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Nucleophilic Behavior of the Phenyl Radical in the Hydrogen Abstraction Reaction from Substituted Toluenes. A Contribution to the Study of the Phenyldiazenyl Radical

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Phenyl radicals derived from benzoyl peroxide (BPO) showed nucleophilic behavior, rho=+0.18 (meta-series) for the hydrogen abstraction reaction from substituted toluenes at 80 °C, and a kinetic deuterium isotope effect, $k_H/k_D=3.73\pm0.2$, was found for toluene. Comparison of these results with those for the phenyl radicals from phenylazotriphenylmethane (PAT) leads to the suggestion that the phenyldiazenyl radicals derived from PAT abstract hydrogen from toluene to yield benzene, which should amount to about 50% of the total benzene formed.

Phenyl radicals have been reported to be electrophilic in hydrogen abstraction reactions based on the results of investigations using phenylazotriphenylmethane (PAT) as the source of the phenyl radicals.[1,2] The phenyl radicals derived from PAT behave, however, differently from those generated from benzoyl peroxide (BPO), as revealed by the fact that the yields of benzene in the thermolysis of PAT in toluene at 60—70 °C, 50—58% per mole PAT,[3,4] are markedly larger than that of BPO, 32% per mole phenyl radicals,[4] in contrast to the very similar yields of methylbiphenyls in both cases, 25% for PAT and 23% for BPO.[4] Appreciable amounts of phenyl radicals from BPO are transformed into esters and quarterphenyls, which are not accounted for in the above measurements. This does not, however, affect the conclusion that the "phenyl" radicals from PAT produce much more benzene in toluene than do those from BPO.

In the thermolysis of PAT, the triphenylmethyl-nitrogen bond dissociates at first to give triphenylmethyl and phenyldiazenyl radicals in a cage.[5] Although the reaction of phenyldiazenyl radicals out of the "cage" is not clear as yet, the hydrogen abstraction reaction of the radicals from toluenes would lead to phenyldiazene, which is known to produce benzene in good yields upon thermal decomposition.[6] PAT could thus receive the cooperation of phenyldiazenyl radicals in the formation of benzene. When the reactions of phenyldiazenyl radicals proceed, the polarity of the "phenyl" radical deduced from the experiments on PAT should be different from that obtained from reactions using BPO, because in the latter studies the precursors of phenyl radicals, benzoyloxy radicals, are converted into benzoic acid upon hydrogen abstraction and can be separated completely from benzene. The intrinsic behavior of the phenyl radicals in the hydrogen abstraction reaction can only be determined using BPO as the radical source.

Results and Discussion

The polar nature of phenyl radicals was determined by the reactivities of substituted toluenes toward phenyl radicals. For the measurement of the reactivities of toluenes, competitive reactions of BPO (4.13 mmol) were carried out at 80 °C between each 100 mmol of a substituted toluene and carbon tetrachloride in a nitrogen atmosphere. Relative rate constants, k_H/k_{Cl}, of Reactions 1 and 2,

$$\mathrm{ArCH_3 + Ph\cdot \xrightarrow{k_H} PhH + ArCH_2\cdot,} \tag{1}$$

$$\mathrm{CCl_4 + Ph\cdot \xrightarrow{k_{Cl}} PhCl + Cl_3C\cdot,} \tag{2}$$

were calculated from the yields of benzene and chlorobenzene with proper corrections, as described below. Duplicate runs afforded the rate ratios listed in Table 1 and the Hammett plot shown in Fig. 1.

TABLE 1. RATES OF HYDROGEN ABSTRACTION FROM TOLUENES RELATIVE TO CHLORINE ABSTRACTION FROM CARBON TETRACHLORIDE AT 80 °C

$XC_6H_4CH_3$ X=	k_H/k_{Cl}	$XC_6H_4CH_3$ X=	k_H/k_{Cl}
m-$(CH_3)_2$	0.214 ± 0.046	*p*-CH_3O	0.389 ± 0.09
H	0.210 ± 0.055	*p*-CH_3	0.270 ± 0.035
m-Cl	0.288 ± 0.055	*p*-Cl	0.277 ± 0.054
m-CN	0.220 ± 0.042	*p*-CN	0.265 ± 0.051
m-NO_2	0.332 ± 0.075	*p*-NO_2	0.646 ± 0.11

