

Supplementary Material Available: two tables (Collisional Activation spectra of the Molecular Ions of Linear Octenes and Label Retention of C₃-Fragment Ions from **1a** as Function of the Decomposition Time (2 pp). Ordering information is given on any current masthead page.

References and Notes

- Isomerization of Hydrocarbons. 9. For part 8 see K. Levsen, H. Heimbach, G. J. Shaw, and G. W. A. Milne, *Org. Mass Spectrom.*, in press.
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- (a) Note that the fragmentation characteristic for the unrearranged ion is partially obscured by isomerization after collision. (b) The close correspondence of the CA spectra from molecular ions produced by EI and FI is remarkable as both sets of spectra were obtained not only with different ion sources, but with different instruments.
- m/e* 29 is the most abundant fragment in the spectrum. As this ion is partially formed by field dissociation at the shortest time,^{15a} it has been omitted from all spectra.
- The remaining differences in the relative abundances are both due to the limited reproducibility of the FI data (see Experimental Section) and differences in the internal energy which may be more pronounced under FI than under EI conditions due to the different polarization of the molecule in the high electric field prior to ionization.
- The terminal hydrogens are preferentially retained.
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- The data from **1c** were corrected for 17% singly labeled material assuming fragmentation from both ends of the molecular ion with equal probability and no H/D exchange at C-1.
- Unspecific fragmentation starts at a shorter time than for C₅ and C₆ ions, which may result from the fact that these ions are partially formed by a secondary decomposition. It has been shown above that complete randomization of all carbon atoms occurs *prior* to such secondary decomposition.
- Some H/D exchange at C-1 occurs at longer times and seems to be especially pronounced *prior* to [C₅H₁₀]⁺ formation (*m/e* 70) where at 1 × 10⁻⁹ s loss of 34% C₃H₄D₂ and 54% C₃H₆, but also 12% C₃H₅D, from **1c** is observed.
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- Part of the fragments the abundance of which shows pronounced differences is also formed by unimolecular decomposition and, hence, may not only reflect the ion structure, but also differences in the internal energy as discussed previously.¹⁴ The metastable ion spectra reported in Table I demonstrate, however, that the internal energy distribution must be identical or very similar for octene molecular ions. Hence the observed differences in the CA spectra exclusively reflect differences in structure.
- However, one of the referees pointed out that the observed differences in the CA spectra which reflect differences in rates need not necessarily result from a higher energy barrier in the isomerization between 1-octene and the other isomers, but may be due to different transition state geometries (entropy-like factors) or forbidden orbital symmetries for the rearrangement.
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- The process with charge migration (*m/e* 71) is negligible in 1-octene.

Polar Effects in Radical Reactions. 7. Positive ρ Values for the Reactions of Isopropyl and *tert*-Butyl Radicals with Substituted Toluenes¹

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Abstract: Hammett equation correlations are reported for the reaction of isopropyl radicals, generated by photolysis of azoisopropane, and *tert*-butyl radicals, generated by photolysis of either *t*-BuN=NBU-*t* or *tert*-butyl peroxyphthalate, with a series of substituted toluenes at 30 °C. Rates of hydrogen abstraction from the toluenes were measured relative to deuterium abstraction from either benzenethiol-*d* or 2-methyl-2-propanethiol-*d*. A plot of log (relative rate constant) vs. σ constants gives for the isopropyl radical, $\rho = 0.8 \pm 0.1$, $s_y = 0.06$ (21 points); and for the *tert*-butyl radical, $\rho = 1.0 \pm 0.1$, $s_y = 0.04$ (23 points). The traditional "polar effects" interpretation of a Hammett equation correlation of an atom abstraction reaction and Zavitsas' recently proposed alternative explanation are discussed. The positive ρ values observed for the systems studied here prove the reality of substituent effects on polar resonance structures in the transition state (SETS). However, we believe that substituent effects on the bond dissociation energy (BDE) of the benzylic C-H bond are also important in these systems. Therefore, we suggest, in contrast to what is rather common practice in the literature, that *both* SETS *and* effects of substituents on BDE should be considered in explaining the results of Hammett equation correlations of these and other radical reactions.

The first observations of the sensitivity of radical reactions to polar substituents were published in 1945–1947. Mayo,³ Price,⁴ Bartlett,⁵ and their co-workers postulated that dipolar resonance structures cause the transition states for certain

radical reactions to be more stable than expected and that these polar structures markedly influence the reactivity patterns observed. In subsequent years, polar effects have been used to rationalize the tendency toward cross-termination reactions,

Table I. ρ Values for Hydrogen Abstraction from Substituted Toluenes by Alkyl Radicals Predicted by the Bond Dissociation Energy (BDE) and Polar Effects Arguments

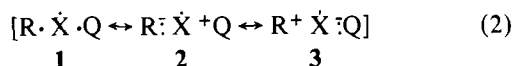
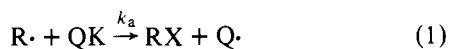
| Radical | BDE ^a | Polar effects |
|-----------------|------------------|--------------------------------|
| Methyl | -0.6 | A near zero value ^b |
| Primary alkyl | -1.0 | Small positive value |
| Secondary alkyl | -1.2 | Positive value |
| Tertiary alkyl | -1.4 | Larger positive value |

^a A. A. Zavitsas and J. A. Pinto, *J. Am. Chem. Soc.*, **94**, 7390 (1972), especially Figure 1. ^b W. A. Pryor, U. Tonellato, D. L. Fuller, and S. Jumonville, *J. Org. Chem.*, **34**, 2018 (1969); W. A. Pryor, D. L. Fuller, and J. P. Stanley, *J. Am. Chem. Soc.*, **94**, 1632 (1972).

certain effects in autoxidations, and experimental results of a variety of other radical reactions.⁶⁻¹¹

Probably the clearest and simplest indication of the polar substituent effect on radical reactions comes from studies of Hammett $\sigma\rho$ equation correlations. This equation, which was developed to allow quantitative study of polar substituent effects on ionic reactions,¹²⁻¹⁴ was, in fact, not anticipated¹² to be useful in correlating radical reactions. In fact, however, the Hammett equation has been found useful in studies of many types of radical reactions, including atom transfers,^{6-11,15,16} additions,^{15,17} copolymerizations,⁶ initiator decompositions,^{6,18} disproportionations,¹⁹ and β -scissions.²⁰ We believe that the clearest evidence for the importance of polar effects on radical reactions can be adduced from studies of the application of the Hammett equation to atom abstraction reactions,^{15,16} and we have examined a series of atom-transfer reactions in a variety of systems for this reason.¹

Substituent Effects on Transition States (SETS). In the earliest studies of polar effects on radical reactions, explicit recognition was made only of the effect of the polar substituent in stabilizing the transition state; effects on bond dissociation energies (BDE), which were thought to be smaller,³⁻⁵ were ignored.²¹ In harmony with this tendency, a summary of the first Hammett treatments of atom-abstraction reactions, published by Russell in 1958,²² also only explicitly dealt with polar effects on transition states. According to this approach, which has now become common, the transition state for an atom abstraction such as shown in eq 1 is described by the three resonance structures shown in eq 2.

