3-Cyano-4-fluorotoluene (3-F). 4-Amino-3-cyanotoluene was converted to the fluoro compound by the Schiemann reaction. Diazotization of 6.3 g (0.046 mol) of 4-amino-3-cyanotoluene in 40% fluoboric acid at 0 °C gave the diazonium salt, which was filtered and dried. The salt was heated slowly with a low flame in a flask fitted with a condenser. After the decomposition, the reaction mixture was dissolved in ether, washed with water and 5% sodium bicarbonate, and dried. Removal of solvent and crystallization from petroleum ether gave 0.9 g (15%) of 3-cyano-4-fluorotoluene: mp 44–46 °C; IR (CCl_4) 2225 cm^{-1} (CN); NMR (CCl_4) δ 6.6–7.8 (m, 3 H, Ar-**H**), 2.3 (s, 3 H, Ar-C**H_3**).

4-Bromo-3-cyanotoluene (3-Br). 4-Amino-3-cyanotoluene, 5.0 g (0.018 mol), was converted to 4.0 g (54%) of 4-bromo-3-cyanotoluene by the Sandmeyer reaction. Steam distillation of the resulting mixture gave a white solid that melted at 64–65 °C (lit.[34] mp 65 °C) after recrystallization from 40% methanol.

Kinetic Procedure. The relative rates of NBS bromination of toluenes **3** were determined by the method of Martin and Pearson.[9a] A mixture of 577.3 mg of 4-chloro-3-cyanotoluene, 297.8 mg of *m*-tolunitrile, 103.7 mg of NBS, and a catalytic amount of AIBN were diluted to 10.0 mL with benzene. The mixture was degassed three times using a freeze–thaw procedure and dry ice–acetone cooling. The tube containing the degassed mixture was sealed and placed in a bath thermostated at 80 °C for 3 h. A UV lamp was placed about 20 cm from the tube to ensure efficient initiation. The cooled mixture was evaporated to 2 mL and then analyzed by NMR using added phthalide (45.1 mg) to determine the yield of the reaction. The relative amounts of benzyl bromide products were determined by integration of the benzyl H's near δ 4.4 with an average of ten integrals taken for each determination. The identity of the benzyl singlets was determined by adding a known solution of *m*-cyanobenzyl bromide and observing the increase in area of one of the singlets. Duplicate runs at different concentrations agreed with 5%.

The relative rates were obtained using the integrated form of the competitive kinetic equation $k/k_0 = \log((A - X)/A)/\log((B - Y)/B)$, where A and B are the amounts of **3**-X and **3**-H, respectively, and X and Y are the amounts of the corresponding benzyl bromide products.

Acknowledgments. The authors would like to thank the U.S. Department of Agriculture Boll Weevil Research Laboratory for allowing us generous use of their NMR spectrometer.

Registry No.—3-Amino-4-chlorotoluene, 95-81-8; 2,5-dimethylaniline, 85-78-3; 3-amino-4-methoxytoluene, 120-71-8; 4-amino-3-nitrotoluene, 89-62-3; 4-cyano-3-nitrotoluene, 26830-95-5; 3-amino-4-cyanotoluene, 26830-96-6; 3-amino-4-iodotoluene, 13194-69-9; 3-nitro-4-phenyltoluene, 39556-87-5; 4-amino-3-cyanotoluene, 5925-93-9; 2-cyano-4-methylbenzenediazonium tetrafluoroborate, 64163-00-4.

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Substituent Effects in Free-Radical Reactions. A Study of 4-Substituted 3-Cyanobenzyl Free Radicals

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Received April 2, 1976

An extended Hammett treatment of the kinetic data of the NBS bromination of 4-substituted 3-cyanotoluenes led to a free-radical substituent constant, $\sigma\cdot$. The substituent order of free-radical stabilization found in this work was: F < OCH_3 < CH_3 < H < Cl < Ph < I < Br < NO_2 < N=NPh < CN < Ac. This order was further analyzed in terms of the ability of each substituent to stabilize a free radical. Two substituents—F and OCH_3—were found to be destabilizing in this system.

