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Kinetic Study of the *N*-Bromosuccinimide Bromination of Some 4-Substituted 3-Cyanotoluenes

T. H. Fisher* and A. W. Meierhoefer

Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762

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Twelve 4-substituted 3-cyanotoluenes (**3**-X) were prepared from 4-substituted 3-aminotoluenes, 4-amino-3-nitrotoluene, or *m*-tolunitrile (**3**-H). The relative rates of NBS bromination of **3**-X vs. **3**-H were determined in benzene at 80 °C. These relative rates, k/k_0, increased in the following substituent order: $NO_2 < CN < Ac < F < Cl < Br < I < H < Ph < CH_3 < N{=}NPh < OCH_3$. The substituent effects were discussed in terms of polar transition state and bond dissociation energy arguments. A linear dependence on σ^+ was found with $\rho = -1.13 \pm 0.12$. Several withdrawing substituents were believed to provide "extra" resonance in this free-radical reaction.

Substituent influences on the homolytic process have been studied in a wide variety of reactions. In spite of this, the effects, both stabilizing and destabilizing, of substituents on free-radical sites are not nearly as well understood as the corresponding substituent influences on positive and negative sites in a molecule. Linear free-energy studies of the Hammett type have proven to be a major tool used to help elucidate organic reaction mechanisms of both the heterolytic and homolytic types. One of the systems that has yielded much valuable information about free-radical substituent effects is the H atom abstraction reactions of substituted toluenes. Most common free radicals have been reacted with substituted toluenes. Russell[1] and Pryor[2] list nearly 20 different free radicals that have been studied in this reaction including: H·, Ph·, CH_3·, *t*-BuO·, Cl·, Br·, etc. Because of this wealth of information available on the benzyl free radical, it was chosen as the substrate in this study.

Many H atom abstraction reactions are known to be dependent on σ or σ^+. The usual explanation of this is illustrated by eq 1, where Y–H represents a substituted toluene, ·Z the abstracting radical, and Y· a benzyl radical. The susceptibility of the transition state to polar influences is represented by **2b** and **2c**, where **2b** is important when Z is electronegative and **2c** is important when Z is electropositive. This explanation had become so well accepted that if polar effects were possible they were expected to overshadow the free radical influences. Recently, a paradigm shift[3] from this polar transition state explanation to a bond dissociation energy (E) explanation was attempted by Zavitsas.[4] Pryor[5] and Henderson[6] have successfully defended the polar transition state explanation by finding several reactions that have positive ρ values consistent with contributions of **2c** above but inconsistent with Zavitsas' explanation. It is also very difficult experimentally to determine accurate bond dissociation energies for benzyl C–H bonds whose only difference is a meta or para substituent.

$$\underset{\mathbf{1}}{\mathrm{Y{-}H}} + \cdot\mathrm{Z} \rightarrow [\underset{\mathbf{2a}}{\dot{\mathrm{Y}}\dot{\mathrm{H}}\dot{\mathrm{Z}}} \leftrightarrow \underset{\mathbf{2b}}{\mathrm{Y^{+}\dot{H}Z^{-}}} \leftrightarrow \underset{\mathbf{2c}}{\mathrm{Y^{-}\dot{H}Z^{+}}}]^{\ddagger} \rightarrow \mathrm{Y}\cdot + \mathrm{H{-}Z} \quad (1)$$

Most attempts to study free-radical influences in H atom abstraction reactions have been to decrease the electronegativity of Z in eq 1 so that the polar effects will become less important. This has been successfully accomplished by using ·Z = ·CH_3,[7] ·Ph,[8] or ·H;[2] and sure enough ρ was found to be near zero in each case. The approach used in this work is to diminish the polar effects by a substrate change (addition of a *m*-CN group) instead of a change in Z. The strongly electron-withdrawing cyano substituent should increase the potential energy of the benzyl cationic contributor **2b**, and consequently the free-radical contributor **2a** should be relatively more important. This is another way of saying the polar effects should not be as important in this free radical reaction.