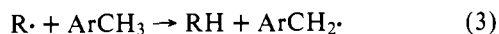


The relative importance of these three structures depends on the nature of R \cdot , X \cdot , and Q \cdot .²³ If Q⁺ is more stable than R⁺ and R⁻ more stable than Q⁻, then **2** makes a more important contribution to the stability of the transition state than does **3**, and a negative Hammett ρ value would be expected. Since negative ρ values were, in fact, observed for hydrogen abstractions from substituted toluenes by radicals that were thought to be electrophilic such as CH₃ \cdot , C₆H₅ \cdot , Br \cdot , and Cl \cdot ,^{15,16} this polar effects concept gained wide acceptance, as evidenced by its use in both monographs⁶⁻¹⁰ and elementary textbooks.²⁴

According to this polar effects argument, the importance of the contribution of resonance structure **2** to the transition state should increase with the electrophilicity of R \cdot . Because the amount of partial positive charge on Q \cdot grows as R \cdot becomes more electronegative, the influence of substituents on this charge and, therefore, on the energy of the transition states (eq 2) also increases. Hence, the magnitude of ρ would be expected to parallel the electron affinity of R \cdot . This trend is

generally observed; the radicals are listed above in the order of increasing electron affinity,²⁵ and the absolute value of ρ increases in the following manner: CH₃ \cdot \approx C₆H₅ \cdot < Cl \cdot < Br \cdot .^{15,16} The discrepancy in these two series for Cl \cdot and Br \cdot has been rationalized in terms of a dependency of ρ values on the heat of the reaction.^{22,26}

Substituent Effects on Bond Dissociation Energy. In 1972, Zavitsas and Pinto challenged this polar effects concept and proposed that the reactivity of toluenes parallels their benzylic C-H bond dissociation energies (BDE) "without postulating charge separation in the transition state".²⁷ In other words, Zavitsas, taking note of the fact that only negative ρ values were then known for reactions of the type



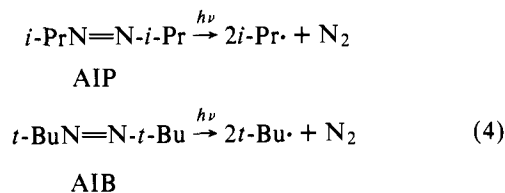
suggested that electron-donating substituents weaken benzylic C-H bonds and electron-withdrawing substituents strengthen these bonds, and that all reactions like eq 3 have negative ρ values purely because of substituent effects on BDE. The magnitude of ρ , according to Zavitsas, only "measures the sensitivity of the rate of hydrogen abstraction to BDE differences in the substituted toluenes".^{27a} Zavitsas also proposed that this sensitivity (and, therefore, the absolute value of ρ) decreases with increasing exothermicity of the abstraction reaction, as would be expected from the Hammond postulate.^{7,22,26}

From this substituent effect on the bond dissociation energies of toluenes and the absence of significant polar substituent effects on the transition state, Zavitsas concluded that "positive ρ values would be impossible for abstractions from toluenes".^{27b} All the ρ values for reactions with toluenes known at the time Zavitsas wrote were negative and, thus, could be rationalized either by Zavitsas' BDE argument or (since only electrophilic radicals had been studied) by the traditional polar effects arguments. Zavitsas noted that a Hammett study of alkyl radicals would provide the data to distinguish between these two approaches. According to the polar effects argument, a ρ of about zero is predicted for hydrogen abstraction from substituted toluenes by methyl radicals; for *tert*-butyl radicals, ρ should be positive. Table I lists ρ values predicted for alkyl radicals by these two opposing arguments.

We have recently reported in preliminary communications the ρ values for reactions of *tert*-butyl^{1a} and undecyl^{1f} radicals with substituted toluenes. Similar studies have been reported by Henderson for the undecyl²⁸ and 1-ethylpentyl²⁹ radicals. Since all these ρ values are positive, it is clear that Zavitsas' ideas must be modified. In this paper we report the full details of our work with the *tert*-butyl radical and also complementary data on the isopropyl radical, and we suggest a detailed rationalization of all the data reported. We believe that the effects of substituents on *both* BDEs and on transition state stabilities should be considered in rationalizing Hammett studies of radical reactions.¹

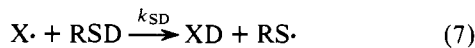
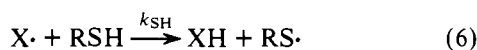
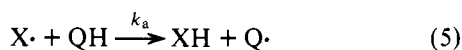
Results

Kinetic Analysis. Isopropyl (*i*-Pr \cdot) and *tert*-butyl (*t*-Bu \cdot) radicals were generated by the photolysis of the corresponding initiator, azoisopropane (AIP) or "azoisobutane", *t*-C₄H₉N=N-C₄H₉-*t* (AIB), in a solution of a substituted toluene and a deuterated thiol.



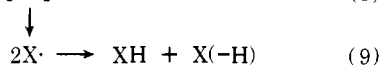
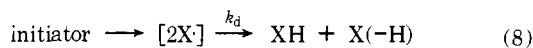
After escaping from the cage, the alkyl radical X \cdot (X = *i*-Pr-

or *t*-Bu·) either may abstract a hydrogen atom from the toluene, QH (eq 5), or from RSH present as an impurity in the deuterated thiol (eq 6) to produce XH (propane or isobutane), or abstract a deuterium atom from the deuterated thiol, RSD (eq 7), to give XD (propane-2-*d* or isobutane-*d*).

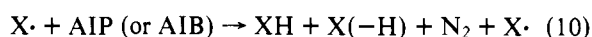


Values of k_a (eq 5) relative to k_{SD} for deuterium abstraction from the thiol (eq 7) were determined by mass spectroscopy from the ratio of peaks corresponding to protonated and deuterated products. For propane (*i*-PrH) and propane-2-*d* (*i*-PrD), these mass to charge ratios (*m/e*) are those for the parent ions, 44 and 45. However, for isobutane (*t*-BuH) and isobutane-*d* (*t*-BuD), fragment peaks at *m/e* 43 and 44 were used. (These are the largest peaks in the spectra. The mass spectral cracking patterns and correction factors are discussed in the Experimental Section.) Assuming that the usual steady-state assumptions are met and that hydrogen abstraction from toluene is the only significant reaction yielding *i*-PrH or *t*-BuH, then plots of the *m/e* 44 to 45 or *m/e* 43 to 44 peaks vs. $[QH]/[RSD]$ should give a straight line with a slope equal to k_a/k_{SD} (see below).

