Phenethyl-1,4-diazabicyclo[2.2.2]octane Ammonium Bromide. Anal. Calcd for $C_{14}H_{21}N_2Br$: C, 56.58; H, 7.12; N, 9.42; Br, 26.88. Found: C, 56.13; H, 7.09; N, 9.46; Br, 27.32.

Phenethyl-1,4-diazabicyclo[2.2.2]octane Ammonium Iodide. Anal. Calcd for $C_{14}H_{21}N_2I$: C, 48.85; H, 6.10; N, 8.15; I, 36.90. Found: C, 48.30; H, 6.10; N, 8.37; I, 37.32. NMR spectra in deuteriowater showed the two expected aromatic (δ 7.9) and aliphatic (δ 3.9) peaks, all signals integrating correctly.

Gas chromatographic analyses were performed on the gas chromatograph Varian Model 1840-1, equipped with a flame ionization detector. The stainless steel column (3 × ⅛ in.) was filled with Porapak Q (150–200 mesh). Uv spectra were performed on a Perkin-Elmer spectrophotometer Model 350.

Kinetic. Equal volumes of a halide solution (ca. 0.580 mol l.$^{-1}$) and an amine solution (ca. 0.200 mol l.$^{-1}$) were placed in a thermostat bath at 54.5° ± 0.2 for 30 min and then were mixed rapidly. The reactions were carried out in stoppered flasks, aliquots of reaction mixture being withdrawn at intervals and titrated.

Rates were determined by following the disappearance of base or the appearance of halide ion. In some instances, both methods were employed for the same reaction to provide an added check. In each case, the two rate constants were identical within the limits of experimental error. The base concentration was determined by titration with hydrochloric acid 0.1 mol l.$^{-1}$ in ethanol solvent using Bromophenol Blue as indicator. The halide ion concentration was determined by the Volhard method.

Second-order rate constants k_2 were calculated by using the integrated form of the rate equation as applied to nonequimolecular concentration, $k_2t = (a - b)^{-1}\,[\ln((a - x)/(b - x)) - \ln(a/b)]$, where a and b are respectively the initial concentration of the halide and the amine, and x is the concentration of the amine at time t.

Rate constants, correlations, and precision of each were obtained in the usual manner by a linear least-squares analysis. The computations were carried out by an IBM 1440 computer and appropriate Fortran programs.

Acknowledgments. We are grateful to Professor D. Decroocq for many suggestions and helpful discussions regarding the interpretation of the experimental results.

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Polar Effects in Radical Reactions. IV. The Reaction of Hydrogen Atoms with Substituted Toluenes[1]

R. W. Henderson[2] and William A. Pryor*

Contribution from the Department of Chemistry, Louisiana State University
at Baton Rouge, Baton Rouge, Louisiana 70803. *Received February 18, 1975*

Abstract: Hydrogen atoms, produced by the photolysis (3500 Å) of *tert*-butyl peroxyformate (BUP) at 35°, were allowed to react with a series of substituted toluenes (QH) in the presence of 2-methyl-2-propanethiol-d_1 (RSD) as a standard reactant. As controls, a similar series of substituted benzenes also was studied. An equation is derived which shows that the relative reactivity of a hydrogen donor QH with the H atom is proportional to the slope of a plot of the ratio of the yields of H_2 to HD as the QH/RSD ratio is varied in the solvent mixture. All of the toluenes studied have about the same relative reactivity (per methyl group), 0.056. The benzenes have a similar but slightly lower relative reactivity, 0.028. Since the reactivity of the benzenes is so close to that of the toluenes, it is clear that some of the H_2 produced from toluenes arises from abstraction of ring hydrogens. Four possible mechanisms by which this might occur are considered, and it is concluded that the most likely is the reaction of an H atom with a cyclohexadienyl radical (eq 9). Despite this complication, an inspection of the data (Table I) makes it clear that the ρ value for the H atom is approximately zero. An empirical treatment of the data in which the reactivity of C_6H_5X is subtracted from that of $X\text{-}C_6H_4\text{-}CH_3$ gives a ρ of -0.1. Thus, it is clear that the H atom, like the methyl and phenyl radicals, shows little polar character in its attack on the benzylic position of substituted toluenes.