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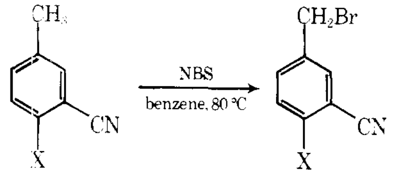
Since the abstracting radical is Br·, **2c** is not important in the transition state of this reaction.

The model system chosen for study was the *N*-bromosuccinimide (NBS) bromination of 4-substituted 3-cyanotoluenes (**3**-X) vs. *m*-tolunitrile (**3**-H) in benzene at 80 °C, see eq 2. This



(2)

3 4

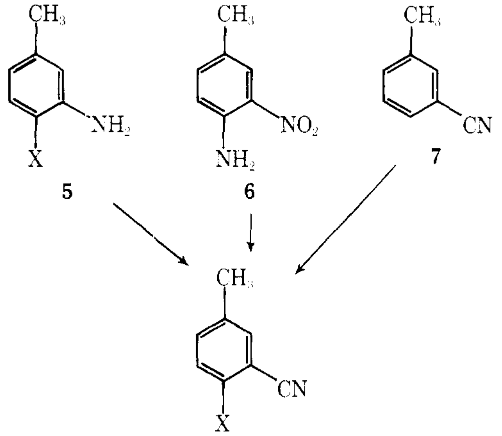
reaction was chosen because its mechanism is well established.[9] Twelve substituents (X) were studied here, covering the entire range of electron donor and acceptor substituents.

Results

Toluene Syntheses. The 4-substituted 3-cyanotoluenes (**3**) used in this work were prepared from one of three different precursors: 4-substituted 3-aminotoluenes (**5**), 4-amino-3-nitrotoluene (**6**), or *m*-tolunitrile (**7**); see eq 3.

Three commercially available amines, 3-amino-4-chlorotoluene, 3-amino-4-methoxytoluene, and 2,5-dimethylaniline, were each diazotized and then reacted with CuCN via a Sandmeyer reaction to give **3** (X = Cl, OCH_3, CH_3).

Three toluenes **3** (X = CN, I, Ph) were prepared from **6** by way of **5**. Diazotization of 4-amino-3-nitrotoluene (**6**) was followed by treatment with CuCN, KI, or benzene and base (Gomberg reaction). Reduction of the 3-nitro group in these three compounds with iron and acetic acid gave the three amines **5** (X = CN, I, Ph). These amines were then converted to **3** (X = CN, I, Ph) by repetition of the sequence used above to convert **5** to **3**.



(3)

3, X = Cl, CH_3, OCH_3, from 5
X = CN, I, Ph, Ac from 6
X = NO_2, –N═NPh, F, Br from 7

4-Acetyl-3-cyanotoluene was prepared by an interesting series of reactions. Hydrolysis of 4-cyano-3-nitrotoluene with 50% sulfuric acid gave the benzoic acid derivative which was then converted to the acid chloride with thionyl chloride. The acid chloride was then added to an ether slurry of ethoxymagnesium malonate to form the benzoyl malonate derivative using a procedure developed by Hauser.[10] Hydrolysis and decarboxylation gave 4-acetyl-3-nitrotoluene in 52% yield. The 3-nitro group was then converted into the nitrile in the same manner as above, giving **3**-Ac.

The last four toluenes were made from *m*-tolunitrile (**7**). Nitration of **7** gave a 60% yield of **3**-NO_2 after removal of 5-cyano-2-nitrotoluene by steam distillation. Reduction of 4-nitro-3-cyanotoluene with iron and acetic acid gave 4-amino-3-cyanotoluene, which was then converted to **3**-N═NPh by addition of nitrosobenzene. 4-Amino-3-cyanotoluene was diazotized and then converted to **3**-F by the Shiemann reaction and to **3**-Br by the Sandmeyer reaction.