One of the major tools available to help elucidate organic reaction mechanisms is that of quantitative structure–reactivity relationships. The ability of a substituent to stabilize a cation, an anion, or a polar transition state by direct resonance is well understood in terms of σ^{+1} and σ^{-}.[2] The comparable influence of a substituent on a free-radical intermediate ($\sigma\cdot$ or σ^{H})[3] is not as well understood. Which substituents best stabilize a free-radical intermediate? Do all substituents

0022-3263/78/1943-0224$01.00/0

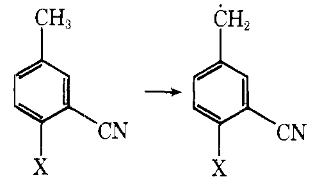
Table I. Model Systems Used to Define Some Free-Radical Substituent Constants

Substituent constant	Ref	Defining eq	Reaction
1. $\sigma\cdot$	25	$\log k/k_0 = \rho\sigma^+ + \sigma\cdot$	**1** → **2**
2. E_R	5c	$\log k/k_0 = \rho\sigma + \gamma E_R$	$XArCH(CH_3)_2$ + polystyryl radical
3. E_D	18	$\log k/k_0 = \rho\sigma^+ + E_D$	$XArCH{=}CH_2 + \cdot CCl_3 \rightarrow$
4. τ_p	19	$\log k/k_0 = \rho\sigma + \tau_p$	$ArX + YPh\cdot \rightarrow$
5. log Q	5a	$\frac{k_{11}}{k_{12}} = \frac{Q_1}{Q_2} e^{-e_1(e_1-e_2)}$	$-CH_2\dot{C}HX + CH_2{=}CHY \rightarrow$

stabilize a free radical in contrast to ionic behavior? Are there some substituents that do not stabilize a free radical? The answers to these fundamental questions concerning free-radical stabilization by substituents are not known with any degree of certainty even though much work has been done on the problem.

Our current understanding of the relationships between structure and reactivity in the homolytic process has been obtained from a wide variety of studies including: bond dissociation energies;[4] free-radical vinyl copolymerizations;[5] decompositions of peroxides,[6] peresters,[7] and azo compounds;[8] spectroscopic[9] and polarographic studies;[3a,10] atom abstraction reactions;[3b,11] etc. One of the most common approaches of those just mentioned is the H-atom abstraction reactions of substituted toluenes.

Our study[12] of the NBS bromination of 4-substituted 3-cyanotoluenes (**1**), see eq 1, led us to consider the general



1 **2** (1)

problem of substituent effects in free-radical reactions. The transition state for this H-abstraction reaction is normally represented as **3** where Y· is **2** and ·Z, the abstracting radical, is Br·. The NBS bromination of monosubstituted toluenes has an excellent correlation with σ^+, where $\rho = -1.46$.[13a] This large negative ρ was interpreted as being consistent with a large contribution of polar form **3b** and dependence on σ^+ because direct resonance was possible between electron-donor substituents and **3b**. The reaction of monosubstituted toluenes with the nucleophilic *tert*-butyl radical[14] has a ρ value of +0.99 consistent with contribution of polar form **3c** to the transition state of this reaction. These two H-abstraction reactions are both *consistent with the polar transition state explanation* just given, whereas only the former is consistent with Zavitsas' BDE explanation.[15]

$$[\dot{Y}\dot{H}\dot{Z} \leftrightarrow Y^{+}\dot{H}\bar{Z} \leftrightarrow \bar{Y}\dot{H}Z^{+}]$$

3a **3b** **3c**

To get a substituent effect that is only related to free-radical stabilities and not polar influences, the latter must be eliminated. Alternatively, a system could be designed where polar effects are not important. This has been accomplished by using an abstracting free radical, ·Z, that has approximately the same electronegativity as ·Y. The reactions of monosubstituted toluenes with $\cdot CH_3$,[16] ·Ph,[17] and ·H[3b] have been studied and ρ was found to be near zero in each case. The remaining rate effects are so small that very accurate measurements are required and interpretation is difficult.

The approach used in this study is not to eliminate the polar effects, but to diminish them. This is to be accomplished by a substrate change (addition of a *m*-cyano group) instead of a change in Z. In our system, polar form **3c** is not important because of the electronegativity of the H-abstracting Br·. The addition of electron-withdrawing groups to Y make the polar form **3b** have a higher energy and therefore not contribute as much to this transition state. Some electron-withdrawing 4-substituents should also be able to destabilize **3b** and at the same time stabilize free radical form **3a** by direct resonance. A free-radical substituent constant is developed in this work to measure this "extra" resonance.

