

Figure 1. A Hammett plot of relative k_H values (eq 4) for the 1-undecyl radical vs. σ substituent constants. The numbers correspond to the entries in Table I.

Table I. Values of k_H/k_{Cl} for Substituted Toluenes toward the 1-Undecyl Radical at 80°

No.	QH	k_H/k_{Cl}	No.	QH	k_H/k_{Cl}
1	<i>p</i> -Xylene	0.023 ^a	6	<i>m</i> -Fluorotoluene	0.021
2	Mesitylene	0.039 ^a	7	<i>m</i> -Chlorotoluene	0.023
3	<i>m</i> -Xylene	0.021 ^a	8	<i>m</i> -Bromotoluene	0.017
4	Toluene	0.011	9	<i>m</i> -Tolunitrile	0.019
5	<i>p</i> -Chlorotoluene	0.018	10	<i>m</i> -Nitrotoluene	0.028

^a The values plotted in Figure 1 for the xylenes were statistically corrected by a factor of 2; the value for mesitylene was corrected by a factor of 3.

system in detail to determine the importance of this chain. The trichloromethyl radicals react readily to produce chloroform, but the chain is evidently broken in the second step.¹⁷ Even in the absence of this chain sequence, a number of species (chloroform, bibenzyl, docosane, etc.) are produced during reaction. Examination of the reactivity and concentration of each showed that only in the case of chloroform was reactivity sufficiently high to overcome the very low concentrations of these products; none of the other products contributed more than a fraction of a per cent to RH or RCl.

Although its reactivity toward chlorine abstraction by the 1-undecyl radical is quite low, chloroform has a relative k_H value of about 30 compared to toluene. The contribution of chloroform to RH production in the kinetic runs, although much higher than that of the other products, was no more than ~2% for [LP] = 0.01 M, the concentration used in the runs from which relative k_H values were obtained.

Addition of alkyl radicals to aromatic rings occurs readily,¹⁸ and it might be suggested that undecane is produced via a sequence in which undecyl radicals abstract hydrogen from the resulting cyclohexadienyl radicals or from nonradical products derived from these radicals. Thermolysis of LP in benzene produces appreciable amounts of undecylbenzene; the corresponding decomposition in toluene produces bibenzyl as the major product along with a small amount of undecyltoluene. However, in carbon tetrachloride-QH solutions the yield of the addition products is less than 1% of the total of RH and RCl, even for [QH]/[CCl₄] ratios as high as 15.¹⁹

A test for ring involvement in RH formation was made by determining k_H/k_{Cl} values for benzene and substituted benzenes. These compounds all had approximately the same reactivity, which amounted to no more than 1 or 2% of that for toluene. This result indicates that the ring contribution to the reactivity of the toluenes is negligible.

Another potential interference is "back-biting" by the 1-undecyl radical, followed by abstraction of H or Cl by the resulting secondary radical. These reactions can be ruled out since only terminally substituted chloroundecane was found. Another source of RH might be reaction of R₁ with peroxide. However, this process can be neglected for [LP] = 0.01 M.^{12d,e}

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- (12) (a) The CCl₄ system has been widely used to determine relative reactivities:^{12b-1} (b) F. G. Edwards and F. R. Mayo, *J. Amer. Chem. Soc.*, **72**, 1265 (1950); R. F. Bridger and G. A. Russell, *ibid.*, **85**, 3754 (1963); (c) W. A. Pryor, K. Smith, J. T. Echols, Jr., and D. L. Fuller, *J. Org. Chem.*, **37**, 1753 (1972), and other papers in this series; (d) D. F. DeTar and D. V. Wells, *J. Amer. Chem. Soc.*, **82**, 5839 (1960); (e) D. F. DeTar and C. Weis, *ibid.*, **79**, 3041, 3045 (1957); (f) C. Walling and A. L. Rieger, *ibid.*, **85**, 3135 (1963); (g) - W. C. Danen, D. Saunders, and K. Rose, *ibid.*, **95**, 1612 (1973); (h) B. R. Kennedy and K. U. Ingold, *Can. J. Chem.*, **44**, 2381 (1966); (i) R. D. Gilliom and J. R. Howley, *ibid.*, **46**, 2752 (1968).
- (13) The [QH]/[CCl₄] ratios were varied from zero to about 15. Analyses were performed on a Hewlett-Packard Model 5712A gas chromatograph equipped with a Disc Integrator.
- (14) Reactions with small ρ values show poor correlations.⁸
- (15) Using a different analytical technique, W. A. Pryor and W. H. Davis, Jr., *J. Amer. Chem. Soc.*, **96**, 7557 (1974), also find a positive ρ for the 1-undecyl radical.
- (16) Since a competitive scheme was employed, those side reactions which consume R₁, but do not produce RH or RCl, will not affect the kinetic expression derived (eq 6).
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- (19) In these runs 90-95% of the undecyl fragments can be accounted for in expected products: undecane, undecyl chloride, ester, etc. Thus the maximum concentration of products containing the remaining fragments (e.g., cyclohexadienyl dimers) is 10⁻³ M, a value much too low for these species to contribute appreciably to RH formation.
- (20) Undergraduate Research Participant.