Table I. Relative Rates of NBS Bromination of Some Toluenes

X	Registry no. (3-X)	k/k_0 3-X	k/k_0 *p*-X-Ph-CH_3[a]
OCH_3	53078-70-9	10.34 ± 0.85	12.39
N═NPh	57495-20-2	3.55 ± 0.06	1.66[b]
CH_3	13730-09-1	2.70 ± 0.04[c]	2.62
Ph	64113-85-5	2.41 ± 0.02	1.83[b]
H	620-22-4	1.00	1.00
I	42872-86-6	0.90 ± 0.01	0.64[b]
Br	42872-83-3	0.90 ± 0.01	0.60[b]
Cl	4387-32-0	0.82 ± 0.04	0.72
F	64113-84-4	0.72 ± 0.02	1.28[b]
C(O)CH_3	64113-87-7	0.63 ± 0.02	0.19[b]
CN	63089-50-9	0.24 ± 0.03	0.11
NO_2	64113-86-6	0.13 ± 0.01	0.07[b]

[a] Reference 9a. [b] Estimated using σ^+ and $\rho = -1.46$. [c] Value for bromination at the 5-methyl only of 2,5-dimethylbenzonitrile.[11]

Kinetic Results. The competitive rates of NBS bromination of each toluene **3**-X vs. the reference toluene **3**-H were done in benzene solvent at 80 °C. These conditions provide a homogeneous solution and thus simplify the kinetics. Good reproducibility was found if the initial amounts of each toluene were precalculated (after a preliminary run) so that approximately equal amounts of benzyl bromide products were formed.

Table I shows the results of these relative rate studies. The most reactive toluene, **3**-OCH_3, was 80 times more reactive than the least reactive one, **3**-NO_2. For sake of comparison, the kinetic data for the monosubstituted toluenes[9a] are also shown in Table I.

Six other toluenes **3**-X were also prepared and relative rate studies were attempted on these. The kinetics of bromination of these compounds were unsuccessful for a variety of reasons. Toluenes **3**-NHAc and **3**-NHBz were insoluble under the reaction conditions. **3**-NH_2 and **3**-SPh underwent side reactions that interfered with the primary reaction. In **3**-CHO the aldehyde H, not the benzylic H, was brominated. **3**-CO_2CH_3 brominated in the correct position, but the carbomethoxy H's interfered with the benzyl H's in the NMR of the benzyl bromide products, making analysis impossible.

Discussion

The NBS bromination of monosubstituted toluenes in benzene at 80 °C was studied by Pearson and Martin.[9a] By studying six substituents they found an excellent correlation with σ^+, $\rho = -1.46$, $r = 0.997$. The mechanism of this reaction has been shown to involve bromine atoms in the H-abstraction step,[9a] with the NBS acting as a source of bromine. The substituent effects for this reaction have normally been explained by the polar transition state argument. This was illustrated earlier in eq 1, where **2b** represented the polar influence on the transition state of this free-radical reaction. This explanation is also illustrated in Figure 1. The placement of a substituent on toluene Y–H causes the transition state of this reaction to be stabilized (OCH_3) or destabilized (CN) with the appropriate increase or decrease in rate. Thus, *p*-methoxytoluene reacts 113 times as fast as *p*-cyanotoluene in the reaction. Zavitsas' bond dissociation energy (E) argument would predict the same result for this reaction by postulating the origin of the substituent effect, residing in the E's of the C–H bonds being broken in the reaction. This explanation is illustrated

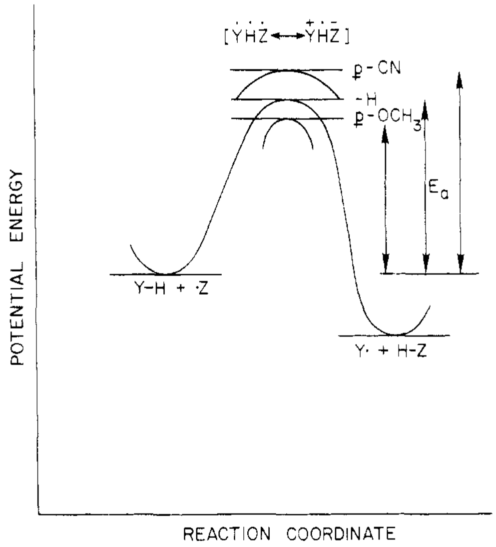


Figure 1. *Potential energy diagram for a H-abstraction reaction showing the polar transition state explanation for substituent effects in free-radical reactions.*