Model Systems. There are many problems associated with establishing a free-radical substituent constant.[3,5c,18–22] What free-radical system is general enough to cover all situations? How are polar effects to be removed? How can transition-state effects be separated from ground-state effects? Is the extended Hammett treatment valid for free-radical reactions? It is doubtful if any system can satisfy all these demands. The two radicals studied most in this context are the benzyl and the cyclohexadienyl systems. Our system has something positive to say on this topic, but is not the ultimate system, and does not answer all of the questions raised. It is hoped that this work will stimulate new approaches that may ultimately lead to the ideal system.

Several attempts to develop a free-radical substituent constant have used an extended Hammett approach that is similar to the Yukawa–Tsuno approach; see Table I. The Yukawa–Tsuno equation,[23] $\log k/k_0 = \rho[\sigma + r(\sigma^+ - \sigma)]$, is used for reactions with variable resonance contributions from one reaction series to another of similar mechanism. When $r = 0$, usual σ dependence is observed; when $r = 1$, σ^+ dependence is found. In general r can vary from zero to values >1. The Yukawa–Tsuno equation is a special example of a general four-parameter linear free-energy equation as illustrated in the equation

$$\log k/k_0 = aX + bY \qquad (2)$$

where aX and bY represent separate influences of the substitutents that directly affect the rates of the reaction. Other examples of eq 2 include the Edwards equation,[2] the Swain–Lupton equation,[24a] and Hansch's multiple parameter analysis.[24b] In Table I, aX represents normal Hammett behavior with dependence on σ or σ^+, and bY represents any deviation from normal behavior. In eq 1, 3, and 4 of Table I, b is taken as 1.0 for the defining equations. Reactions that are different from the model systems could have different values of b.

A good variety of free-radical reactions are represented in Table I. Two reactions involve H-atom abstractions from toluene and cumene systems, respectively; two reactions involve free-radical additions to vinyl monomers; and one is a homolytic aromatic substitution reaction. Equation 2 of Table I is the work of Yamamoto and Otsu[5c] and their substitution constant is called E_R for resonance substituent constant. Sakurai[18] studied the effects of substituents on styrene to the addition of $\cdot CCl_3$ and developed a delocalization substituent constant, E_D, related to the Q value of Alfrey and Price. Simamura[19] has suggested the substituent constant τ to measure the free-radical stabilizing effect of substituents to phenylation. The last entry in Table I is the Qe scheme of Alfrey and

Table II. Values of Some Free-Radical Substituent Constants[a]

Substituent	Registry no.	$\sigma\cdot$	E_R	E_D	τ_p	Log Q	σ^2[c]
F	64113-73-1	−0.25					0.00
OCH_3	64113-74-2	−0.12	0.11	0.19	0.14	0.13	0.07
CH_3	64113-75-3	−0.02	0.03	0.11	0.09	0.04	0.03
H	61142-85-6	0.00	0.00	0.00	0.00	0.00	0.00
Cl	64113-76-4	0.08	0.10	0.07	0.16	0.01	0.05
Ph	64113-77-5	0.12					0.00
I	64113-78-6	0.16	0.12			0.07	0.03
Br	64113-79-7	0.17	0.12			0.04	0.05
NO_2	64113-80-0	0.27	0.41	0.27	0.90	0.21	0.61
N=NPh	64113-81-1	0.33			0.9[b]		0.07
CN	64113-82-2	0.34	0.24	0.32		0.27	0.44
Ac	64113-83-3	0.53	0.24				0.25

[a] See Table I for the definitions of these substituent constants. [b] Reference 27. [c] Reference 20.

Price,[5a] which has found much utility in the study of vinyl copolymerizations.

The extended Hammett approach[18] as applied to free-radical reactions has been used mainly to separate inductive and resonance effects. The inductive effects are usually measured experimentally by ρ_m found by using only meta substituents. Then any deviations of para substituents from this line are assumed to be resonance effects. A major problem with this approach arises in free-radical reactions because the resonance effects measured can involve both polar and radical stabilization. The term "extra" resonance[26] is often used to refer to any direct resonance between the substituent and the reaction site that is not possible in the reactant. The Hammett substituent constants σ^+ and σ^- measure this "extra" resonance as it applies to positive and negative reaction sites. The Hammett free-radical substituent $\sigma\cdot$ is the analogous measure of the "extra" resonance between a substituent and a free-radical site. A separation of the polar and radical "extra" resonance is required for a measure of $\sigma\cdot$. In this work we are attempting to separate the resonance effects on radical form **3a** from the resonance effects on polar form **3b** by use of a substrate change.