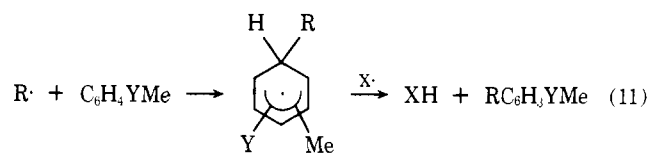
However, the protonated alkane, XH, may also be produced by disproportionation of X· both in the cage (eq 8) and in free solution (eq 9). We will deal with this problem below. Although



induced decomposition of AIP or AIB by the corresponding X· is, in theory, another possible source of XH, this process evidently does not occur under our conditions. Neither 2-cyano-2-propyl nor *tert*-butyl radicals, produced by thermolysis of azoisobutyronitrile or *tert*-butyl peroxyphthalate at 80 °C in a solution of AIP or AIB in toluene, causes the concentration of AIP or AIB to decrease.



Addition of a radical to an aromatic ring to give a cyclohexadienyl radical followed by hydrogen abstraction by a X· could also give XH (eq 11). However, since neither cymene



($\text{RC}_6\text{H}_3\text{YMe}$, R = *i*-Pr; Y = H) nor *tert*-butyltoluene (R = *t*-Bu; Y = H) could be detected by VPC in a reacted solution of 0.5 M AIP or AIB in toluene and benzenethiol ($[QH]/[\text{PhSD}] = 19.6$), reaction 11 can be neglected. The insignificance of reaction 11 is also indicated by $k_a/k_{SD} < 1 \times 10^{-4}$ for benzene as a QH.

The ratios of rates of formation of XH and XD are given by

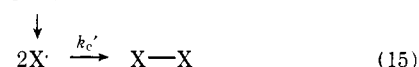
$$\frac{d[XH]}{d[XD]} = \frac{k_d f_c [\text{initiator}] + k_a [X\cdot] [QH] + k_{SH} [X\cdot] [RSH] + k_d' [X\cdot]^2}{k_{SD} [X\cdot] [RSD]} \quad (12)$$

where f_c is the fraction of the radicals that react in the cage. Since RSH is a fixed impurity in RSD, $k_{SH}[RSH]/k_{SD}[RSD]$ is independent of the QH/RSD ratio. Therefore, the relative yields of XH and XD are given by

$$\frac{[XH]}{[XD]} = \frac{k_a [QH]}{k_{SD} [RSD]} + \frac{k_{SH} [RSH]}{k_{SD} [RSD]} + \frac{k_d f_c [\text{initiator}]}{k_{SD} [X\cdot] [RSD]} + \frac{k_d' [X\cdot]}{k_{SD} [RSD]} \quad (13)$$

A plot of $[XH]/[XD]$ vs. $[QH]/[RSD]$ will be a straight line with a slope of k_a/k_{SD} and intercept $k_{SH}[RSH]/k_{SD}[RSD]$ if the last two terms on the right in eq 13 are insignificant relative to the first two terms.

The amount of XH formed by disproportionation (eq 8 and 9) may be monitored by observing the yield of dimer, 2,3-dimethylbutane or 2,2,3,3-tetramethylbutane, produced by the combination reactions (cage, eq 14, and free solution, eq 15) because the partitioning of X· between these two processes is known.³⁰



For example, using both 1:1 and 23:1 molar ratios of *p*-chlorotoluene to PhSD and 0.5 M AIP, the same yield of 2,3-dimethylbutane, 2×10^{-3} M, was obtained; with both 1:1 and 30:1 molar ratios of *p*-fluorotoluene to PhSD, and 0.1 M AIB, the same yield of 2,2,3,3-tetramethylbutane, 1.2×10^{-3} M, was obtained. Since the amount of these combination products remained small and constant as the concentration of radical scavengers (RSD and QH) was varied, only negligible combination and disproportionation of X· radicals occurs in the cage and virtually none occurs in free solution. This conclusion is not unexpected; on observing that the dimer yield from thermolysis of AIBN was constant for a similar range of thiol concentrations, Hammond et al. concluded that only cage combination was occurring.³¹ Therefore, the free-solution disproportionation term of eq 13 is negligible.

The yield of dimer can be used to estimate the extent of cage disproportionation since free-solution combination and disproportionation are not important. After correcting for the ratio of disproportionation to combination for the isopropyl ($\Delta \approx 1$)^{30,32} or *tert*-butyl ($\Delta \approx 5$)^{30,33} radical, the cage yield of XH is found to be only about 5% of the total XH formed (about 0.1 M). Also, if cage disproportionation (eq 8) were important, the ratio of the yields of XH to XD should increase with increasing initiator concentration (see eq 13). However, this ratio is the same within experimental error for AIP concentrations ranging from 0.1 to 0.5 M in toluene/*t*-BuSD and for AIB concentrations of 0.05 to 0.3 M in toluene/PhSD. This consistency combined with the negligible cage yield of XH reported above indicates that the cage disproportionation term in eq 13, $k_d f_c [\text{initiator}]/k_{SD} [RSD]$, must not be significant.

Therefore, eq 13 relating the yields of alkane and deuterated alkane to $[QH]/[RSD]$ can be simplified to

$$\frac{[XH]}{[XD]} = \frac{k_a [QH]}{k_{SD} [RSD]} + \frac{k_{SH} [RSH]}{k_{SD} [RSD]} \quad (16)$$

Since the last term in this equation is a constant, k_a/k_{SD} for each QH can be obtained from the slope of a plot of $[XH]/[XD]$ vs. $[QH]/[RSD]$.

In an effort to provide an entirely independent system for generating and studying the *tert*-butyl radical, both the photolysis and thermolysis of *tert*-butyl peroxyphthalate (BPP) were examined. Photolysis of this initiator proved to be a cleaner

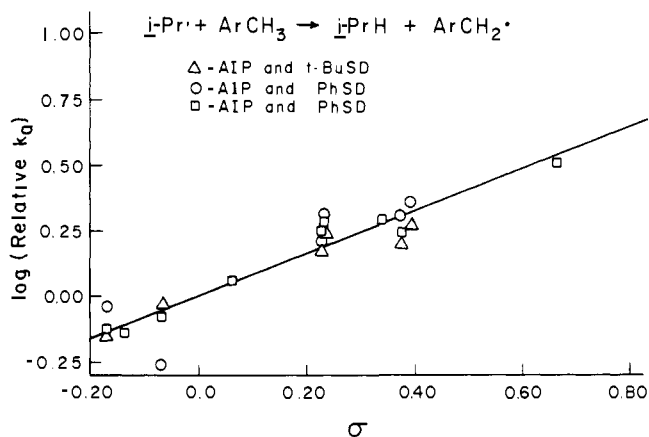


Figure 1. A Hammett equation plot of \log (relative k_a) values for hydrogen abstraction from substituted toluenes by isopropyl radicals at 30 °C vs. σ . For each system, $\log(k_a/k_a^0)$ is plotted, where $\log(k_a^0)$ is the intercept of the least-squares line for that system: system I (Δ) is azoisobutane (AIP) and 2-methyl-2-propanethiol-*d* (*t*-BuSD); system II (\circ) is AIP and benzenethiol-*d* (PhSD) before the filament current of the mass spectrometer was adjusted; system III (\square) is AIP and PhSD after the filament current was adjusted. The least-squares treatment gives $\rho = 0.8 \pm 0.1$; $s_y = 0.06$; 21 points.