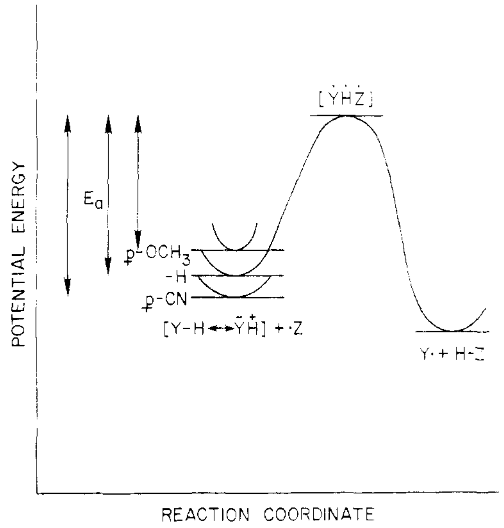


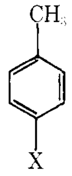
Figure 2. Potential energy diagram for a H-abstraction reaction showing the bond dissociation energy explanation for substituent effects in free-radical reactions.

in Figure 2. In this case the transition state is assumed to be the same for each substituent, but the benzyl C–H bond of *p*-cyanotoluene is considered stabilized by the cyano substituent. This argument puts the emphasis on ground-state influences instead of transition-state influences. Note the net result is the same in each case: the cyanotoluene is slowest. Essentially the BDE argument places the polarity in the ground state instead of in the transition state. The point of agreement is that the activation energy for *p*-cyanotoluene is larger than that of *p*-methoxytoluene.

Our system compares the relative rates of NBS bromination of 4-substituted 3-cyanotoluenes (**3**-X) with the reference substrate *m*-tolunitrile (**3**-H). Compounds **3**-X are disubstituted toluenes with a *m*-cyano group on each toluene in addition to the variable 4-substituent. The *m*-cyano group was added because it is a strong electron-withdrawing group and should increase the activation energy of **3**-X relative to the toluenes without the *m*-cyano group. In the polar transition state explanation, this increase in E_a for the cyano group makes the polar form **2b** of higher energy and therefore less important. This diminished importance would be seen experimentally as a smaller value of ρ in the disubstituted series **3**. Two other factors that normally affect the magnitude of ρ were kept constant here. These are the amount of bond breaking in the transition state and the electronegativity of the H-abstracting species ·Z. The linear geometry of the cyano group provided a minimum steric interference with adjacent 4-substituents compared to other electron-withdrawing groups like nitro or acetyl.

Some substituents are known to give "extra" resonance to free-radical sites due to strong direct resonance between the substituent and the free-radical site. The *p*-cyano group has been postulated to provide such additional stability in the free-radical methylation of benzonitrile[12] and the unusual stability of the tricyanomethyl radical.[13] This type of "extra" resonance would be possible for a 4-substituent that can directly resonate with a benzyl free-radical site. This "extra" resonance would also stabilize free-radical form **2a** in a manner analogous to that given the polar form **2b** already discussed. Substituents that stabilize **2a** but destabilize **2b** would be of special interest. Electron-withdrawing substituents fit this category.

Some of the kinetic data of Table I will be cited here that relates to the concept of "extra" resonance. The compounds whose rates are to be compared are formed by placing a 4-substituent on toluene and *m*-tolunitrile, respectively. The first two cases, CN and Ac, provide a relative rate increase in **3** that is 2.2 and 3.3 times that seen in **8**. This is a fairly large increase. In contrast F causes a rate decrease in **3** relative to **8**. The "extra" resonance of the Ac group is probably also retarded by steric inhibition of resonance from the 3-cyano group.