Reactions of the hydrogen atom in the gas phase have been extensively studied,[3,4] but the solution chemistry of this radical has come under intensive investigation only relatively recently.[5-8] The hydrogen atom is of great theoretical interest; for example, data on its reactions are necessary to test calculations of absolute rate theory.[3] In addition, it is desirable to compare the behavior of the H atom with that of other, larger free radicals.

A considerable effort has been expended toward understanding the role of the H atom in radiation chemistry and biology.[6-8] In the radiolysis of aqueous solutions, the H atom is produced along with various other species, e.g., the solvated electron, the hydroxyl radical, and excited molecules.[9] In order to interpret the chemical effects resulting from radiation, it is essential that the reactions of the different transient species be isolated and studied independently.

The Hammett $\sigma\rho$ treatment is particularly useful for classifying the polar characteristics of chemical species[4,10] and has been found to correlate the reactions of free radicals unexpectedly well.[4,5f,11,12] Hammett equation correlations have been reported for the hydrogen abstraction reaction from the side chain of ring-substituted toluenes by a variety of radicals (eq 1).[5f,11,12]

$$R\cdot + CH_3\text{-}C_6H_4X \rightarrow RH + \cdot CH_2\text{-}C_6H_4X \quad (1)$$

However, comparable data for the simplest of radicals, the hydrogen atom, are not available. We have now studied this reaction and find the H atom to be essentially electroneutral, with ρ approximately zero.[5f,13]

Experimental Section

Materials. The procedure of Ruchardt and Hecht[14] was used to synthesize *tert*-butyl peroxyformate (BUP). 2-Methyl-2-propanethiol-d_1 was prepared by vigorously stirring the unlabeled thiol with 99.8% D_2O. Hydrogen gas (H_2 and D_2) was purchased from the Matheson Co. Deuterium hydride (HD) was generated by the addition of a solution of 99.8% D_2O in *n*-butyl ether to a slurry of *n*-butyl ether and lithium aluminum hydride;[15] analysis of the resulting gas by mass spectrometry indicated a composition of ~98% HD and about 1% each of H_2 and D_2. The aromatic hydrocarbons were dried and distilled immediately prior to use. In some runs, aromatics purified by sulfuric acid treatment were used; however, the relative reactivities were not affected by the additional purification.

Kinetic Procedure. A solution containing a hydrogen donor (QH), 2-methyl-2-propanethiol-d_1, and 0.02 *M* BUP was placed in a Pyrex ampoule and degassed by three freeze-pump-thaw cycles. The ampoule was sealed off under vacuum and irradiated for 1 hr at 35° in a Rayonet photochemical reactor. Sixteen 3500-Å region, "black-light" lamps (GE No. F8T5BL) provided illumination, and a "merry-go-round" apparatus was used to ensure that all of the tubes received equal exposure. After irradiation, the samples were frozen in liquid nitrogen and degassed into a CEC Model 21-620 mass spectrometer, and an analysis for H_2 and HD was made. Calibration curves for these gases were prepared from known synthetic mixtures; since machine reproducibility varied slightly over a period of time, standards were run with the unknowns. Some D_2 was also produced in these runs, arising from the reaction of D atoms, generated by the photolysis of thiol-*d*, with labeled thiol. However, the amount of D_2 never exceeded 1% of the H_2 and HD yield and usually was less than 0.5%. Each hydrogen donor was irradiated neat under conditions similar to those used to photolyze the BUP solutions, but in no case was hydrogen gas (or any gas) produced.

A difficulty encountered in this study was that of obtaining k_H values for the toluenes which had substituents with σ values at the extremes of the range. Some groups with reactive hydrogens (e.g., hydroxy and alkoxy) are not suitable since the correction for the contribution of the substituent depends on the effect of the methyl group on the substituent's reactivity. Also, the nitro and cyano groups consumed such a large fraction of the H atoms that the yields of H_2 and HD were inadequate for quantitative determination.

Results and Discussion

The BUP-thiol-*d* system[5e] was used to determine the relative reactivities of a series of substituted benzenes and toluenes. The reactions are given in eq 2-5

$$\underset{\text{BUP}}{H\text{-}CO_2\text{-}OC(CH_3)_3} \xrightarrow{h\nu} H\cdot + \text{other products} \quad (2)$$

$$H\cdot + QH \xrightarrow{k_H} H_2 + Q\cdot \quad (3)$$

$$H\cdot + RSD \xrightarrow{k_1} H_2 + \cdot RSD \quad (4)$$

$$H\cdot + RSD \xrightarrow{k_2} HD + RS\cdot \quad (5)$$

where ·RSD is the radical which results when a hydrogen atom is abstracted from RSD. Note that the rate constant k_1 reflects hydrogen abstraction not only from the *tert*-butyl moiety, but also from the sulfhydryl position of the small amount of undeuterated thiol present (2%).