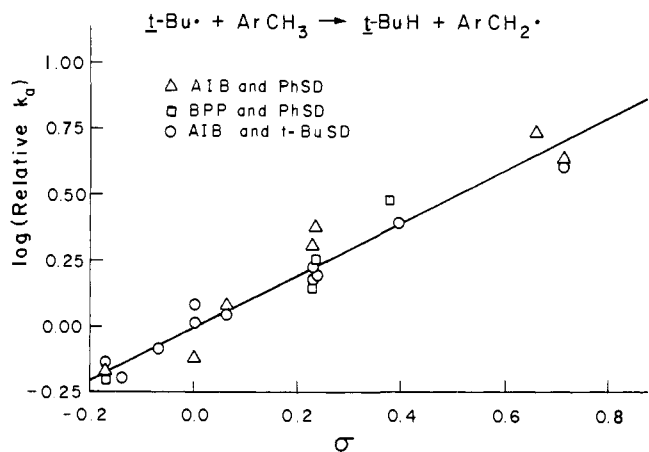
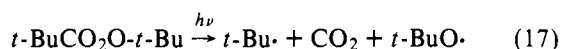


Figure 2. A Hammett equation plot of \log (relative k_a) for hydrogen abstraction from substituted toluenes by *tert*-butyl radicals at 30 °C vs. σ . For each system, $\log(k_a/k_a^0)$ is plotted where $\log(k_a^0)$ is the intercept of the least-squares line for that system: system I (Δ) is azoisobutane (AIB) and benzenethiol-*d* (PhSD); system II (\square) is *tert*-butyl peroxyvalate (BPP) and PhSD; system III (\circ) is AIB and 2-methyl-2-propanethiol-*d*. The least-squares treatment gives $\rho = 1.0 \pm 0.1$; $s_y = 0.04$; 23 points.

source of *t*-Bu \cdot than thermolysis. Since neither abstraction



of chlorine from CCl_4 nor of deuterium from toluene-*d*₈ were useful standard reactions, the semi-independent system of peroxy ester photolysis in toluene/thiophenol-*d* was used to obtain relative reactivities, k_a/k_{SD} (eq 5 and 7). Only the reactions indicated by eq 5–7 are likely in this system because BPP does not give a cage yield of isobutane,³⁴ and, as in the AIB/thiol system, the concentrations of the radical scavengers QH and RSH are sufficiently high to prevent any free-solution disproportionation of *t*-Bu \cdot . Therefore, eq 16 relating the yields of isobutane and isobutane-*d* to $[\text{QH}]/[\text{RSD}]$ is valid for both the AIB and BPP systems.

Data Treatment. The ratio of rate constants for hydrogen abstraction from a substituted toluene (QH) and deuterium abstraction from a deuterated thiol (RSD), k_a/k_{SD} , was obtained from the slope of the least-squares line of $[\text{XH}]/[\text{XD}]$

Table II. Relative Rate Constants (k_a^X/k_a^0) for Hydrogen Abstraction from Substituted Toluenes (XQH) by the Isopropyl Radical at 30 °C^a

| X | System ^b | Log (k_a^X/k_a^0) ^c | |
|---------------------|---------------------|------------------------------------|-------|
| <i>p</i> -Me | I | -0.14 | |
| | II | -0.04 | |
| | III | -0.14 | |
| 3,5-Me ₂ | III | -0.14 | |
| | <i>m</i> -Me | I | -0.06 |
| | | II | -0.26 |
| III | | -0.08 | |
| <i>p</i> -F | III | 0.06 | |
| | <i>p</i> -Cl | I | 0.17 |
| | | II | 0.21 |
| III | | 0.24 | |
| <i>p</i> -Br | I | 0.24 | |
| | II | 0.30 | |
| | III | 0.29 | |
| <i>m</i> -F | III | 0.29 | |
| | <i>m</i> -Cl | I | 0.20 |
| | | II | 0.31 |
| III | | 0.24 | |
| <i>m</i> -Br | I | 0.27 | |
| | II | 0.35 | |
| | III | 0.51 | |
| <i>p</i> -CN | III | 0.51 | |

^a Rate constants (k_a^X) were measured relative to the rate constant for abstraction of deuterium from a deuterated thiol (k_{SD}), 2-methyl-2-propanethiol-*d*, *t*-BuSD (system I^b), or benzenethiol-*d*, PhSD (systems II and III^b). ^b System I is azoisobutane (AIP) and *t*-BuSD; system II is AIP and PhSD before the filament current of the mass spectrometer was adjusted; system III is AIP and PhSD after the filament current was adjusted. ^c For each system, the intercept of the least-squares line of the Hammett equation for that system, $\log(k_a^0)$, was subtracted from the logarithm of the relative rate constants to give $\log(k_a^X/k_a^0)$.

vs. $[\text{QH}]/[\text{RSD}]$ for $X = i\text{-Pr}$ and $X = t\text{-Bu}$. The values of k_a/k_{SD} for the toluenes studied in each system of radical initiator and thiol are given in tables which appear in the microfilm edition.

The k_a values from the various systems cannot be directly combined to produce a single Hammett equation for each radical because they were measured relative to k_{SD} 's for different thiols. Therefore, a Hammett equation was calculated by the method of least squares from $\log(k_a/k_{SD})$ and σ constants for each radical and each system. The "overall" Hammett equation was constructed by subtracting from the $\log(k_a/k_{SD})$ values for each system the intercept of its least-squares lines³⁵ and combining the resulting data. The equation obtained by the least-squares treatment of these points in the Hammett equation format is for the isopropyl radical (Table II and Figure 1), $\rho = 0.8 \pm 0.1$; $s_y = 0.06$ (21 points);³⁶ and for the *tert*-butyl radical (Table III and Figure 2), $\rho = 1.0 \pm 0.1$; $s_y = 0.04$ (23 points).^{1a,36}

Discussion

The positive ρ values which we obtained for the isopropyl and *tert*-butyl radicals are listed along with ρ values for other alkyl radicals in Table IV. On the basis of these positive ρ values and their increase in magnitude with decreasing electrophilicity of the radical, the importance of substituent effects in the transition state (SETS) is established.^{38a} However, it is no more likely that substituents would exert their influence *only* on transition states (the traditional polar effects argument) than it is that they would only affect bond strengths as Zavitsas has argued.

