

ground state or excited state conformer or (b) a single, highly reactive conformer are less compelling from examination of molecular models and the observed stereospecificity of the rearrangement. Instead, the spin inversion may occur on the same single energy barrier surface which leads to product similar to that postulated for radiationless decay of excited benzene.¹⁹

Acknowledgments. Research grants from the National Institutes of Health (GM-16611) and the National Science Foundation (GP 38643) are gratefully acknowledged.

References and Notes

- (1) A preliminary account of this work was given at the 167th National Meeting of the American Chemical Society Los Angeles, Calif., March 31, 1974, Abstract ORGN 080.
- (2) Previous paper in the β,γ -unsaturated ketone series, R. G. Carlson, R. L. Coffin, W. W. Cox, and R. S. Givens, *J. Chem. Soc., Chem. Commun.*, 501 (1973).
- (3) For a recent review, see S. S. Hixon, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).
- (4) For example, see E. Baggiolini, K. Schaffner, and O. Jeger, *Chem. Commun.*, 1103 (1969).
- (5) R. S. Givens and W. F. Oettle, *J. Amer. Chem. Soc.*, **93**, 3963 (1971); J. R. Williams and G. M. Sarkisian, *Chem. Commun.*, 1564 (1971).
- (6) J. I. Seeman and H. Ziffer, *Tetrahedron Lett.*, 4413 (1973).
- (7) (a) J. Ipaktschi, *Tetrahedron Lett.*, 3179 (1970); (b) H. Sato, K. Nakanishi, J. Hayashi, and Y. Nakadaira, *Tetrahedron*, **29**, 275 (1973); (c) S. Domb and K. Schaffner, *Helv. Chim. Acta*, **53**, 677 (1970); (d) D. A. Plank and J. C. Floyd, *Tetrahedron Lett.*, 4811 (1971).
- (8) The synthesis of **1b-d** was carried out by alkylation of cyclopentylidene-cyclopentanone with ethyl bromoacetate to give **1d**. Saponification to **1b** followed by esterification with diazomethane gave the methyl ester **1c**.
- (9) Three of the four studies⁷ have been on steroid systems where axial methyl groups, the rigid steroid nucleus, or other sites of unsaturation may influence the rearrangement (see, for example, the discussion of ref 6). Of the concerted mechanisms, only the $\sigma_2a + \pi_2a$ is possible for **1** due to the restriction of the cyclic olefin, a feature of most of the known oxa-di- π -methane substrates.⁹ The other factors are absent.
- (10) A preliminary report on the photochemistry of **1a** is given in ref 2.
- (11) E. Bunnenburg, C. Djerassi, K. Mislou, and A. Moscowitz, *J. Amer. Chem. Soc.*, **84**, 2823, 5003 (1962).
- (12) R. R. Fraser, M. A. Petit, and M. Miskow, *J. Amer. Chem. Soc.*, **94**, 3253 (1972); H. L. Goering, J. N. Eikenberry, and G. S. Koermer, *ibid.*, **93**, 5913 (1971).
- (13) Work is in progress on this interesting difference in photoreactivity. Others have noted a difference in the photoepimerization process due to ring size and stereochemical constraints.^{6,14} The present reaction may be another example of this phenomenon.
- (14) See, for example, N. C. Yang and R. H. K. Chen, *J. Amer. Chem. Soc.*, **93**, 531 (1971).
- (15) A small amount of photoepimerization of the recovered starting ketone is noted. The extent and nature of this reaction is under investigation.
- (16) (a) P. Crabbé, "ORD and CD in Chemistry and Biochemistry," Academic Press, New York, N.Y., 1972, pp 40-42. (b) J. J. Plattner and H. Rapoport, *J. Amer. Chem. Soc.*, **93**, 1758 (1971).
- (17) H. E. Zimmerman, J. D. Robbins, R. D. McKelvey, C. J. Samuel, and L. R. Sousa, *J. Amer. Chem. Soc.*, **96**, 1974 (1974); *ibid.*, **96**, 4630 (1974). It should be noted that the $\pi_2a + \sigma_2a + \pi_2a$ pathway is followed in this acyclic diene where there are no restrictions concerning the concerted pathways available.
- (18) This may also be termed a $\pi_2a + \sigma_2a + \pi_2a$ rearrangement involving the carbonyl π -orbital, a necessary component of the oxa-di- π -methane rearrangement. Because the configuration about the carbonyl π -bond cannot be determined and for illustrative purposes, we have used the $\pi_2a + \sigma_2a$ diagram. (See also R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Academic Press, Germany, 1970, pp 96-97.)
- (19) D. Phillips, J. Lemaire, C. S. Burton, and W. A. Noyes, *Advan. Photochem.*, **5**, 329 (1968).