Kinetic analysis of eq 2-5 leads to eq 6.

$$[H_2]/[HD] = (k_1/k_2) + (k_H/k_2)([QH]/[RSD]) \quad (6)$$

Thus, relative values of k_H can be obtained from a plot of $[H_2]/[HD]$ against [QH]/[RSD]. It is assumed in this derivation that the QH and RSD concentrations (which were varied from 1 to 9 *M*) do not change significantly during reaction. Since the concentration of BUP was 0.02 *M*, and hence the total concentration of radicals was limited, this is an excellent assumption. For the same reason, there was no appreciable buildup of products (disulfide, QD, etc.), which could potentially donate H or D to the H atom. (Side reactions which consume H atoms but do not produce H_2 or HD do not interfere in the competitive scheme.)

Table I presents data on relative k_H values both for substituted toluenes and for substituted benzenes, and Figure 1 shows typical plots of the data. The benzenes all have essentially the same reactivity, 0.028 ± 0.002 (excluding *tert*-butylbenzene, which has reactive aliphatic hydrogens). The toluenes also all have about the same reactivity per methyl group, 0.056 ± 0.006. (After correction for the *tert*-butyl moiety, the reactivity of *p-tert*-butyltoluene is the same as that of the other toluenes.)

The high reactivity of the benzenes indicates that a substantial portion of the H_2 resulting from reaction with toluenes comes from abstraction of ring hydrogens. There are several possible mechanisms by which this H_2 could arise: (1) direct abstraction of phenyl hydrogens; (2) abstraction of hydrogen from cyclohexadienyl radicals produced by radical addition to the ring; (3) hydrogen abstraction from nonradical products; and (4) an H_2-producing reaction between BUP and a cyclohexadienyl radical.

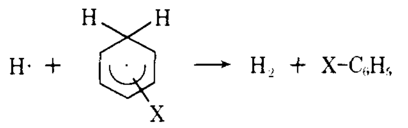
Mechanism 1. Direct hydrogen abstraction of ring hydrogens (eq 7) does not seem likely to compete with abstraction of side chain hydrogens (eq 8); reaction 7 is endothermic[16] by approximately 8 kcal/mol, whereas reaction 8 is exothermic by 19 kcal/mol. Thus, k_7 and k_8 would be expected to differ by several orders of magnitude

$$H\cdot + ArH \xrightarrow{k_7} H_2 + Ar\cdot \quad (7)$$

$$H\cdot + ArCH_3 \xrightarrow{k_8} H_2 + ArCH_2\cdot \quad (8)$$

whereas the data show benzene to be 44% as reactive as toluene. Although direct abstraction of phenyl hydrogens has been postulated in some cases,[17,18b] isotope effect and product studies[18] indicate that direct abstraction probably is not important under the conditions used in our experiments.

Mechanism 2. Reaction of H atoms with cyclohexadienyl radicals (eq 9) could be important.



(9)

For this to occur, the cyclohexadienyl radical concentration would have to be on the order of 10^{-4} *M*. (This calculation assumes a value for k_H of $10^7\ M^{-1}\ \text{sec}^{-1}$ for toluene[13c,18c] and a value of about $10^{10}\ M^{-1}\ \text{sec}^{-1}$, the diffusion-control limit,[19a] for hydrogen abstraction from a cyclohexadienyl radical by the H atom.) Radical concentrations are generally lower than this value;[4,19b] however, resonance delocaliza-

Table I. Relative Reactivities of Aromatic QH Compounds toward the Hydrogen Atom at 35°