$\sigma\cdot$. Some general criteria that need to be met in a model system used to define $\sigma\cdot$ are: (1) the effect studied must involve a direct interaction between the substituent and the free-radical site; (2) the mechanism of the reaction should be well understood; (3) the kinetic effects should be reasonably large, and an accurate method should be available to measure the kinetic effects; (4) a wide range of substituents should be studied to give generality to the study; (5) outside influences (like steric effects, solvent effects, etc.) should be kept to a minimum.

The 4-substituted 3-cyanotoluene system (**1**) chosen here, while not the ultimate choice of a model system, nonetheless measures up nicely to each of the five criteria just listed. A benzyl free radical can be directly stabilized by resonance with para substituents on it. The mechanism of NBS bromination of toluenes has been determined by a variety of studies[13] and is believed to involve a hydrogen-atom abstraction by a bromine atom. The use of benzene solvent in this reaction provides a homogeneous medium and accurate kinetics are easily obtained. Twelve substituents were chosen varying from methoxyl to nitro on the extremes. Steric inhibition of resonance can come into play for only three substituents, and this will be discussed in more detail later.

Using the form of a general four-parameter linear free-energy equation, $\sigma\cdot$ is defined by the equation

$$\log k/k_0 = \rho\sigma^+ + \sigma\cdot \qquad (3)$$

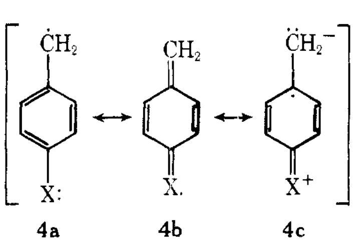
The relative rate data for **1** given in Table I of our earlier work[12] provides the log term on the left. The aX term is represented by $\rho\sigma^+$, which is $-1.46\sigma^+$ for the NBS bromination of monosubstituted toluenes. By rearranging the terms in eq 3, the definition of $\sigma\cdot$ results as $\sigma\cdot = \log k/k_0 - \rho\sigma^+$. This is a measure of the difference in substituent effects between the monosubstituted toluenes and the 4-substituted 3-cyanotoluenes for the NBS bromination reaction. The values of $\sigma\cdot$ thus calculated are listed in Table II along with values of the other substituent constants mentioned in Table I. There are other ways $\sigma\cdot$ could be defined that more closely resemble the Yukawa–Tsuno equation, but eq 3 seems the simplest and is more in harmony with the other extended Hammett equations of Table I.

The ρ^+ for monosubstituted toluenes is believed to contain both inductive and direct resonance effects between electron-donor groups and **3b**. Probably some direct resonance between the 4-substituents and radical form **3a** is present, but it is believed to be overshadowed by the polar resonance as indicated by the excellent σ^+ correlation. The "extra" resonance looked for here is that which is possible in the transition state of the bromination of **1** but is not important in the transition state of the same reaction with the monosubstituted toluenes. Our reference value of ρ in eq 3 is not a ρ_m because we were not interested in only separating inductive and resonance effects of the polar type. It was assumed that the ρ^+ value of −1.46 has both resonance and inductive polar influences in it.

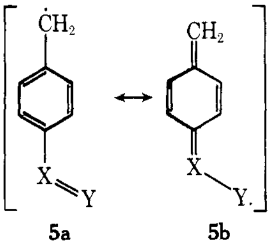
Of the six substituent constants in Table II, only $\sigma\cdot$ has negative values. A negative value indicates destabilization by a substituent. The idea that all substituents should stabilize a free radical originated in studies of homolytic aromatic substitution reactions. Free-radical substitution of monosubstituted benzenes are normally faster than benzene, and the ortho and para products are more favored than the meta products for virtually all substituents. Cammarata[20] has suggested that this is equivalent to saying that free-radical substituent effects should be correlated with σ^2. Several such correlations were found,[20] but some substituents such as $N\text{-}Me_3^+$ and S–Me must not be used in this type of correlation. These exceptions raise questions about the generality of direct resonance between both electron-donor and electron-acceptor substituents and free-radical sites.

The electron-withdrawing groups NO_2, CN, and Ac are good free-radical stabilizing substituents as measured by all six substituent constants of Table II. The relative order of the three vary, however, and each is favored in at least one system.