Rick L. Coffin, Richard S. Givens,* Robert G. Carlson*

Department of Chemistry, University of Kansas
Lawrence, Kansas 66045

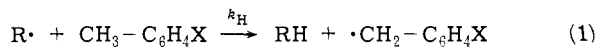
Received July 13, 1974

Polar Effects in Radical Reactions. II. Nucleophilic Character of the Undecyl Radical¹

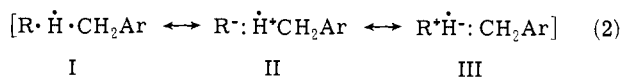
Sir:

Substituent effects on radical reactions are well known.²⁻⁹ In particular, Hammett ρ values have been mea-

sured for a variety of radicals in their attack on substituted toluenes (eq 1).^{8,9} These effects have been ascribed to the



resonance stabilization of the transition state by structures such as II and III. According to this model, those radicals for which form II is more important would exhibit electro-



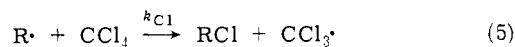
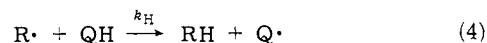
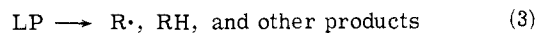
philic character, while those for which structure III is more significant would be nucleophilic. The absolute magnitude of the polar effect in either case would be dependent upon the reactivity of the particular radical.

Recently, an alternative rationalization of the data was proposed,¹⁰ one in which partial charge separation in the transition state is considered to be unimportant. It was postulated that ρ merely reflects differences in the bond dissociation energies of the benzylic hydrogens in the substituted toluenes and that the magnitude of ρ is a measure of the sensitivity of the abstracting radical to those differences. Unlike the other model, this treatment leads to the prediction that radicals are limited to negative (or zero) ρ values. As before, the size of ρ would be dependent upon radical reactivity.

A key test of the two models was provided by Pryor, Davis, and Stanley in their study of the *tert*-butyl radical.¹¹ A ρ value of 0.99 was found; this was the first positive ρ value reported for hydrogen abstraction from toluenes.

We have studied the 1-undecyl radical and here report the second positive ρ value observed for hydrogen abstraction from toluenes. This result provides additional support for the argument that radical reactions are susceptible to polar influences.

The undecyl radicals ($R\cdot$) were generated by thermolysis at 80° of *n*-lauroyl peroxide (LP) in a mixture of a toluene (QH) and carbon tetrachloride.^{12a} The equations for the reactions are as follows

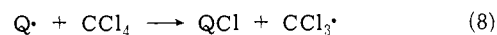


Kinetic analysis of eq 3-5 leads to eq 6. Some RH is produced even when the peroxide is allowed to decompose in

$$\frac{[RH] - [RH]_0}{[RCl]} = \frac{k_H}{k_{C1}} \frac{[QH]}{[CCl_4]} \quad (6)$$

neat carbon tetrachloride. The concentration of RH was corrected for this material, designated $[RH]_0$. The k_H/k_{C1} values given in Table I were obtained from the slope of a plot of $([RH] - [RH]_0)/[RCl]$ vs. $[QH]/[CCl_4]$.¹³ A Hammett $\sigma\rho$ plot of the relative k_H values (see Figure 1) gives $\rho = 0.45 \pm 0.07$ ($r = 0.92^{14}$).¹⁵