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Polar Effects in Radical Reactions. III. A Positive ρ for the Reaction of Undecyl Radicals with Substituted Toluenes¹

Sir:

Hydrogen abstraction, the ubiquitous process all radicals undergo, is the most useful model for studying factors which affect the reactivity of radicals.²⁻⁴ Although the bond dissociation energies (BDE) of the bonds broken and formed in the reaction are the most important factors con-

trolling hydrogen transfer rates, other influences such as polar effects on transition states (PETS) frequently cause important perturbations.⁵⁻⁷ Hammett-type correlations of the rate constants for radical reactions, which often have been accepted as *prima facie* evidence for predominant importance of PETS, have been observed in atom transfers,⁵⁻¹¹ additions,^{8,9,12} copolymerizations,^{7b} disproportionations,¹³ and β -scissions.¹⁴

We believe that the ρ value in Hammett correlations of radical reactions is determined *both* by PETS and by substituent effects on the ground states of molecules through their influence on BDE.^{5,15} The effects of ring substituents on the BDE of benzyl hydrogens can only produce negative ρ values,^{16a} whereas PETS can make either a positive or a negative contribution to ρ .^{1,15} Although most of the ρ values which have been reported are negative,^{8,9} we recently reported $\rho = +0.99$ for the reaction of *tert*-butyl radicals with toluenes.¹ Clearly, it is desirable to show that this positive ρ is not unique. The ρ values for the reaction of other alkyl radicals with toluenes can serve this purpose. Zavitsas, disregarding PETS, has predicted that alkyl radicals react with toluenes with ρ values ranging from -0.6 for methyl to -1.6 for *tert*-butyl;^{16b} if the perturbations due to PETS are considered, ρ values for alkyl radical reactions should lie between the ρ observed for *tert*-butyl radicals, $+0.99$, and that for methyl radicals,¹⁷ about 0 . In this paper we report on a study of the reaction of undecyl radicals with toluenes which gives a ρ of $+0.5$, consistent with the PETS arguments.

Our kinetic system involves heating lauroyl peroxide, LPO ($0.6 M$), at 81° for 10 hr in *tert*-butylbenzene solvent containing two substituted toluenes ($0.4 M$ each) in an nmr tube. The relative rates of hydrogen abstraction from the toluenes by the undecyl radicals, $U\cdot$, are equal to the ratio of logarithms of the fractional amounts of the two toluenes remaining, as measured by nmr.^{18,19}

There are two types of reactions which could invalidate our kinetic analysis. (1) The first is benzylic hydrogen abstraction by radicals other than $U\cdot$; other radicals which might abstract benzylic hydrogens are benzyl radicals and undecylcarboxy ($UCO_2\cdot$) radicals. In similar systems, abstraction of hydrogen by a benzyl radical has been shown not to be important.²⁰ Abstraction by $UCO_2\cdot$ is not significant since the amount of undecanoic acid formed in the reaction mixture is only a tenth of the toluenes consumed and the undecane produced.

(2) The second reaction which might interfere is addition of $U\cdot$ to the aromatic ring of substrates to produce a cyclohexadienyl radical which can (a) form a substituted undecyltoluene by loss of a hydrogen atom or (b) dimerize to produce a cyclohexadienyl dimer, which can be further oxidized to form biphenyls.

(2a) Undecyltoluene is not a significant product; glpc analysis showed that thermolysis of $0.6 M$ LPO and $0.8 M$ toluene in benzene solvent ($7.8 M$) produced $0.18 M$ undecane and only $0.024 M$ undecylbenzene.²¹ Since the rate constants for $U\cdot$ addition to benzene and toluene are approximately equal,^{23,24a} even less undecyltoluene must be produced in this control experiment than undecylbenzene. (2b) Formation of biphenyls does not interfere with our kinetics method since the chemical shift of their benzylic protons is virtually identical with that in their substituted toluene precursors, and they would be counted as unreacted toluenes in our analysis. Cyclohexadienyl dimers might well interfere, both because their CH_3 groups are shifted relative to the toluenes', and because they could be important hydrogen donors; however, they are not important products since we found no proton signals at 5-6 ppm where cyclo-