Individual Substituents. The benzyl free radical is a class S radical in the classification of Walter,[28] in spite of the fact that a large number of Hammett correlations have been observed for it. A class S radical is one that both electron-donor and -acceptor substituents affect in the same manner. Transition state **3** would, however, be class O. It is well established that only donor substituents can stabilize a positive site and only acceptor substituents can stabilize a negative site by direct resonance. It is often stated that both electron-donor and acceptor substituents can have direct resonance with a free radical. The situation is illustrated in structure **4** with an electron-donor substituent and in structure **5** with an electron-acceptor substituent. Resonance in **5** is directly analogous to negative ion delocalization and looks favorable for a single electron also. For electron donor substituents the situation is different. When an electron-donor group stabilizes a free radical in the same manner as a positive site, **4c** results which is charge separated and consequently is considered to be of higher energy than noncharge-separated structures like **4a** and **4b**. Structure **4b** involves delocalization of the odd electron to the donor atom and results in an expansion of its octet by one electron. This is possible with higher period elements with low-lying d orbitals and by hyperconjugation when the substituent is methyl. However, when the donor atom is a first-row element like O, N, or F, no such stabilization is possible. These general considerations seem to be confirmed by the results of this study.



4a **4b** **4c**



5a **5b**

The values of $\sigma\cdot$ in Table II vary from F to Ac with the former the least stabilizing and the latter the most stabilizing substituent. In general the electron acceptor substituents stabilized the benzyl free radical the best, presumably by resonance structures like **5**. Of the resonance electron donor groups, the phenylazo and all of the halo substituents but fluoro also provide stabilization for the free radicals. Two substituents, fluoro and methoxyl, are actually destabilizing in this study.

The best four free-radical-stabilizing substituents found here were NO_2, N=NPh, CN, and Ac, respectively, with Ac decidedly the best. These four substituents are all good electron-withdrawing substituents as measured by σ. Inductively, the nitro substituent is the best electron acceptor of the group as measured by σ'. The ability to withdraw electrons by resonance is usually measured by $\sigma_R = \sigma_p - \sigma'$. The Ac substituent is the best of the four at resonance electron withdrawal. The σ_R values for N=NPh, CN, NO_2, and Ac are +0.05, +0.07, +0.15, and +0.25, respectively.[25,29] Even though steric inhibition of resonance is probably important for both the nitro and acetyl substituents, its effect should be about the same for each substituent. The linear CN group should not have steric problems and this would relatively enhance its ability at "extra" resonance. It is concluded that the Ac substituent is the best substituent of those studied here at stabilizing a free radical because it can best delocalize the odd electron by resonance.

Steric inhibition of resonance is possible in **3** for the three substituents NO_2, Ac, and Ph. The 4-substituents must be in the plane of the benzyl ring to effectively resonate with the odd electron at the benzyl position. The 3-cyano substituent in **2** can interfere with the planarity of these three 4-substituents. This steric effect should be most pronounced for phenyl, since it is the largest of the three. It is estimated that the 4-phenyl substituent is about 60° out of plane. Correction for this steric effect would enhance the value of $\sigma\cdot$ for Ph by a factor of several fold. Undoubtedly this steric effect is the reason the phenyl group is not more prominent in this study. Correction for the steric effects of the Ac and NO_2 substituents would enhance their $\sigma\cdot$ values by an approximately equal amount and would not affect the relative positions of these two substituents.

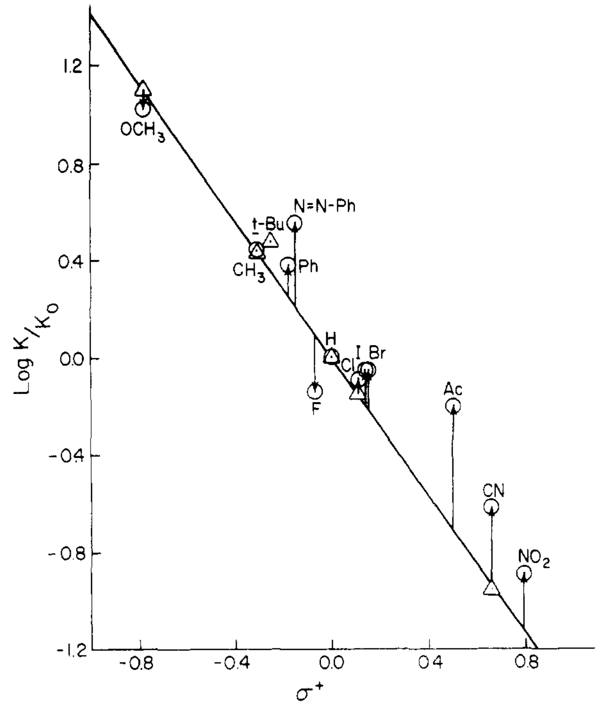


Figure 1. Plot of log k/k_0 vs. σ^+ for monosubstituted toluenes (triangles) and for 1-X (circles). The line is for the monosubstituted toluene data where $\rho = -1.46$. The vertical arrows represent the sign and magnitude of $\sigma\cdot$.