A basic assumption in this derivation is that the only sources of RH and RCl are the reactions in eq 3-5.¹⁶ It has been observed that a chain sequence (eq 7 and 8) can occur in the CCl_4 system.^{12d} If the chain length is high, these reactions could produce appreciable levels of potential hydrogen and chlorine donors. We studied the CCl_4 -toluene



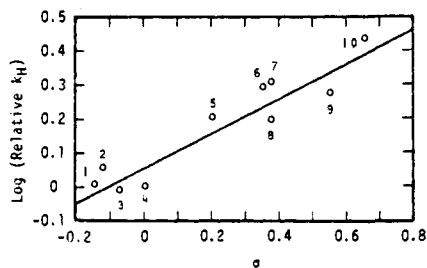


Figure 1. A Hammett plot of relative k_H values (eq 4) for the 1-undecyl radical vs. σ substituent constants. The numbers correspond to the entries in Table I.

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 R• with peroxide. However, this process can be neglected for [LP] = 0.01 M.^{12d,e}

Acknowledgment. The authors wish to thank Professor W. A. Pryor and W. H. Davis, Jr., for many helpful discussions. This work was supported by a Faculty Research Grant from Francis Marion College.

References and Notes

- (1) Part I. R. W. Henderson and R. Ward, Jr., Abstracts of Papers, Southeastern Regional American Chemical Society Meeting, Charleston, S.C., Nov 1973, No. 384.
- (2) C. Walling, "Free Radicals in Solution," Wiley, New York, N.Y., 1957, pp 132-140, 365-369, 375-376, 474-491.
- (3) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N.Y., 1966, p 170 ff.
- (4) R. Breslow, "Organic Reaction Mechanisms," 2nd ed, W. A. Benjamin, New York, N.Y., 1969, pp 235-242.
- (5) K. U. Ingold and B. P. Roberts, "Free-Radical Substitution Reactions," Wiley-Interscience, New York, N.Y., 1971, p 158.
- (6) G. A. Russell in "Free Radicals," Vol. I, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 7.
- (7) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N.Y., 1963, pp 176-177, 185-187.
- (8) W. A. Pryor, T. H. Lin, J. P. Stanley, and R. W. Henderson, *J. Amer. Chem. Soc.*, **95**, 6993 (1973).
- (9) (a) I. B. Afanes'ev, *Russ. Chem. Rev.*, **40**, 216 (1971); (b) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).
- (10) A. A. Zavitsas, *J. Amer. Chem. Soc.*, **94**, 2779 (1972); A. A. Zavitsas and J. A. Pinto, *ibid.*, **94**, 7390 (1972); A. A. Zavitsas, *Chem. Tech.*, **434** (1972); see also J. D. Unruh and G. J. Gleicher, *J. Amer. Chem. Soc.*, **93**, 2008 (1971); R. B. Roark, J. M. Roberts, D. W. Croom, and R. D. Gilliom, *J. Org. Chem.*, **37**, 2042 (1972).
- (11) W. A. Pryor, W. H. Davis, Jr., and J. P. Stanley, *J. Amer. Chem. Soc.*, **95**, 4754 (1973).
- (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 R•, but do not produce RH or RCl, will not affect the kinetic expression derived (eq 6).
- (17) W. A. Pryor, U. Tonellato, D. Fuller, and S. Jumonville, *J. Org. Chem.*, **34**, 2018 (1969).
- (18) (a) W. A. Pryor, D. L. Fuller, and J. P. Stanley, *J. Amer. Chem. Soc.*, **94**, 1632 (1972), and references cited therein; (b) J. R. Shelton and C. Uzelmeier, *ibid.*, **88**, 5222 (1966); (c) S. H. Wilen and E. L. Eliel, *ibid.*, **80**, 3309 (1958); (d) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, New York, N.Y., 1960, Chapter 6.
- (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.

Richard W. Henderson,* R. D. Ward, Jr.²⁰

Department of Chemistry and Physics
Francis Marion College
Florence, South Carolina 29501

Received May 20, 1974

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-