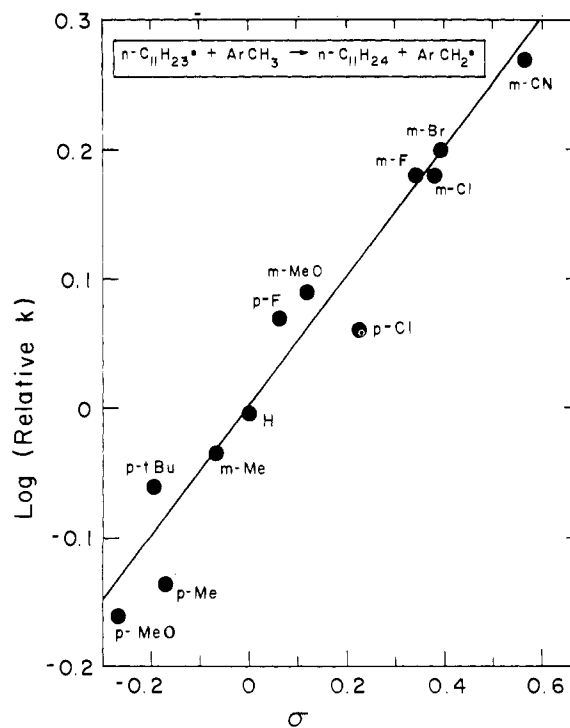


Figure 1. A Hammett equation plot of log (relative rate constants) vs. σ for hydrogen abstraction from substituted toluenes by the undecyl radical at 81° . The least-squares treatment gives $\rho = 0.50 \pm 0.02$ ($r = 0.97$).

hexadienyl vinylic hydrogens absorb. Thus, although some addition must occur, our nmr method is insensitive to this process.²⁵

A Hammett $\sigma\rho$ correlation of our data at 81° (Figure 1) gives $\rho = 0.50 \pm 0.02$ (12 points, $r = 0.97$). Henderson and Ward, studying this reaction by a completely independent method, report $\rho = 0.47 \pm 0.07$ ($r = 0.91$).²⁶ The fact that these two methods, with very different experimental difficulties and possible interfering reactions, give the same ρ value is strong evidence for the accuracy of this value.²⁷

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- (21) (a) Since only 0.24 *M* docosane is produced, and since k_d/k_c for primary radicals is 0.15,²² only 0.036 *M*, or 20%, of the undecane is produced in disproportionation reactions. This undecane does not interfere because we follow substrate disappearance, not product appearance. (b) The average decrease in the concentration of the substituted toluenes, 12% (0.1 *M*), is less than the amount of undecane formed (0.18 *M*). We cannot account for all of the excess undecane, but ca. 0.03 *M* of it arises from disproportionation. (c) In a solution of 0.8 *M* toluene in benzene, the amount of undecylbenzene formed (0.024 *M*) is less than half that formed by thermolysis of 0.6 *M* LPO in neat benzene (0.053 *M*). Shelton, in his study of homolytic aromatic cyclohexylation, reports a similar change in addition product (arylcyclohexane) yield when the solvent was changed from toluene to benzene. J. R. Shelton and C. W. Uzelmeier, *J. Amer. Chem. Soc.*, **88**, 5222 (1966), especially p 5223. (d) Important termination reactions are U• combinations to give docosane and benzyl radical combination to form bibenzyls.
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- (23) Preliminary studies of methyl radical addition to substituted benzenes indicate a $\rho \approx 0$ and an abstraction to addition ratio for toluene greater than ten.^{24a} Other studies of addition/abstraction ratios have been reported: (1) Pryor's compilation of his work^{24b} and that of Szwarc^{24c} for methyl radicals predicts a relative reactivity of toluene to benzene of 2:1. Since these workers obtained data at different temperatures, this ratio may not be very accurate. (2) Eliel approximates a ratio of rate of methyl radical abstraction from the side chain of toluene to rate of abstraction of hydrogen from the toluene ring of 7.5.^{24d} (3) In his study of homolytic aromatic cyclohexylation,^{21c} Shelton reports that addition to toluene is a minor process compared to abstraction of benzylic protons. Thus, although the precise magnitude of the addition/abstraction ratio is uncertain, it is evident that alkyl radicals abstract benzylic hydrogens in preference to addition to the aromatic ring. Therefore, addition occurs to a lesser extent than abstraction in our system. Furthermore, some addition does not prevent our nmr analysis from determining the amount of toluene which undergoes abstraction.
- (24) (a) W. A. Pryor, W. A. Davis, Jr., and J. H. Gleaton, unpublished data; (b) W. A. Pryor, D. L. Fuller, and J. P. Stanley, *J. Amer. Chem. Soc.*, **94**, 1632 (1972); (c) M. Szwarc and J. H. Binks, "Theoretical Organic Chemistry," Kekule Symposium, 1958, Butterworths, London, 1958, p 262; (d) S. H. Wilen and E. L. Eliel, *J. Amer. Chem. Soc.*, **80**, 3309 (1958).
- (25) The nmr method is also insensitive to other reactions which do not affect the benzylic proton peak such as abstraction of methoxy protons from the methylanisoles. These methoxy protons are about as reactive as the benzylic protons. See note 24 in ref 8.
- (26) R. W. Henderson and R. D. Ward, Jr., *J. Amer. Chem. Soc.*, **96**, 7556 (1974).
- (27) NOTE ADDED IN PROOF. A. A. Zavitsas has informed us (private communication) that he has obtained a rho of about +0.4 for this reaction.