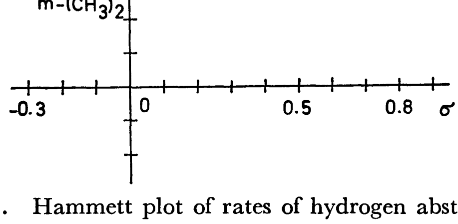
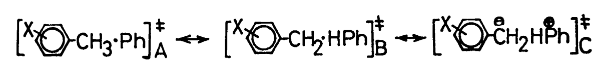
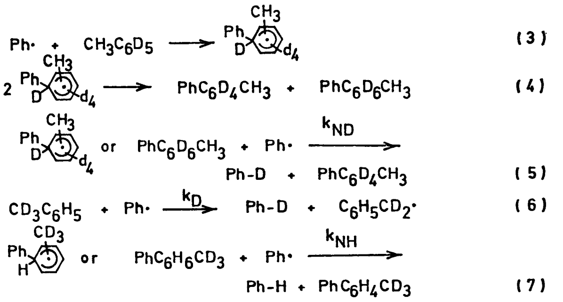


Fig. 1. Hammett plot of rates of hydrogen abstraction by phenyl radicals from toluenes relative to rates of chlorine abstraction from carbon tetrachloride.

The polar character of the phenyl radicals obtained from the results of meta-substituted toluenes was slightly nucleophilic, rho=+0.18, in contrast to the results of earlier reports, −0.1,[1] −0.4,[2] and −0.5.[7] The reactivities of para-substituted toluenes are larger than the values expected from the rates of the meta-series. Definite extra resonances are operative in the transition state of the hydrogen abstraction reaction and they are especially effective in the cases of *p*-nitro- and *p*-methoxytoluenes. The effect of the extra resonances play an important role in the manifestation of B.



In the calculation of the rate ratios, the following were taken into consideration. Phenyl radicals from BPO can also take up hydrogen from the aromatic ring of a substrate molecule during the course of homolytic phenylation. Because the homolytic phenylation by BPO proceeds by means of the disproportionation reaction *via* substituted phenylcyclohexadienyl radicals,[8] and an appreciable amount of dihydrobiaryls are formed, phenyl radicals can abstract hydrogen from the cyclohexadienyl radicals and from dihydrobiaryls.



The extent of Reactions 5 and 7 can be estimated by examining benzene and deuteriobenzene formed from experiments using toluene-nuclear-d_5 and toluene-α-s_3 as the substrate, together with rate ratios ($k_{\text{total benzene}}/k_{\text{Cl}}$) for the toluene–carbon tetrachloride and toluene-α-d_3–carbon tetrachloride systems.[9]

From the reaction using toluene-d_5 (d_5-fraction 90.3 %), the ratio C_6H_6: C_6H_5D=93.8: 6.2 was obtained for the benzene formed. For the benzene formed from toluene-α-d_3 (d_3-fraction 90.0%), the ratio C_6H_6: C_6H_5D =54.5: 45.5 was found. The kinetic deuterium isotope effect for Reactions 7 and 5 (k_{NH}/k_{ND}) was calculated to be 2.97, and the hydrogen abstraction reaction at the nuclear positions (k_{NH}) contributes *ca.* 10% of the total formation of benzene.

It is tentatively assumed, that the participation of nuclear hydrogen in the formation of benzene in the system containing substituted toluenes is proportional to the rates of phenylation of the substituted toluenes, and that the rates of phenylation can be estimated using partial rate factors for phenylation.[10] The rates of phenylation of substituted toluenes (R_X) relative to that of toluene were calculated to be as follows:

R_X:	*p*-MeO	1.13	*p*-Me	1.01	*m*-Me	1.01
	p-Cl	1.19	*m*-Cl	1.03	*p*-CN	1.96
	m-CN	2.04	*p*-NO_2	2.02	*m*-NO_2	2.13

Measurements on benzene using GLPC for competitive reactions were corrected by substracting from them the amounts of benzene formed from the nuclear hydrogen by phenyl radicals:

$$(\text{benzene})_{\text{corr}} = (\text{benzene})_{\text{total}} \cdot (1 - \text{Corr})$$

$$\text{Corr}_{\text{toluene}} = 0.10.$$

Similarly, the corrections for X-substituted toluenes are

$$\text{Corr}_{\text{X-toluene}} = R_X \cdot \text{Corr}_{\text{toluene}} = 0.10 \cdot R_X.$$

The values in Table 1 have been corrected in this manner.