QH	[QH]/ [*tert*-BuSD]	$[H_2]/[HD]$	Relative reactivity[a]
Benzene	0	0.142	0.025
	2.11	0.194	
	4.66	0.239	
	7.32	0.330	
	10.2	0.393	
	13.2	0.428	
	15.8	0.522	
Toluene	2.64	0.280	0.057
	5.80	0.483	
	8.00	0.594	
	10.1	0.738	
	13.3	0.881	
	16.5	1.10	
m-Xylene	2.18	0.342	0.098
	4.69	0.601	
	7.41	0.855	
	11.0	1.24	
	15.5	1.66	
p-Xylene	2.63	0.381	0.097
	5.62	0.674	
	8.93	0.997	
	12.4	1.35	
	16.2	1.69	
tert-Butylbenzene	2.48	0.272	0.056
	5.73	0.448	
	9.96	0.730	
	13.7	0.887	
	16.4	1.05	
p-tert-Butyltoluene	3.21	0.398	0.089
	6.18	0.713	
	9.30	0.966	
	12.5	1.23	
	16.1	1.62	
Bromobenzene	4.55	0.250	0.029
	7.84	0.386	
	11.4	0.482	
	15.8	0.591	
m-Bromotoluene	2.89	0.286	0.057
	6.10	0.493	
	10.4	0.681	
	13.1	0.944	
	16.7	1.14	
Chlorobenzene	3.03	0.220	0.030
	6.69	0.361	
	10.1	0.433	
	13.2	0.526	
	16.5	0.638	
m-Chlorotoluene	3.16	0.328	0.062
	6.39	0.540	
	8.51	0.662	
	11.7	0.855	
	16.0	1.19	
p-Chlorotoluene	2.22	0.263	0.059
	5.40	0.458	
	8.75	0.626	
	12.4	0.872	
	15.9	1.08	
Fluorobenzene	3.29	0.221	0.028
	7.64	0.363	
	10.0	0.417	
	12.1	0.503	
	16.4	0.585	
m-Fluorotoluene	2.70	0.278	0.056
	5.84	0.482	
	9.61	0.654	
	12.7	0.839	
	16.6	1.11	

[a] Slope of a plot of $[H_2]/[HD]$ vs. [QH]/[RSD]; see text.

tion may stabilize this radical sufficiently to allow it to reach 10^{-4} *M*. The stabilization energy of the cyclohexadienyl radical is about 25 kcal/mol.[20]

Mechanism 3. A number of nonradical products such as cyclohexadienes and cyclohexadienyl dimers are produced during reaction. Since BUP initially is present at only 10^{-2} *M*, the maximum possible concentration of these products is less than 10^{-2} *M*. In order to compete with abstraction of benzylic hydrogens, the k_H values for these compounds would have to be more than 10^3 times larger than k_H for toluene; however, the observed values are less than this by at least an order of magnitude.[18b,21]

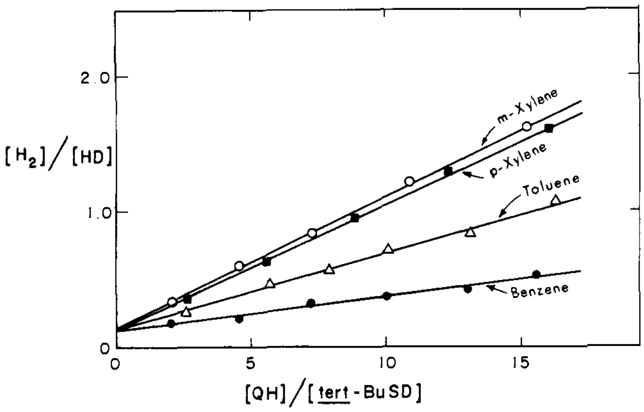
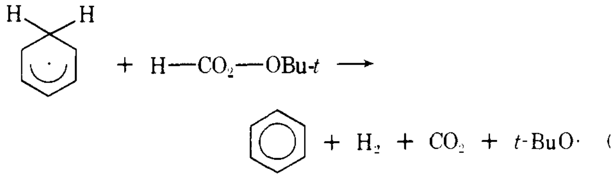


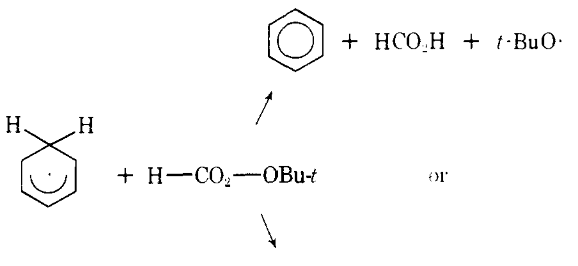
Figure 1. Plots of eq 6 for benzene, toluene, and *m*- and *p*-xylene.