The methoxyl substituent is an interesting case. It is such a strong electron donor by resonance that its σ^+ value is −0.78 vs. a σ value of −0.27. From theoretical calculations, Taft[30] has estimated the methoxyl substituent to be less than one-third as efficient at stabilizing a free radical as a positive charge when either is located on the carbon atom adjacent to the substituent. Timberlake,[8b] in a study of azo compounds, found little if any stabilization by the methoxyl substituent in both aliphatic and benzylic systems. Delocalization of the benzylic odd electron to the OCH_3 group would necessitate placing it on a higher energy orbital of oxygen, such as the 3s orbital. This should be unfavorable but has been suggested by Gould[31] to be important for substituted triphenylmethyl radicals.[32] Resonance structures of the type **4** would be unfavorable here due to the electronegativity of the hydrogen-abstracting atom (Br·). Our value of $\sigma\cdot$ lends support to Timberlake's conclusion that the methoxyl substituent cannot effectively stabilize a free radical, and in fact seems to destabilize it.

Hyperconjugation would be required for the methyl substituent to resonance stabilize this benzyl free radical. The lack of any enhancement by the methyl substituent ($\sigma\cdot$ is essentially zero for methyl) is interpreted as the lack of hyperconjugation in this case.

The halo substituents provide an interesting insight into the problem of free-radical stabilization. The σ^+ value of F is negative. The other three halo substituents have positive σ^+ values, indicating that F being a first-row element is the most efficient cation stabilizing substituent by resonance, and this outweighs the fact the F is also the most electronegative of the halogens. To stabilize a free radical, however, electron withdrawal is required, not electron donation. The odd electron ends up being delocalized into a d orbital on the halo substituent. Since F cannot expand its octet, it does not stabilize the benzyl free radical, but the other three halo substituents with low-lying d orbitals have favorable $\sigma\cdot$ values.

Because of the importance of the azo linkage, –N=N–, to azo dyes and some free-radical initiators, the phenylazo substituent has been discussed elsewhere.[25,33] The phenylazo substituent can both donate and accept electrons by resonance, and consequently stabilize cations, anions, and free radicals.

In summary, the free-radical stabilizing ability of the 12 substituents studied here is graphically illustrated in Figure 1. The straight line in Figure 1 is for the NBS bromination of monosubstituted toluenes. The deviation from this line is shown by an arrow for each substituent, where the up direction represents free-radical stabilization and the down direction destabilization. The direction and magnitude of these vectors represent the sign and magnitudes of the $\sigma\cdot$'s. It is not claimed that complete separation of the polar and radical effects was achieved here, but progress was made in that direction. The relative order of substituent stabilization found here is probably more significant than the magnitudes of the $\sigma\cdot$'s. Also, comparisons within the series of electron-withdrawing substituents and within the series of electron-donor substituents is probably more significant than comparisons between the two series, because of the polar nature of the transition state **3** found in the NBS brominations of toluenes.

Registry No.—**1** (R = F), 64113-84-4; **1** (R = OMe), 53078-70-9; **1** (R = CH_3), 13730-09-1; **1** (R = H), 620-22-4; **1** (R = Cl), 4387-32-0; **1** (R = Ph), 64113-85-5; **1** (R = I), 42872-86-6; **1** (R = Br), 42872-83-3; **1** (R = NO_2), 64113-86-6; **1** (R = N=NPh), 57495-20-2; **1** (R = CN), 63089-50-9; **1** (R = Ac), 64113-87-7; **1** (R = *t*-Bu), 64113-88-8.

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(32) The dimers of the triphenylmethyl radicals discussed by Gould[31] are now known not normally to be hexaphenylethanes, but this does not affect the argument of whether the oxygen atom of a methoxyl group can easily expand its octet by resonance with a free radical site para to it.

(33) The $\sigma\cdot$ value reported earlier[25] of 0.28 is slightly different from the value of 0.33 reported here due to a difference in the kinetic equation used. In the earlier work, the kinetic equation $k/k_0 = M_HA_X/M_XA_H$ was used, where M_X is the moles of X and A_X is the area of the X benzyl H's in the NMR of the product mixture. This equation is used in competative reactions involving small conversions of reactants to products.