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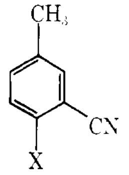

3

8	3	$k(3)/k(8)$
$k_{CN/H} = 0.11$	$k_{CN/H} = 0.24$	2.2
$k_{Ac/H} = 0.19$	$k_{Ac/H} = 0.63$	3.3
$k_{F/H} = 1.28$	$k_{F/H} = 0.72$	0.6

Some general comments need to be made about the importance of steric inhibition of resonance in those benzyl radicals where the 3-cyano substituent can interfere with the planarity of the 4-substituent. This interference should be important for three substituents—NO_2, Ac, and Ph. The effect should be most pronounced for phenyl, since it is the largest of the three. This steric situation is analogous to optically active ortho-substituted biphenyls where coplanarity is not possible due to the steric interaction. In the benzyl free-radical from **3**-Ph, it is estimated that that the two phenyl groups are about 60° out of plane. This steric effect and the small electron-withdrawing nature of the phenyl group probably account for the lack of much "extra" resonance from the phenyl substituent.

A statistical analysis was performed to see if our kinetic data of Table I was linearly correlated with some of the more common Hammett substituent constants. The results are shown in Table II. The best correlation was found with σ^+ as expected, with $\rho = -1.13 \pm 0.12$, $r = 0.950$. The other correlations fall into the so-called region of noncorrelation with $r < 0.9$. This ρ^+ value of -1.13 is appreciably less than the value of -1.46 found in the monosubstituted toluene series, see Figure 3. This smaller ρ^+ value is consistent with polar influences being less important in **3**-X than in **8**-X. The correlation with σ was much poorer than σ^+ as measured by both correlation coefficient and standard deviation of ρ. This was

Table II. Correlations of Log k/k_0 with Some Hammett Substituent Constants for 3-X

Substituent constant	Ref[a]	ρ	r	n
σ^+	17	-1.13 ± 0.12	0.950	12
σ^n	18	-1.43 ± 0.29	0.869	10
σ	19, 20	-1.38 ± 0.27	0.854	12
σ^-	19, 21	-0.92 ± 0.31	0.774	8
σ'	22	-1.52 ± 0.55	0.659	12
σ_R[b]	19, 20, 22	-1.32 ± 0.61	0.566	12
E_s	22	0.29 ± 0.25	0.399	9

[a] Values of substituent constants used are given in these references. [b] $\sigma_R = \sigma_p - \sigma'$.

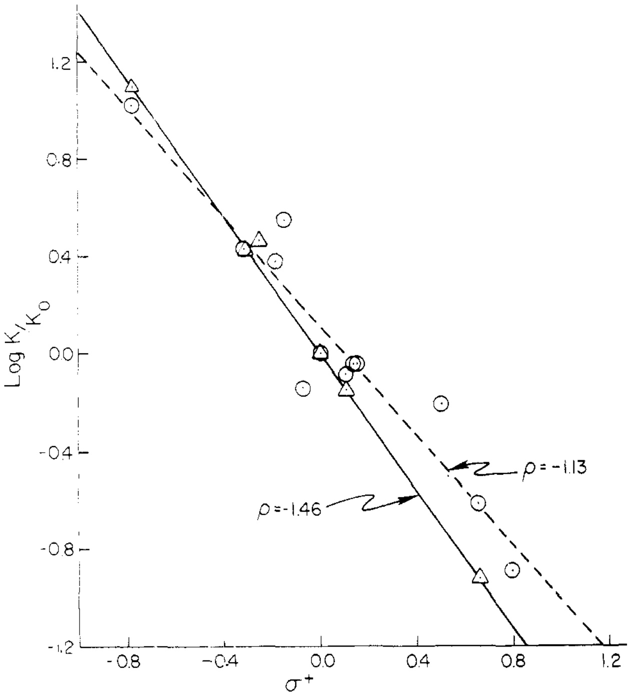

Figure 3. Plot of rates of NBS bromination vs. σ^+ for monosubstituted toluenes (triangles) and for **3**-X (circles).

also the case with monosubstituted toluenes **8**. Some other parameters were also checked for correlations and found to be poorer than those listed in Table II. These include $\sigma_R{}^+$,[14] molar refractivity,[15] van der Waals volume,[16] and lipophilicity.[15]

In conclusion, the rates of NBS bromination of toluenes **3**-X are adequately explained by the usual polar transition state explanation involving a reduced dependence on polar effects compared with monosubstituted toluenes. "Extra" resonance is believed to be found for several electron-withdrawing substituents.