The effect of the methoxyl substituent of methoxytoluene in the formation of benzene was checked using the isotope tracer technique with *p*-deuteriomethoxytoluene as the substrate. For the benzene formed, a molar ratio C_6H_6: C_6H_5D of 92.3: 7.7 was found. The corrected value is listed in the table. The benzene from the methoxyl group amounts to about 33% of the total benzene formed.

The difference in the polar nature of the phenyl radical found here (+0.18) from that of Trosman and Bagdasar'yan[7] (−0.5) arises from different experimental conditions. The determination of benzene separately from one by-product, chloroform, is one of the key points in the present study. The column used by Bridger and Russell[1] was found to be unsuccessful in this laboratory. A 2-m column of ODPN (20% on C-22 AW), in combination with a 1-m column of Apiezon Grease L (25% on C-22 AW) was used at 80 °C with helium as the carrier gas. Much more chloroform was formed than benzene, when toluenes with electron-donating groups were used as the substrate. The rate ratios k_H/k_{Cl} found for nitrotoluene by Trosman and Bagdasar'yan[7] 0.80 for para- and 0.475 for meta-compounds, gave 0.64 and 0.36 after the correction described above, which are in good accord with the present values of 0.646 and 0.332. Their values of the rate ratios for toluene and xylenes are by far larger than the present values.

The slightly nucleophilic nature of the phenyl radical for the hydrogen abstraction reaction in the present findings is in very good agreement with the results reported by Ito *et al.* for homolytic phenylation (rho= +0.05),[10] and with the results reported by Migita *et al.* for bromine abstraction from substituted benzyl bromides (rho=+0.15 for meta-series).[11] Thus, a parallel relationship in the polar nature of phenyl radicals was established between the addition reaction to benzene nuclei and the abstraction reaction from benzylic compounds.

The kinetic deuterium isotope effect was found to be 3.73±0.2. This is a little smaller than the value, 4.5± 0.5, found by Bridger and Russell.[1]

The nucleophilic nature of phenyl radicals from BPO for the hydrogen abstraction reaction contrary to the electrophilic radicals from PAT, suggests the coexistence of phenyldiazenyl radicals together with phenyl radicals in the thermolysis of PAT. In measuring the electrophilicity of phenyldiazenyl radicals, amino radicals should be taken as a reference. For example dimethylamino radicals are reported to be electrophilic for hydrogen abstraction from toluenes: rho=−1.08 (sigma plus) and k_H/k_D=4.0 at 130 °C.[12] Diphenylmethyleneamino radicals were also found to be electrophilic (rho=*ca.* −2.5).[13] Phenyldiazenyl radicals are, therefore, probably electrophilic in the abstraction of hydrogen from toluenes. Based on these assumptions, the results of Bridger and Russell[1] and Pryor *et al.*[2] appear to be explainable.

Another electrophilic property of particular radicals, X·, derived from PAT were also found for hydrogen abstraction from solvent molecule toluenes giving benzyl radicals during the thermolysis of PAT. The relative rates of formation of benzyl and substituted benzyl radicals, $k_{\mathrm{ArCH_2\cdot}}/k_{\mathrm{PhCH_2\cdot}}$, were measured by determining the amount of 1-aryl-2,2,2-triphenylethane, which was isolated by column chromatography in a 66% yield per mole of benzene as determined by GLPC. Because a fairly large amount of triphenylmethyl radicals were present in solution during the PAT thermolysis, it appears plausible to assume that the radical-scavenging step is effective, so that hydrogen abstraction is rate determining in the reaction,

$$\mathrm{ArCH_3} \xrightarrow{\mathrm{X\cdot}} \mathrm{ArCH_2\cdot} \xrightarrow{\mathrm{Ph_3C\cdot}} \mathrm{ArCH_2CPh_3}. \qquad (8)$$