We recently suggested the following hypothesis:^{1b,f} Hammett correlations of reactions like eq 3 can be rationalized as

Table III. Relative Rate Constants (k_a^X/k_a^0) for Hydrogen Abstraction from Substituted Toluenes (XQH) by the *tert*-Butyl Radical at 30 °C^a

| X | System ^b | Log (k_a^X/k_a^0) ^c |
|---------------------------|---------------------|------------------------------------|
| <i>p</i> -Me | I | -0.17 |
| | II | -0.16 |
| | III | -0.16 |
| 3,5-Me ₂ | III | -0.20 |
| <i>m</i> -Me | III | -0.09 |
| | I | -0.13 |
| H | I | 0.01 |
| | III | 0.08 |
| | III | 0.08 |
| <i>p</i> -F | I | 0.05 |
| | III | 0.04 |
| <i>p</i> -Cl | I | 0.31 |
| | II | 0.17 |
| | III | 0.18 |
| | III | 0.17 |
| <i>p</i> -Br | I | 0.38 |
| | II | 0.21 |
| | III | 0.17 |
| <i>m</i> -Cl | II | 0.48 |
| <i>m</i> -Br | III | 0.39 |
| | III | 0.39 |
| <i>p</i> -CN | I | 0.71 |
| <i>m</i> -NO ₂ | I | 0.63 |
| | III | 0.61 |

^a Rate constants (k_a^X) were measured relative to the rate constant for abstraction of deuterium from a deuterated thiol (k_{SD}), benzenethiol-*d*, PhSD (system I and II^b), or 2-methyl-2-propanethiol-*d*, *t*-BuSD (system III^b). ^b System I is azoisobutane (AIB) and PhSD; system II is *tert*-butyl peroxyvalate (BPP) and PhSD; and system III is AIB and *t*-BuSD. ^c For each system, the intercept of the least-squares line of the Hammett equation for that system, $\log k_a^0$, was subtracted from the logarithm of the relative rate constants to give $\log (k_a^X/k_a^0)$.

arising from two causes that may act in opposing directions. The first is that substituents alter the bond dissociation energy of the benzylic C–H bond; since electron-donating substituents weaken the benzylic bond,³⁹ this factor predicts a negative ρ value, regardless of the nature of the radical. This is the effect stressed by Zavitsas.²⁷ However, SETS, arising from the presence of the attacking radical in the transition state, can provide selective resonance stabilization of some transition states and perturb the BDE-determined ρ . This perturbation can lead to a more negative ρ , or it can overcome the BDE effect and produce a positive ρ .^{1b} Generally, the usual representation of dipolar structures correctly predicts the direction of the perturbation due to SETS.^{1a,b,f,38b} For nucleophilic radicals such as *tert*-butyl, the negative ρ value for eq 3 which is inherent from the substituent effects on BDEs is converted to a positive value by SETS.

Figure 3 graphically illustrates these ideas. It shows the Evans–Polanyi plot for hydrogen abstraction from *p*-methoxy- and *p*-nitrotoluenes by both methyl and *tert*-butyl radicals. (For a description of the theory of these plots, see the discussions by Evans and Polanyi, Bell, and Dewar.⁴⁰) In the toluenes, an electron-withdrawing nitro group strengthens the BDE of the benzylic C–H bond; thus, the curves for bond breaking in the two toluenes reflect the larger BDE of *p*-nitrotoluene. The methyl radical is relatively nonpolar, and hydrogen abstraction by methyl is mainly governed by the BDE effects. Figure 3a shows that the difference in the BDEs of the two toluenes leads to a lower activation energy for hydrogen abstraction from *p*-methoxytoluene. However, the *tert*-butyl radical is more nucleophilic than is methyl, and the transition state for its reaction with *p*-nitrotoluene is stabilized to a larger

Table IV. Hammett ρ Values for Hydrogen Abstraction from Substituted Toluenes by Alkyl Radicals

| Radical | ρ^a | Temp, °C | Electron affinity, eV |
|--------------------|------------------|----------|-----------------------|
| Methyl | -0.2 ± 0.2^b | 100 | 1.13 ^c |
| Undecyl | 0.5 ± 0.1^d | 81 | 1.0 ^{c,e} |
| Undecyl | 0.5 ± 0.2^f | 80 | |
| Isopropyl | 0.8 ± 0.1^g | 30 | <0.34 ^h |
| 1-Ethylpentyl | 0.7 ± 0.2^i | 80 | |
| <i>tert</i> -Butyl | 1.0 ± 0.1^j | 30 | |

^a ρ values are reported according to the format we have suggested as $\rho \pm$ the uncertainty in ρ at the 95% confidence level. See ref 36. ^b W. A. Pryor, U. Tonellato, D. L. Fuller, and S. Jumonville, *J. Org. Chem.*, **34**, 2018 (1969). ^c F. M. Page, "Free Radicals in Inorganic Chemistry", *Adv. Chem. Ser.*, No. **36**, 68 (1962). ^d W. A. Pryor and W. H. Davis, Jr., *J. Am. Chem. Soc.*, **96**, 7557 (1974). ^e The value given is for the ethyl radical. ^f R. W. Henderson and R. D. Ward, Jr., *J. Am. Chem. Soc.*, **96**, 7556 (1974). ^g This work. ^h The value given is for the cyclohexyl radical. D. K. Bohme, E. Lee-Ruff, and L. B. Young, *J. Am. Chem. Soc.*, **94**, 5153 (1972). ⁱ R. W. Henderson, *ibid.*, **97**, 213 (1975). ^j This work and W. A. Pryor, W. H. Davis, Jr., and J. P. Stanley, *J. Am. Chem. Soc.*, **95**, 4754 (1973).

degree, relative to others in these series, by the additional polar resonance structure $t\text{-Bu}^+ \text{H} \cdot \text{CH}_2\text{C}_6\text{H}_4\text{X}$. Thus, in this case, SETS stabilize the transition state and reverse the order of activation energies from that predicted by the BDE effect; thus, a positive ρ value is obtained.

Conclusions

The positive ρ values observed for hydrogen abstraction from substituted toluenes by isopropyl and *tert*-butyl radicals indicate that Hammett studies of atom transfers cannot be satisfactorily explained by consideration of the effects of substituents on BDE alone. At least one other factor, which can act in opposition to the BDE effect, must be considered. We believe that it is most consistent with the prior literature, as well as most economical, to regard this second effect as the substituent effect on the transition state (SETS).^{1b}

Table V presents a summary of the ρ values predicted from consideration of BDE and SETS effects for hydrogen abstraction from toluenes or iodine abstraction from aryl iodides by alkyl free radicals. Since electron-donor substituents weaken the benzylic C–H bond in toluenes but strengthen the Ar–I bond in the iodides, the BDE effect leads to a prediction of negative ρ values, regardless of attacking radical, for the toluenes, but positive ρ values, regardless of the radical, for the aryl iodides. Table V shows that this BDE effect often dominates (e.g., for the last entry), but in many cases the polar substituent effect due to the presence of the radical in the transition state dominates the BDE effect and a ρ value with sign opposite to that expected from BDE effects alone is observed (e.g., the first entry).