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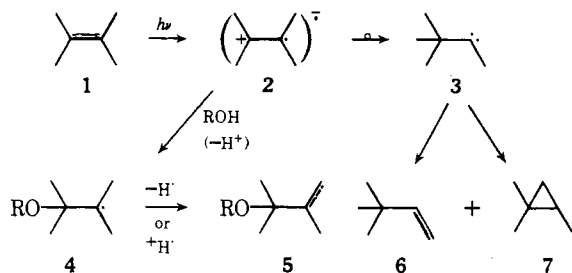
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Photochemistry of Alkenes. III. Formation of Carbene Intermediates¹

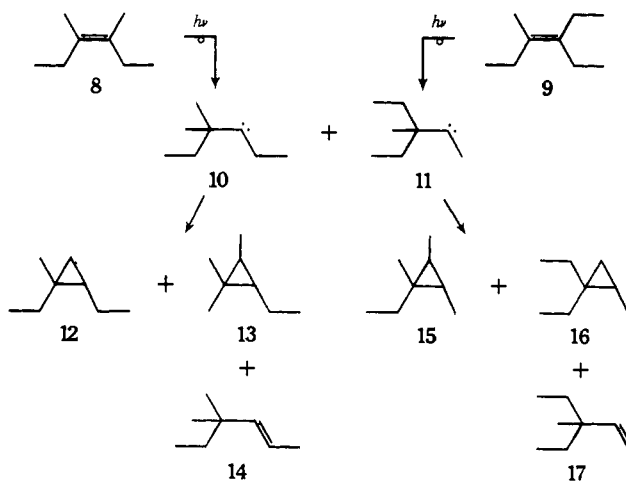
Sir:

Recent reports from these laboratories have shown that tri- and, especially, tetrasubstituted alkenes display a novel behavior on direct irradiation in hydroxylic media which leads principally to the formation of a mixture of saturated

Scheme I



Scheme II



and unsaturated ethers, as depicted in Scheme I for the conversion of 2,3-dimethyl-2-butene (**1**) to the mixture of ethers **5**.¹ By contrast, in nonhydroxylic media, such as ether or octane, rearrangement to a 1.03:1 mixture of the 1-butene **6** and the cyclopropane **7** occurs.² Moreover, in alcoholic solvents of low nucleophilicity substantial amounts of **6** and **7** are formed in competition with the ethers **5**; thus the ratio **5**:(**6** + **7**) decreases in the order methanol > ethanol > 1-propanol > 1-butanol.

The formation of ether products **5** has been interpreted in terms of nucleophilic trapping of the $\pi, R(3s)$ Rydberg excited state (**2**).¹ It is attractive to interpret the formation of **6** and **7** in terms of competing rearrangement of the excited state **2** to the carbene intermediate **3**, especially since **3** is known to undergo rearrangement to afford **6** and **7** in the same ratio when generated by other means.³ We wish now to report additional evidence which strongly supports the generation of carbene intermediates and indicates that the process is general for most tetrasubstituted alkenes on direct irradiation in nonnucleophilic media.

Thus, as shown in Table I, 3,4-dimethyl-3-hexene (**8**) is converted on irradiation in pentane solution to a mixture of the cyclopropyl and olefinic products **12**–**17**,⁴ as would be expected from initial photorearrangement to the two possible carbene intermediates **10** and **11** (Scheme II). Moreover, the isomeric olefin **9**, which should undergo rearrangement to the same two carbene intermediates, affords a mixture of the same products **12**–**17**. Furthermore, although the carbene intermediates **10** and **11** are apparently formed in different relative amounts from olefins **8** and **9**, the three products **12**–**14** are formed in similar ratios from each olefin and by independent generation of carbene **10** from the corresponding tosylhydrazone. Likewise the products **15**–**17** are formed in similar ratios on irradiation of either olefin or on independent generation of carbene **11**.⁵

We have observed photoarrangement of a number of other tetrasubstituted alkenes to carbene-derived products, as exemplified in Scheme III for 1,2-dimethylcyclohexene.⁶ Although the proposal that the carbene intermediates arise via rearrangement of the $\pi, R(3s)$ excited state requires fur-

Scheme III