A mixture of aryltriphenylethanes from a competitive reaction mixture was obtained by column chromatography and analyzed using NMR or the ^{14}C-tracer technique. The rate ratios, $k_{\mathrm{ArCH_2\cdot}}/k_{\mathrm{PhCH_2\cdot}}$, are listed in Table 2. A Hammett plot is shown in Fig. 2. The polar nature of particular free radicals, X·, derived from PAT in the formation of benzyl radicals at 50 °C was electrophilic (rho=−0.49 (sigma plus)). The results are in good accord with those of Pryor *et al.* for the hydrogen abstraction reaction.[2)]

Table 2. Relative rate of formation of substituted benzyl radicals, $k_{\mathrm{ArCH_2\cdot}}/k_{\mathrm{PhCH_2\cdot}}$, by PAT at 50 °C

Substrate	Chemical shift of $\mathrm{CH_2}$ in $\mathrm{ArCH_2CPh_3}$ in pyridine (δ)	$k_{\mathrm{ArCH_2\cdot}}/k_{\mathrm{PhCH_2\cdot}}$
p-Methoxytoluene[a)]	4.05	3.52
p-Xylene	4.05	1.46[b)]
Toluene	4.05	1.00
p-Chlorotoluene	4.10	0.67
m-Chlorotoluene	3.98	0.79
p-Nitrotoluene	4.10	0.65

a) Measured by the ^{14}C-tracer technique. b) Corrected per methyl group.

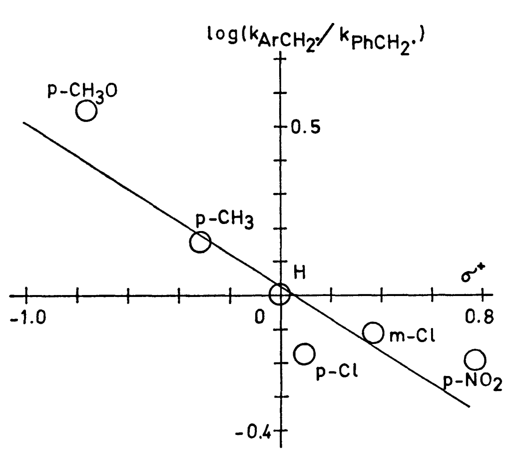
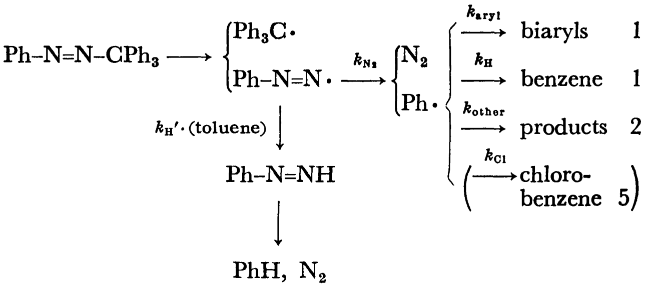


Fig. 2. Hammett plot (against sigma plus) of formation of substituted benzyl radicals from toluenes through hydrogen abstraction by particular radicals derived from PAT.

Assuming the phenyldiazenyl radical as the intermediate, the reaction scheme for thermolysis of PAT in toluene at 60 °C can be formulated as follows:



Scheme 1.

The reactions of phenyl radicals (k_{aryl}, k_{H}, and k_{other}) should be referred to the results of BPO, *i.e.*, the rate ratios with respect to each other are *ca.* 1 : 1 : 2 at 80 °C, and $k_{\mathrm{N_2}}$ is rate-determining. Because the benzene yield per mole of PAT is about twice that of BPO (Table 4), the rate, $k_{\mathrm{N_2}}$, is about four times as large as the rate of hydrogen abstraction of phenyldiazenyl radicals, $k_{\mathrm{H}}'\cdot$(toluene). This gives $k_{\mathrm{N_2}}=40\cdot k_{\mathrm{H}}'$, using a toluene concentration of 10 M. When carbon tetrachloride is present as a co-solvent, k_{Cl} should also be taken into consideration and was about five times as large as k_{H}, because the $k_{\mathrm{H}}/k_{\mathrm{Cl}}$ found was 0.210.