Experimental Section

Chemicals. The substituted toluenes were washed several times with concentrated sulfuric acid followed by washings with 10% sodium bicarbonate and distilled water. They were dried over anhydrous magnesium sulfate and vacuum distilled. 2-Methyl-2-propanethiol-*d* (*t*-BuSD) and benzenethiol-*d* (PhSD) were prepared by repeatedly adding 99.8% D₂O to each thiol, stirring the mixture, and separating the immiscible liquids until the deuterium content at the exchangeable hydrogen position was shown by NMR to be approximately 98%. The thiols were then dried over the minimum amount of anhydrous magnesium sulfate, decanted, and distilled. The NMR spectra of the purified thiols showed them to be more than 95% deuterated. Approximately 1 mL of 99.8% D₂O per 100 mL of thiol was added to the thiols so that they were saturated with D₂O. Therefore, the reaction solutions, prepared by mixing a toluene and a thiol, were slightly wet with

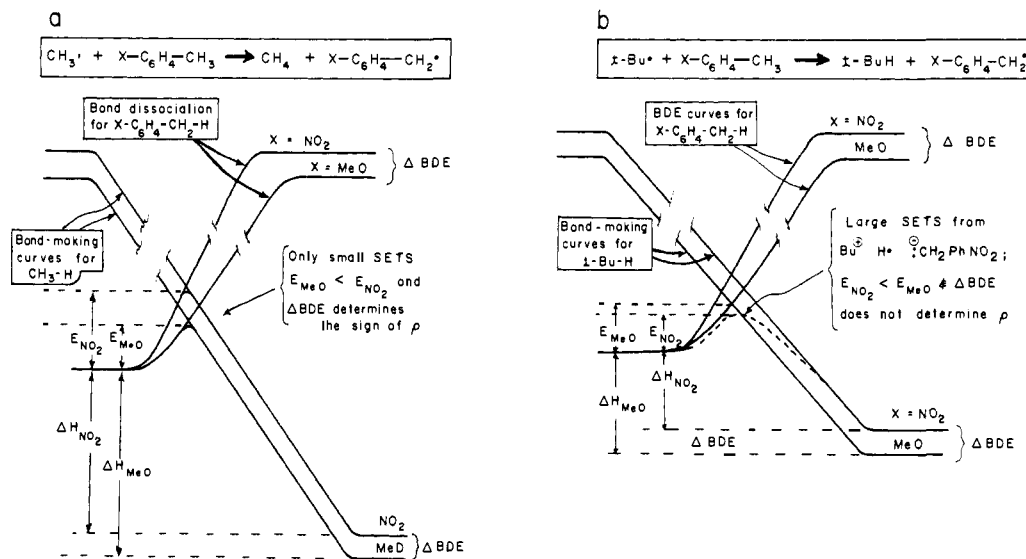


Figure 3. Evans-Polanyi⁴⁰ plots of potential energy vs. reaction coordinate for hydrogen abstraction from toluenes by methyl and *tert*-butyl radicals. The BDE of the two toluenes differ, with *p*-nitrotoluene having the strongest benzylic C-H bond; thus, the bond-breaking curves are shown aligned at their bottoms but diverging at their tops by an amount equal to the difference in BDEs, ΔBDE . Since the difference in heat of reaction of a given radical with the two toluenes is equal to ΔBDE , the bond-making curves for reaction of either radical with the two toluenes also are displaced from one another by ΔBDE . For the reaction of the methyl radical, BDE effects determine the relative activation energies, and a negative ρ value can be seen to result. For *tert*-butyl, an appreciable substituent effect on transition state stability (SETS) lowers the potential energy of the transition state for *p*-nitrotoluene owing to the added resonance of the dipolar structure $\text{Bu}^+\text{H}\cdot\text{CH}_2\text{Ar}$. This has the effect of rounding the intersection of the two curves for this reaction profile at the area of the transition state, and the order of activation energies is reversed from the order of the BDEs. A positive ρ value results.

Table V. The Influence of SETS and Substituent Effects on BDE on the Sign of ρ Values of Atom Transfer Reactions

| Attacking radical | Substrate | Sign of ρ predicted by consideration of | | |
|-----------------------|-----------------|--|------------------|---------------------|
| | | SETS only | BDE effects only | Obsd ρ |
| <i>tert</i> -Butyl | ArCH_3 | Positive | Negative | $1.0 \pm 0.1^{a,b}$ |
| Isopropyl | ArCH_3 | Positive | Negative | 0.8 ± 0.1^b |
| Undecyl | ArCH_3 | Positive | Negative | $0.5 \pm 0.2^{c,d}$ |
| <i>p</i> -Nitrophenyl | ArI | Negative | Positive | 0.1 ± 0.2^e |
| Phenyl | ArI | Near zero | Positive | 0.57^f |

^a W. A. Pryor, W. H. Davis, Jr., and J. P. Stanley, *J. Am. Chem. Soc.*, **95**, 4754 (1973). ^b This work. ^c W. A. Pryor and W. H. Davis, Jr., *J. Am. Chem. Soc.*, **96**, 7557 (1974). ^d R. W. Henderson and R. D. Ward, Jr., *ibid.*, **96**, 7556 (1974). ^e W. H. Davis, Jr., J. H. Gleaton, and W. A. Pryor, *J. Org. Chem.*, **42**, 7 (1977). ^f W. C. Danen and D. G. Saunders, *J. Am. Chem. Soc.*, **91**, 5924 (1969); W. D. Danen, D. G. Saunders, and K. A. Rose, **96**, 4558 (1974).

D_2O . During the course of the reaction, it is possible that the deuterium content of the thiols could decrease because of hydrogen abstraction by thyl radicals. However, this excess D_2O ensures that the exchangeable sulfhydryl hydrogen positions remained deuterated.

tert-Butyl peroxyvalate (BPP) was purchased from Lucidol as a 75% solution in "mineral spirits" and purified by three passes down a Woelm neutral alumina column with hexane as the eluent. The "mineral spirits" eluted from the column very shortly before the BPP. The chromatographed BPP was shown to be 95% pure by iodometric titration.^{41a}

Azoisopropane (AIP) and azoisobutane (AIB) were prepared via the method of Ohme and Schmitz from the corresponding *N,N'*-dialkylsulfamide.^{41b,42} Vacuum distillation gave AIP [bp 40–41 °C (120 mm); NMR (CCl_4) δ 1.2 (d, $J = 6.5$ Hz, 5.8 H, $-\text{CH}(\text{CH}_3)_2$) and 3.5 (septet, $J = 6.5$ Hz, 1 H, $-\text{CH}(\text{CH}_3)_2$); UV (C_6H_6) λ_{max} 359 nm (ϵ 15)] [lit. bp 88.5 °C;⁴³ NMR (neat) δ 1.188 (d, $J = 6.5$ Hz) and 3.525 (septet, $J = 6.5$ Hz);⁴⁴ UV ("saturated hydrocarbon solvent") λ_{max} 359 nm (ϵ 14.5⁴⁵)] and AIB [bp 52–53 °C (96 mm); n_{D}^{25} 1.3951; NMR (CCl_4) δ 1.18 (s, $-\text{C}(\text{CH}_3)_3$); UV (cyclohexane) λ_{max} 367 nm (ϵ 15)] (lit. bp 98–109,⁴² 109–110 °C;⁴⁶ n_{D}^{25} 1.3940⁴²).

