence of other factors, *e.g.*, solvent and temperature, on the rates of radical abstraction processes.[17]

Registry No.—N-Bromosuccinimide, 128-08-5.

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Benzylic Bromination in the Reactions of Benzyl Methyl Ether and Related Compounds with N-Bromosuccinimide

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Through application of nmr analysis of reaction products it has been established conclusively, as is strongly suggested by earlier work of Huang and Lee, that the benzaldehyde formed in the reaction of benzyl methyl ether and N-bromosuccinimide in carbon tetrachloride is derived mainly, if not exclusively, by breakdown of α-bromobenzyl methyl ether, the primary reaction product. The alternate reaction path in which the aldehyde is formed by direct breakdown of a radical intermediate ($C_6H_5\dot{C}HOCH_3 \rightarrow C_6H_5CHO + \dot{C}H_3$) is unimportant. When dibenzyl ether is substituted for benzyl methyl ether, the aldehyde is generated, in a similar fashion. No bromo ether is found in the products of reactions of benzyl *t*-butyl ether, but the path by which benzaldehyde forms is thought to involve the bromo ether as an intermediate. Benzyl *p*-chlorophenyl ether reacts to form a thermally stable α-bromo derivative and no aldehyde. Benzyl acetate is converted in part by N-bromosuccinimide into α-bromobenzyl acetate, but benzaldehyde and acetyl bromide are also formed in quantity by a process in which the bromo acetate is not an intermediate. α-Bromobenzyl methyl ether is readily hydrolyzed, but treatment of its carbon tetrachloride solution with a small amount of water results in its decomposition to benzaldehyde and methyl bromide rather than its hydrolysis. Evidence has been obtained that $C_6H_5CH(NC_4H_4O_2)OR$ formed during the reaction of benzyl ethers ($C_6H_5CH_2OR$) and N-bromosuccinimide is produced from $C_6H_5CH(Br)OR$ and the brominating agent by a process which is reversible.

Benzyl alkyl ethers have been found to react with N-bromosuccinimide and other halogenating agents to produce benzaldehyde.[1–5] Formation of the aldehyde in the reaction with N-bromosuccinimide is presumed to