Table 3. Calculated rate ratios, $k_{\mathrm{benzene}}/k_{\mathrm{Cl}}$ for thermolysis of PAT in toluene–carbon tetrachloride

Substrate	$k_{\mathrm{benzene}}/k_{\mathrm{Cl}}$
p-Methoxytoluene	2.80
p-Xylene	1.36
Toluene	1.00
p-Chlorotoluene	0.75
p-Cyanotoluene	0.68
p-Nitrotoluene	0.68

Based on this scheme, setting $k_{\mathrm{N_2}}$, k_{Cl}, and k_{other} constant, the rho value for k_{H} to +0.18, the rho for k_{H}' to −2.5,[13)] and k_{aryl} proportional to R_x, as described previously, we can estimate the rate ratios, $k_{\mathrm{benzene}}/k_{\mathrm{Cl}}$, as shown in Table 3. These results are in very good agreement with the results shown in Table 2 and also with the results of Bridger and Russell[1)] and of Pryor *et al.*[2)] The data for PAT may thus be interpreted in terms of phenyldiazenyl and phenyl radicals.

Experimental

Gas Chromatographic Determination of Benzene and Chlorobenzene. Benzene and chlorobenzene were measured with apparatus of the KGL-2A (HITACHI) and JGC-1100 (JEOL) types using a 2-m column of ODPN (20% on C-22 AW) connected to a 1-m column of Apiezon Grease L (25% on C-22 AW), with the He carrier gas flowing at a rate of 90 ml/min at 80 °C. For the determination of chlorobenzene, only a 2-m column of ODPN was used with He at a flow rate of 150 ml/min at 80 °C. Their internal standard was selected from toluene, *p*-xylene, and *o*-xylene according to the reaction mixture.

Table 4.

Radical source	mmol	Toluene mmol	Temp (°C)	Benzoic acid mmol (%)	Benzene mmol (%/Ph·)	Methylbiphenyls mmol (%/Ph·)
PAT	4.017	760	50	—	1.515 (37.7)	—
PAT	2.04	200	60	—	—	0.514 (24.9)[a]
PAT	4.017	760	70	—	2.33 (58.0)	—
BPO	4.13	200	80	1.85 (43)	2.13 (33.2)	1.46 (22.6)[b]

a) *o*-:*m*-:*p*-=59.6:25.6:14.8. b) *o*-:*m*-:*p*-=46.5:18.5:34.7.

Yields of Benzene and Methylbiphenyls. The benzene and methylbiphenyls yields from the thermolysis of PAT and BPO in toluene were determined by GLPC (Table 4).

Competitive Reactions in the Substituted Toluene–Carbon Tetrachloride System. Benzoyl peroxide (4.13 mmol) was dissolved in a mixture of 100 mmol each of carbon tetrachloride and substituted toluene in a nitrogen atmosphere and heated for 42 h at 80±1.0 °C.

The reaction mixture was distilled with steam after a certain amount of mesitylene had been added to the mixture to assure the separation of chlorobenzene from high-boiling products. When nitrotoluenes were subjected to competitive reactions, the distillate was treated with a stannous chloride-concd. hydrochloric acid mixture to remove the nitro-compound. The purified distillates were subjected to GLPC determinations of benzene and chlorobenzene.

GC-MS Spectrometry. Mass spectrometric measurements were made on an apparatus of the LKB-9000 (SHIMADZU) type for a) the deuterated benzene formed, b) toluene-α-d_3, c) toluene-d_5, and d) *p*-deuteriomethoxytoluene.

a) The determination of the deuteriobenzene formed from the substrates, deuteriotoluene and deuteriomethoxytoluene, was made at 14 eV using a 3-m column of Apiezon Grease L on Chromosorb W (AW) at 42 °C. The He flow rate was 60 ml/min.

b) Toluene-α-d_3 was prepared by reduction of benzylidyne trichloride with a zinc dust-acetic acid-*d* solution according to the method of Renaud and Leitch.[14] The fraction of toluene-α-d_3 was found to be 90.0% at 12 eV.

c) Toluene-d_5 from Merk, Sharp and Dohme, Canada, Ltd., was used for the studies. The sample contained a 90.3% fraction of toluene-d_5 measured at 12 eV. Toluene-d_6 was present in a 2.3% fraction.

d) *p*-Methoxy-d_3-toluene was prepared from *p*-cresol and dimethyl-d_6 sulfate. Its boiling point was 80.5 °C at 37 Torr. The fraction of trideuteriomethoxytoluene was determined at 12 eV to be 98.1%.