Experimental Section

Materials. Benzene, *N*-bromosuccimimide (Aldrich), phthalide (Aldrich), and 2,2'-azobisisobutyronitrile (K&K) were all purified by standard procedures prior to use. *m*-Tolunitrile (K&K) was distilled and a center cut used.

All infrared spectra were obtained with a Perkin-Elmer 137 spectrophotometer. Nuclear magnetic resonance spectra were recorded with a Varian A-60. Elemental analyses were performed by Galbraith Laboratories, Inc.

4-Chloro-3-cyanotoluene (3-Cl). 3-Amino-4-chlorotoluene (Eastman), 21.2 g (0.15 mol), was added to a cold solution of sulfuric acid and diazotized with 11.25 g (0.16 mol) of sodium nitrite. The diazonium solution was added to a warm solution of 44.5 g (0.5 mol) of cuprous cyanide and 33.5 g (0.5 mol) of potassium cyanide in a typical Sandmeyer reaction. After heating for 1 h on a steam bath, the mixture was cooled, extracted with ether, washed with water, 6 M hydrochloric acid, and 5% sodium bicarbonate, and dried with magnesium sulfate. Removal of solvent followed by recrystallization from 50% ethanol gave 6.3 g (28%) of 4-chloro-3-cyanotoluene: mp 56–57 °C; IR (CCl_4) 2225 cm^{-1} (C≡N); NMR (CCl_4) δ 7.2–7.5 (m, 3 H, Ar-**H**), 2.3 (s, 3 H, Ar-CH_3).

Anal. Calcd for C_8H_6ClN: C, 63.38; H, 4.00; N, 9.24. Found: C, 63.31; H, 3.84; N, 9.05.

2,5-Dimethylbenzonitrile (3-CH$_3$). A Sandmeyer reaction was used to convert 12.0 g (0.1 mol) of 2,5-dimethylaniline to the nitrile: yield 6 g (47%); bp 66–67 °C (1.4 Torr) [lit.[23] bp 104–105 °C (18 Torr)].

3-Cyano-4-methoxytoluene (3-OCH$_3$). Using the Sandmeyer procedure as above, 3-amino-4-methoxytoluene, 20.5 g (0.15 mol), was converted into 9 g (41%) of 4-cyano-4-methoxytoluene: bp 85–86 °C (0.4 Torr) [lit.[24] bp 148–150 °C (18 Torr)].

3,4-Dicyanotoluene (3-CN). 4-Amino-3-nitrotoluene (Baker), 75 g (0.5 mol), was converted to 4-cyano-3-nitrotoluene by the Sandmeyer procedure. Reduction of the crude 4-cyano-3-nitrotoluene with iron and acetic acid followed by recrystallization from 30% ethanol gave 15 g (23%) of 3-amino-4-cyanotoluene: mp 93–95 °C (lit.[25] mp 92.0–94.5 °C). The method of Findeklee[26] was then used to convert 3.0 g (0.022 mol) of 3-amino-4-cyanotoluene into 0.75 g (23%) of 3,4-dicyanotoluene: mp 118–120 °C (lit.[26] mp 118–120 °C).

3-Cyano-4-iodotoluene (3-I). 4-Iodo-3-nitrotoluene was prepared from 4-amino-3-nitrotoluene in 67% yield by the procedure of Carlin and Foltz.[27] 4-Iodo-3-nitrotoluene, 25 g (0.095 mol), was added to 28 g of iron filings and 140 mL of 50% aqueous acetic acid. The mixture was heated for a few minutes to start the reaction and was kept below 50 °C for 1 h. Neutralization followed by steam distillation gave 18 g (81%) of the amine, mp 33–35 °C (lit.[28] mp 37.5 °C). The method of Hodgson[29] was then used to convert the amine to 3-cyano-4-iodotoluene in 28% yield. Recrystallization from petroleum ether gave orange crystals: mp 49–51 °C; IR (CCl_4) 2225 cm^{-1} (C≡N); NMR (CCl_4) δ 7.0–8.0 (m, 3 H, Ar-**H**), 2.4 (s, 3 H, Ar-CH_3).