Procedures for Kinetic Runs. For a single kinetic run for 1-substituted toluene, reaction solutions of five to seven different toluene (QH) to thiol (RSD) ratios were prepared by mixing toluene and thiol solutions of the same initiator (AIP, AIB, or BPP) concentration. (The [QH]/[RSH] ratio varied from 0.8 to 30. The concentration of AIP in various runs was 0.1, 0.2, 0.25, 0.5 M; the concentration of AIB or

BPP was 0.05, 0.1, 0.2, or 0.3 M.) After placing the reaction mixtures in Pyrex sample tubes and degassing by four freeze-pump-thaw cycles, the solutions were photolyzed in a Rayonet photochemical reactor equipped with a "merry-go-round" to ensure that all tubes received equal irradiation. The Rayonet RPR 3500 or General Electric 8T5/BL lamps used were found to have an emission curve consisting of sharp mercury emission line spikes superimposed on a broad fluorescence emission from 300 to 440 nm. Since these lamps have very little output below 300 nm, the reaction tubes are Pyrex, and the thiols and most of the toluenes studied have small extinction coefficients at wavelengths greater than 300 nm, excitation of the azo compound is the dominant photolytic process. Some excitation of benzenethiol (PhSD) and some toluenes may occur, but these processes are not important in our photolysis times (3 h for AIB, 8 h for BPP, and 11 h for AIP); even *m*-nitrotoluene, which is a pale yellow, gives a relative reactivity which is near the least-squares line for the Hammett plot of the *tert*-butyl radical data (Table II and Figure 3). Since 2-methyl-2-propanethiol-*d*₁ (*t*-BuSD) does not absorb light of these wavelengths, the insignificance of these excitations is further proved by the similarity of ρ values for the PhSD and *t*-BuSD systems (Tables II and III and Figures 1 and 2).

After photolysis, the sample tubes were frozen in a CCl_4 (or acetone)/dry ice or EtOH/liquid N_2 slush bath. The gas over the solution was then transferred directly⁴⁷ into a Consolidated Engineering Corp. Model 21-620 mass spectrometer. The ratio of mass/charge (m/e) peaks 44 to 45 was measured and converted to a propane (*i*-PrH) to

propane-2-*d* (*i*PrD) ratio. Since the cracking pattern for propane and propane-2-*d* is such that the *m/e* 45 peak is due to *i*-PrD (with only a minor contribution from *i*-PrH) while the *m/e* 44 peak is mostly due to *i*-PrH but with a contribution from *i*-PrD that is 60% of the *m/e* 45 peak,^{48a} the equation used to effect this conversion is

$$\frac{[i\text{-PrH}]}{[i\text{-PrD}]} = \frac{H_{44} - 0.64H_{45}}{H_{45}} = \frac{H_{44}}{H_{45}} - 0.64 \quad (18)$$

in which H_{44} is the height of the *m/e* 44 peak and H_{45} is the height of the *m/e* 45 peak.^{49a} The *m/e* 44 and 45 (M^+) peaks were chosen for this analysis because, although they are not the largest peaks in the propane and propane-2-*d* spectra, they are the best indicators of the extent of isotopic substitution. Since the cracking pattern for isobutane and isobutane-*d* results in the *m/e* 44 peak arising from *t*-BuD (with a minor contribution from *t*-BuH) and the *m/e* 43 peak mostly from *t*-BuH but with a contribution from *t*-BuD that is 30% of the *m/e* 44 peak,^{48b} the equation used to effect the conversion to an isobutane (*t*-BuH) to isobutane-*d* (*t*-BuD) ratio is

$$\frac{[t\text{-BuH}]}{[t\text{-BuD}]} = \frac{H_{43} - 0.3H_{44}}{H_{44}} = \frac{H_{43}}{H_{44}} - 0.3 \quad (19)$$

in which H_{43} is the height of the *m/e* 43 peak and H_{44} is the height of the *m/e* 44 peak.^{49b} The *m/e* 43 and 44 ($M^+ - 15$) peaks were chosen because they not only indicate the extent of isotopic substitution but also are the largest peaks in the isobutane and isobutane-*d* spectra.

In order to test the mass spectrometry analysis, solutions of AIB in *p*-chlorotoluene/*t*-BuSD and *p*-xylene/*t*-BuSD were photolyzed and then analyzed on a Du Pont residual gas analyzer. The H_{43}/H_{44} values measured with this instrument compare favorably with the values obtained from the CEC instrument.⁵⁰

Since it is important to our method of analysis that the peaks of these *m/e* values result from the corresponding protonated and deuterated alkanes only and not from any other compounds, several precautions were taken. Firstly, only toluenes and thiol whose cracking patterns showed negligible contributions to these peaks were used. Secondly, the reaction mixtures were frozen in slush baths of temperatures as low as -117°C (EtOH/liquid N_2) so that only very low-boiling gases could be transferred into the mass spectrometer. Since VPC analyses identified propane, propene, 2,3-dimethylbutane, and disulfide [(PhS) \rightarrow_2 or (*t*-BuS) \rightarrow_2] as the primary reaction products from the AIP system, and since propene, the only low-boiling component of the system other than propane, does not give a *m/e* 44 or 45 peak, we feel confident that the peaks of these *m/e* values are only due to propane and propane-2-*d*.⁵¹ In the *tert*-butyl radical systems, VPC showed the main products to be isobutane, isobutylene, 2,2,3,3-tetramethylbutane, and disulfide, (PhS) \rightarrow_2 or (*t*-BuS) \rightarrow_2 . Because isobutylene, the only low-boiling component of the system other than isobutane, does not give a *m/e* 43 or 44 peak, we are confident that these peaks of these *m/e* values are only due to isobutane and isobutane-*d*.

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Supplementary Material Available: Values of k_a/k_{SD} for the substituted toluenes studied in each system of radical initiator and deuterated thiol (7 pages). Ordering information is given on any current masthead page.