Evaluation of Kinetic Deuterium Isotope Effects on Hydrogen Abstraction from the Methyl Group of Toluene, the Fraction of Hydrogen Abstraction from the Nuclear Position of Toluene, and the Fraction of Hydrogen Abstraction from the Methoxyl Group of p-*Methoxytoluene.* Kinetic deuterium isotope effect, (k_H/k_D), the relative rate of abstraction from the nuclear position, (k_{NH}/k_H) ((nuclear-H)/(toluene)), and the relative rate of abstraction from the methoxyl group of *p*-methoxytoluene, ($k_{\text{O-CH}_3}/k_H$), were evaluated using the following equations:

$$\frac{k_H(\text{CH}_3)+k_{NH}(\text{n-H})}{k_D(\text{CD}_3)+k_{ND}(\text{n-D})}=\frac{93.8}{6.2} \tag{9}$$

for benzene from toluene-d_5,

$$\frac{k_H(\text{CH}_3)+k_{NH}(\text{n-H})}{k_D(\text{CD}_3)}=\frac{54.5}{45.5} \tag{10}$$

for benzene from toluene-d_3,

$$\frac{k_H(\text{CH}_3)+k_{NH}(\text{n-H})}{k_D(\text{CD}_3)+k_{NH}(\text{n-H})+k_H(\text{CH}_3)}=2.91, \tag{11}$$

for the ratio of the rate ratios, $k_{\text{toluene}}/k_{\text{Cl}}$ and $k_{\text{toluene-}d_3}/k_{\text{Cl}}$,

$$\frac{k_H(\text{CH}_3)+k_{NH}(\text{n-H})+k_{\text{O-CH}_3}(\text{O-CH}_3)}{k_{\text{O-CD}_3}(\text{O-CD}_3)}=\frac{92.3}{7.7}, \tag{12}$$

for benzene from methoxy-d_3-toluene, and

$$\frac{k_H(\text{CH}_3)+k_{NH}(\text{n-H})+k_{\text{O-CH}_3}(\text{O-CH}_3)}{k_H(\text{CH}_3)+k_{NH}(\text{n-H})+k_{\text{O-CH}_3}(\text{O-CH}_3)+k_{\text{O-CD}_3}(\text{O-CD}_3)}=1.35, \tag{13}$$

for the ratio of the rate ratios, $k_{\text{methoxytoluene}}/k_{\text{Cl}}$ and $k_{\text{methoxy-}d_3\text{-toluene}}/k_{\text{Cl}}$, here ($\text{CH}_3$), ($\text{CD}_3$), (n-H), (n-D), (O-$\text{CH}_3$), and (O-$\text{CD}_3$) denote the concentrations for the CH_3 and CD_3 groups of toluene or methoxytoluene, the nuclear-hydrogen and nuclear deuterium atoms of toluene or methoxytoluene, and the methoxyl group and deuteriomethoxyl groups of methoxytoluene, respectively. k_x represents the rate constants for hydrogen abstraction from the corresponding groups. The nuclear hydrogen concentrations were expressed by the yields of the biaryls formed during the thermolysis of BPO (4 mmol) in 200 mmol of toluene, *i.e.*, 1.43 mmol (n-H) in 200 mmol of toluene.

We obtain from Eqs. 9, 10, and 11, the following results:

$$k_H/k_D = 3.73\pm0.2, \quad k_{NH}/k_H = 17.6.$$

Using the same k_{NH} for Eqs. 12 and 13, as for Eqs. 9—11, we obtain

$$k_H/k_{\text{O-CH}_3} = 2.07\pm0.02.$$

The participation of the nuclear hydrogen of toluene in the hydrogen abstraction reaction was found from (k_{NH}/k_H) ((n-H)/(CH_3)) to be 0.125, *i.e.*, about 10% of the benzene was formed from nuclear hydrogen. The participation of the methoxyl group of methoxytoluene in the benzene formation is about 33%.