Anal. Calcd for C_8H_6IN: C, 39.53; H, 2.49; N, 5.76. Found: C, 40.42; H, 2.36; N, 6.00.

3-Cyano-4-phenyltoluene (3-Ph). Using the procedure of Ritchie,[30] 71 g (0.46 mol) of 4-amino-3-nitrotoluene was converted to 46 g (46%) of 3-nitro-4-phenyltoluene, bp 140–142 °C (0.3 Torr) [lit.[30] bp 207–208 °C (28 Torr)]. 3-Nitro-4-phenyltoluene, 20 g (0.094 mol), 20 g of mossy tin, and 100 mL of concentrated HCl were refluxed overnight. The mixture was filtered, made basic, and extracted with ether. Evaporation of the solvent left 10 g of the crude amine, which was converted to the nitrile by the usual diazotization procedure. Recyrstallization from hexane gave 2.0 g (19%) of 3-cyano-4-phenyltoluene: mp 79–80 °C; IR (CCl_4) 2225 cm^{-1} (CN); NMR (CCl_4) δ 7.3–8.1 (m, 8 H, Ar-**H**), 2.5 (s, 3 H, Ar-CH_3).

Anal. Calcd for $C_{14}H_{11}N$: C, 87.00; H, 5.75; N, 7.25. Found: C, 87.10; H, 5.52; N, 7.19.

4-Acetyl-3-cyanotoluene (3-Ac). The procedure of Joachim and Claus[31] was used to convert 4-cyano-3-nitrotoluene to 4-methyl-2-nitrobenzoic acid. The acid chloride was then obtained from the acid and thionyl chloride. An ether solution of the acid chloride was treated with an ether solution of ethoxymagnesium malonate using the method of Hauser.[10] After refluxing for 1 h, the magnesium complex was hydrolyzed with 20% sulfuric acid. Removal of the ether gave a dark oil which was hydrolyzed and decarboxylated by refluxing with an aqueous mixture of acetic and sulfuric acid. Purification gave a 59% yield of 4-acetyl-3-nitrotoluene. The reduction of 4-acetyl-3-nitrotoluene to the amine was carried out by the procedure of Kenneford.[32] A 46% yield of 4-acetyl-3-aminotoluene, mp 54–55 °C (lit.[32] mp 55–56 °C), was obtained. The amine was then converted to 4-acetyl-3-cyanotoluene by the method of Hodgson and Heyworth.[29] 4-Acetyl-3-cyanotoluene was obtained as a white solid: mp 73–74 °C; IR ($CHCl_3$) 2225 (CN), 1710 cm^{-1} (C=O); NMR (benzene) δ 3.0 (s, 3 H, Ar-CH_3), 1.2 (s, 3 H, Ac).

Anal. Calcd for $C_{10}H_9NO$: C, 75.44; H, 5.71; N, 8.80. Found: C, 75.76; H, 5.63; N, 8.88.

3-Cyano-4-nitrotoluene (3-NO$_2$). *m*-Tolunitrile, 15 g (0.13 mol), was nitrated by the method of Macovski[33] to give 13 g (65%) of the nitro product. Recrystallization from 50% ethanol (charcoal) gave the white solid 3-cyano-4-nitrotoluene: mp 93–94 °C (lit.[26] 93–94 °C).

4-Amino-3-cyanotoluene (3-NH$_2$). 3-Cyano-4-nitrotoluene, 14 g (0.086 mol), was reduced with iron and acetic acid to give a yellow solid. Recrystallization from 30% ethanol (charcoal) yielded 8.0 g (71%) of 4-amino-3-cyanotoluene as a white solid: mp 59–61 °C (lit.[26] 63 °C).

3-Cyano-4-phenylazotoluene (3-N=NPh). 4-Amino-3-cyanotoluene was converted to 3-cyano-4-phenylazotoluene in 22% yield:[19] mp 100–102 °C.

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-$C\mathbf{H}_3$).

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.

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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

T. H. Fisher* and A. W. Meierhoefer

Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762

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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