Mechanism 4. A possible H_2-producing reaction of cyclohexadienyl radicals with BUP is shown in eq 10. An induced decomposition in which a radical donates a hydrogen atom to the O–O bond of a peroxide has been reported in several systems[22] and provides a partial analogy for eq 10.



(10)

While eq 10 cannot be entirely eliminated as a possibility, it does not appear likely for two reasons. Firstly, the literature analogies suggest that attack would occur at a peroxidic oxygen (eq 11a or 11b) which would not lead to H_2 formation.



(11a)

(11b)

Secondly, the importance of eq 10 was tested by varying the concentration of BUP at a fixed value of [PhH]/[RSD] and monitoring the $[H_2]/[HD]$ ratio after irradiation. The latter ratio remained constant over a fivefold decrease in BUP concentration, from 0.02 to 0.004 *M*, an indication that reaction 10 is not important in this system. This control experiment also indicates that attack on BUP (or its decomposition products) by H atoms is not the source of the reactivity of the benzenes.

Thus, of the possible sources of H_2 from substituted benzenes, the second mechanism, hydrogen atom attack on a cyclohexadienyl radical (eq 9), seems to be the most reasonable. Radical-radical interactions of this type are common in systems involving aromatic substrates; e.g., such reac-

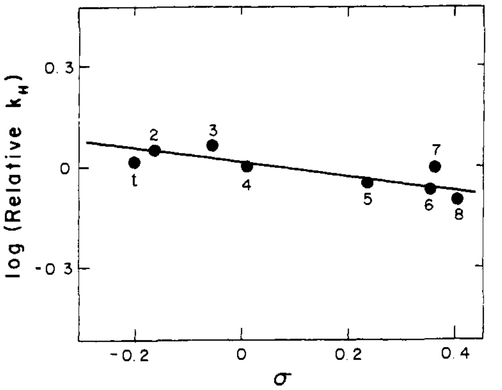


Figure 2. A Hammett plot of log relative k_H values (eq 3) for the hydrogen atom vs. σ substituent constants. The code is as follows: 1, *p*-*tert*-butyltoluene; 2, *p*-xylene; 3, *m*-xylene; 4, toluene; 5, *p*-chlorotoluene; 6, *m*-fluorotoluene; 7, *m*-chlorotoluene; 8, *m*-bromotoluene. The values for the xylenes were statistically corrected by a factor of 2.

tions are responsible for product formation in homolytic aromatic substitution reactions.[23]

Regardless of the mechanism by which the aromatic hydrogens are abstracted, it is clear that ring substituents have essentially no effect on the reactivity of the hydrogens in the methyl groups of the toluenes. One explanation might be that the rate constant for abstraction of a benzylic hydrogen by the quite reactive hydrogen atom is very near the diffusion-controlled limit. If this were the case, substituents might not be expected to affect the rate.[24] Sauer and Ward[18c] have calculated that, for toluene, the rate of abstraction from the side chain by the H atom is an order of magnitude lower than the rate of ring addition. Since the rate constant for addition is about 10^9 M^{-1} sec^{-1},[13b,c,18c,21b] the rate constant for abstraction is well below the diffusion-controlled limit of $\simeq 10^{10}$ M^{-1} sec^{-1}.[19a] In fact, it is possible to calculate the approximate magnitude of k_H from our data. Use of *t*-BuSD as RSD in our system gives values of k_H/k_2 of about 0.1. The value of k_2 is 10^8–10^9 M^{-1} sec^{-1},[25] and k_H again is obtained as being less than 10^8 M^{-1} sec^{-1}. In this calculation, it is assumed that the H atoms are thermolyzed before reaction. Although "hot" H atoms are known,[26a] this excited species should not be important in our system.[26b] Thus, we conclude that the relative values of k_H reported here are not merely diffusion-controlled values, and that these data can be analyzed by the Hammett equation.

It is clear from an inspection of the raw data in Table I that the ρ value for abstraction of benzylic hydrogens from toluenes by the H atom is approximately zero. The similarity in reactivities of substituted benzenes and toluenes makes it very difficult to analyze the data to yield a ρ value of great precision. (Fortunately it is seldom if ever necessary to know ρ to more than one significant figure.[5f]) Nevertheless, one method of treating our data appears worthy of report since it indicates that, to the extent that the data can be subjected to algebraic analysis, the conclusion that $\rho \simeq 0$ is supported.