^{14}C-Tracer Experiments. Triphenylmethanol-α-^{14}C was prepared from benzoate-carbonyl-^{14}C by the Grignard reaction and its specific activity was measured. ^{14}C-PAT was derived from triphenylmethanol-^{14}C and used for thermolysis without dilution.

^{14}C-PAT (13.5 mmol) was heated to 50 °C in nitrogen in a mixture of toluene and *p*-methoxytoluene (a) 1:1, b) 2:1, total 3.0 mmol) and treated according to the standard dilution method.

a) The reaction mixture was divided into two equal parts and to each of them was added 1.00 g of unlabelled $\text{PhCH}_2\text{CPh}_3$ or $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CPh}_3$.

b) The reaction mixture was divided into two parts in a 2:1 volume ratio, and to each was added 1.00 g of unlabelled $\text{PhCH}_2\text{CPh}_3$ or $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CPh}_3$. The results were as follows:

Radioactivity (dpm/mg)

	Starting Ph_3COH	Isolated		$k_{ArCH_2\cdot}/k_{PhCH_2\cdot}$
		$CH_3OC_6H_4$-CH_2CPh_3	$PhCH_2CPh_3$	
a)	4080	559.5	191.8	3.48
b)	4080	313.3	357.8	3.56
			av.	3.52

The radioactivity was measured using a scintillation counter of the Beckman LS-200 type. The NMR spectra were recorded on Varian A-60 instrument, with TMS as the internal standard.

For the radio assay, we are grateful to Dr. N. Morikawa of the University of Tokyo.

References

1) R. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963).

2) W. A. Pryor, J. T. Echols, Jr., and K. Smith, *J. Am. Chem. Soc.*, **88**, 1189 (1966).

3) J. F. Garst and R. S. Cole, *Tetrahedron Lett.*, **1963**, 679.

4) The results in the present paper.

5) A. Tsolis, S. G. Mylonakis, M. T. Nieh, and S. Seltzer, *J. Am. Chem. Soc.*, **94**, 829 (1972); R. C. Neuman, Jr., G. D. Lockyer, Jr., and M. J. Amrich, *Tetrahedron Lett.*, **1972**, 1221; N. A. Porter, M. E. Landis, and L. J. Marnett, *J. Am. Chem. Soc.*, **93**, 795 (1971); W. A. Pryor and K. Smith, *ibid.*, **92**, 5403 (1970); **89**, 1741 (1967); K. Tagaki and R. J. Crawford, *ibid.*, **93**, 5910 (1971); S. Seltzer and F. T. Dunne, *ibid.*, **87**, 2628 (1965).

6) E. M. Kosower, *Acc. Chem. Res.*, **4**, 193 (1971); B. Kaiser, Dissertation of the University of Münster (1970).

7) E. A. Trosman and Kh. S. Bagdasar'yan, *Russ. J. Phys. Chem.*, **38**, 1466 (1964).

8) K. H. Pausacker, *Aust. J. Chem.*, **10**, 49 (1957); E. L. Eliel, S. Meyerson, Z. Welvart, and S. H. Wilen, *J. Am. Chem. Soc.*, **82** 2936 (1960).

9) The evaluation of the rate ratios is shown in the experimental section.

10) R. Ito, T. Migita, N. Morikawa, and O. Simamura, *Tetrahedron*, **21**, 955 (1965).

11) T. Migita, T. Nagai, and Y. Abe, *Chem. Lett.*, **1975**, 543.

12) C. J. Machejda and W. P. Hoss, *J. Am. Chem. Soc.*, **92**, 6298 (1970).

13) Diphenylmethyleneamino radicals have a rho value of *ca.* −2.5 for the hydrogen abstraction reaction from methyltoluenes at 70 °C. (T. Suehiro *et al.*, to be published)

14) R. Renaud and L. C. Leitch, *Can. J. Chem.*, **34**, 98 (1956).