References and Notes

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- (35) A single line could also be constructed by forcing the $\log(k_a/k_{SD})$ values for a single QH to be the same. However, this treatment places too much emphasis on the experimental values of these $\log(k_a/k_{SD})$ values. The advantage of the intercept method is that all $\log(k_a/k_{SD})$ values are used to determine the value of the intercept.
- (36) (a) The results of the least-squares analysis are reported according to the format we have recently suggested. The slope of the least-squares line, its uncertainty at the 95% confidence level, the average standard deviation in the logarithms of the relative rates (s_y),^{37e} and the number of points are given.^{36b,37} (b) W. H. Davis, Jr., and W. A. Pryor, *J. Chem. Educ.*, **53**, 285 (1976). (c) The slope of the least-squares line is b_1^{37a} and the standard deviation of the slope is s_{b_1} .^{37b} It may be said with 95% confidence that the true value of the slope lies within $(t_{n-2}, 0.05)(s_{b_1})$ of the calculated slope, b_1^{37c} . The Student's *t* value for *n* points and a confidence level of 95% can be obtained from a table of the distribution of *t* (two-tailed tests).^{37d}
- (37) G. W. Snedecor and H. G. Cochran, "Statistical Methods", 6th ed, Iowa State University, Ames, Iowa, 1967: (a) p 136; (b) p 138; (c) p 153; (d) p 549; (e) p 44.
- (38) (a) The ρ values for Br· and Cl· reacting with toluenes are in the inverse order to that predicted from their electron affinities. This can be rationalized by recognizing that the reactions of Br· are less exothermic, and therefore have transition states that involve more bond breaking and are more sensitive to the effects of substituents.^{7,22,26b} In the case of *tert*-butyl and isopropyl, the ρ values do lie in the order predicted by the electron affinities of these two radicals. However, the larger ρ value for *tert*-butyl relative to isopropyl in this case as well may arise in part from the fact that the *tert*-butyl reactions are less exothermic and involve more bond breaking relative to those of the isopropyl radical. (b) The importance of SETS can be equal to or greater than the BDE effect. Consider the ρ values of Cl· (about -0.8) and methyl (about -0.2).¹⁵ These two radicals have equivalent BDE effects.
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- (41) (a) L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958); (b) R. Ohme and E. Schmitz, *Angew. Chem., Int. Ed. Engl.*, **4**, 433 (1965).
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- (47) Carbon dioxide produced by photolysis of BPP was removed by an Ascarite trap in the inlet system of the mass spectrometer.
- (48) "Mass Spectral Data", American Petroleum Institute Research Project 44, Serial No. (a) 62 and 548; (b) 5 and 131; (c) 13.

- (49) (a) The factor of -0.64 in eq 18 can be neglected because it appears in every measurement of H_{44}/H_{45} and affects only the intercept and not the slope of the plot of $[i\text{-PrH}]/[i\text{-PrD}]$ (or H_{44}/H_{45}) vs. $[\text{QH}]/[\text{RDS}]$. (b) The factor of -0.3 in eq 19 can likewise be neglected.
- (50) With the Du Pont instrument, H_{43}/H_{44} for the *p*-chlorotoluene solution was 1.40 and H_{43}/H_{44} for the *p*-xylene solution was 1.57. With the CEC spectrometer, these values were 1.36 and 1.47, respectively. Both of the values measured on the Du Pont analyzer are larger than those measured on the CEC instrument, but the ratios are about equal ($1.40/1.57 = 0.892$ and $1.36/1.47 = 0.925$).
- (51) Although 2,3-dimethylbutane is rather low boiling (bp 58°C), it does not have significant m/e 44 and 45 peaks^{46c} and, therefore, does not interfere with the mass spectral analysis even if it is transferred into the mass spectrometer.

Substituent Effects on a Sigmatropic Reaction. Rearrangement of Some 3-Substituted 1,1-Diphenylindenes

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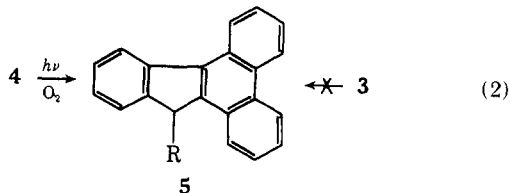
Abstract: The products of the irradiation of a series of 3-substituted 1,1-diphenylindenes **1** (substituents: H, CH₃, COCH₃, CO₂CH₃, CN) in benzene are either 3-substituted 1,2-diphenylindenes **3** (for COCH₃, CO₂CH₃, and CN) or 1-substituted 2,3-diphenylindenes **4** (for H and CH₃). The product-determining step is the thermal sigmatropic migration of a hydrogen atom on the middle carbon of an isoindene intermediate, **2**, to either neighboring carbon. The dependence of the direction of the hydrogen migration on the nature of the substituent is correlated with the substituent-dependent symmetry of the highest occupied molecular orbital of a model for the transition state. In methanol-benzene the irradiation of acetyl- and carbomethoxy-substituted **1** produced isomer **4**, the isomer not formed in benzene. In benzene-methanol-*O-d* the irradiation of 3-acetyl-1,1-diphenylindene yielded **4** that contained 10% deuterium. An anionic intermediate has been postulated to account for the results in methanol. The thermal, photochemical, and base-catalyzed interconversions of **3** and **4** have been examined also.

When a 3-substituted 1,1-diphenylindene (**1**) is irradiated in benzene solution, the primary product is either a 1,2-diphenyl 3-substituted indene (**3**)¹ or a 2,3-diphenyl 3-substituted indene (**4**)² (Scheme I). The reaction occurs in two steps. An isoindene **2**, shown to be an intermediate in a number of photochemical^{1,3} and thermal⁴⁻¹¹ rearrangements of indenes,¹² is formed here in a photochemical step. The second step is a thermal rearrangement of **2** to either **3** or **4** depending on the direction of the hydrogen migration. McCullough¹ observed that **4a** was the major product from **1a**, whereas Huhtanen² found that **3c** was the only product from **1c**.

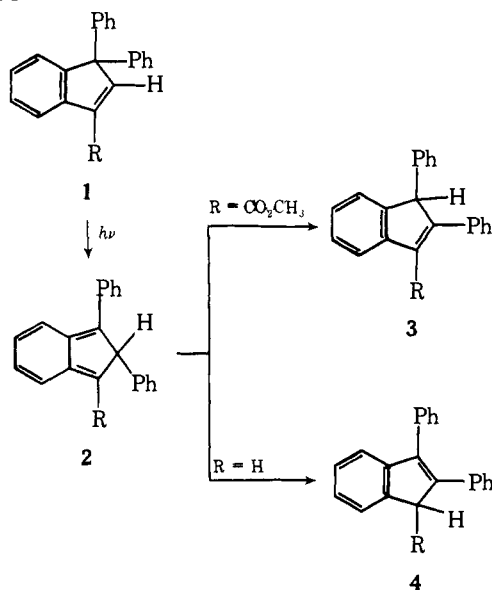
The general question of how substituents affect the course of a sigmatropic hydrogen migration was raised by these observations. The products of the series **1b-e** were identified and these results were correlated with the perturbing effects of the substituents on the symmetry of the highest occupied molecular orbital of a model for isoindene **2**.

Results

Structure Assignment. The series **1b-e** was prepared by classical methods from 3,3-diphenyl-1-indanone. Both possible products (**3** and **4**) of the irradiation of **1** were prepared in each



Scheme I



a (R = H), b (R = CH₃), c (R = CO₂CH₃), d (R = COCH₃),
e (R = CN), f (R = CO₂H)

case. Where possible, structures were assigned to these isomeric pairs by method of synthesis, by photocyclization of isomer **4** to indenophenanthrene **5** (and by the absence of photocyclization for isomer **3**), and by an NMR correlation. The NMR