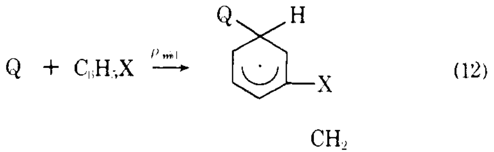
The analysis involves subtraction of the reactivity of C_6H_5–X from that of the analogous toluene, CH_3–C_6H_4X. The ρ value obtained by this treatment (see Figure 2) is −0.14 ± 0.04. In view of the small value of ρ, the standard deviation of ρ is excellent.[27] However, it is doubtful if ρ for this reaction can be known with an accuracy greater than −0.1 ± 0.1.

Table II. Comparison of ρ Values for Hydrogen Abstraction from Ring-Substituted Toluenes and for Addition to Substituted Benzenes[a]

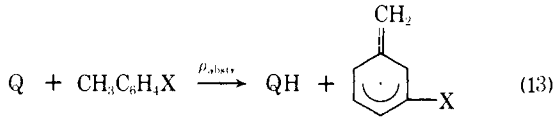
	H abstraction from toluenes		Addition to benzenes	
Radical	ρ	Temp, °C	ρ	Temp, °C
Hydrogen atom	−0.1[b]	35	−0.3[c]	40
Phenyl	−0.3[d,e]	60	0.1[f]	80
			0.0[g]	g
			0.1[h]	20
p-$CH_3C_6H_4$·	−0.1[d]	60	0.0[h]	20
p-XC_6H_4·	−0.3[d,i]	60	−0.3[h,j]	20
p-$NO_2C_6H_4$·	−0.6[d]	60	−0.7[h]	20
Cyclopropyl	0.2[k,l]	100	0.1[k]	100
Cyclohexyl			1.1[m]	90
3-Heptyl	0.7[n]	80		

[a] This correlation is based on meta substituents, except for a few cases in which an insufficient number of meta derivatives were studied. In those instances the ρ values are based on both meta- and para-substituted compounds. [b] This work. [c] W. A. Pryor, T. H. Lin, J. P. Stanley, and R. W. Henderson, *J. Am. Chem. Soc.*, **95**, 6993 (1973). [d] W. A. Pryor, J. T. Echols, and K. Smith, *ibid.*, 88, 1189 (1966). [e] R. F. Bridger and G. A. Russell, *ibid.*, 85, 3754 (1963). [f] Data summarized by G. H. Williams, *Chem. Soc., Spec. Publ.*, No. 24, 36 (1970). [g] G. Martelli, P. Spagnolo, and M. Tiecco, *J. Chem. Soc. B*, 1413 (1970) (temperature not given). [h] R. Ito, T. Magita, N. Morikawa, and O. Simamura, *Tetrahedron*, 21, 955 (1965). [i] X is bromine. [j] X is chlorine. [k] T. Shono and I. Nishiguchi, *Tetrahedron*, **30**, 2183 (1974). [l] Value for 2-phenylcyclopropyl radical. [m] J. R. Shelton and C. W. Uzelmeier, *Intra-Sci. Chem. Rep.*, 3, 293 (1969). [n] R. W. Henderson, *J. Am. Chem. Soc.*, 97, 213 (1975).

Comparison of ρ Values for Reactions with Toluenes and Benzenes. Recently we suggested[5f] that the ρ value for addition of a given radical to substituted benzenes (eq 12, meta addition shown) is very similar to the ρ value for hydrogen abstraction by that radical from ring-substituted toluenes (eq 13). Table II presents all the data now available for radicals for which both addition to benzenes and hydrogen abstraction from toluenes have been studied. The last three radicals are particularly interesting; cyclohexyl, for which $\rho_{add} = 1.1$, probably has a similar reactivity to the 3-heptyl radical, for which $\rho_{abstr} = 0.7$. The cyclopropyl radical has much smaller values of both ρ_{add} and ρ_{abstr}, probably because it more closely resembles a vinylic radical than it does a secondary alkyl radical.[28]



(12)



(13)

It should be noted that the correspondence in Table II is only approximate. Many of the pairs of ρ values were not determined at the same temperature or in the same solvent, and these factors certainly would affect the magnitude of ρ. Nevertheless, there is a rather surprising correspondence of the pairs of ρ values. This relationship probably has not previously been noted because Hammett equation correlations are most often applied to ionic reactions, and the same ion would not be expected both to attack a side-chain benzylic position and add to a benzene ring.

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References and Notes

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