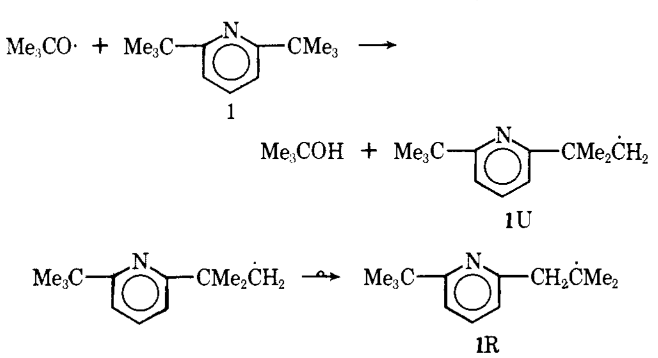
Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XXIV. Neophyl Rearrangements[1]

B. Maillard[2] and K. U. Ingold*

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Canada. *Received June 7, 1975*

Abstract: The rate constants for isomerization of 2-aryl-2-methylpropyl-1 to 1-aryl-2-methylpropyl-2 radicals have been measured by EPR spectroscopy over a range of temperatures. The radicals were derived by hydrogen abstraction from the following compounds: *tert*-butylbenzene, 1,3-di-*tert*-butylbenzene, 4-*tert*-butylpyridine, 2,6-di-*tert*-butylpyridine, and 2-*tert*-butylnaphthalene. The rates of isomerization of the radicals derived from the two pyridines and the naphthalene are significantly faster than the rates of isomerization of the radicals from the two benzenes.

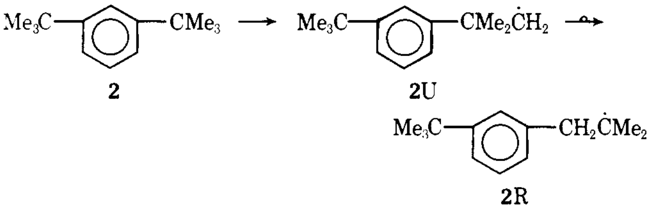
During the course of an EPR spectroscopic study of radical additions to hindered aromatic compounds,[3] we had cause to study the reaction of photochemically generated *tert*-butoxy radicals with 2,6-di-*tert*-butylpyridine (**1**). At room temperature, the predominant species was the rearranged tertiary alkyl radical **1R** rather than the unrearranged primary alkyl radical **1U** which must be formed initially.


1

1U

1R

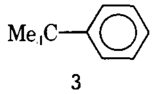
Under the same conditions, 1,3-di-*tert*-butylbenzene (**2**) gave predominantly the primary alkyl **2U** as we would expect on the basis of previous EPR studies on *tert*-butylbenzene (**3**).[4-8]

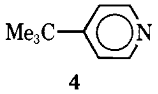

2

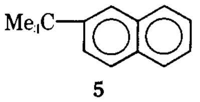
2U

2R

The more rapid "neophyl rearrangement"[9] of the pyridine intrigued us and prompted a careful kinetic EPR spectroscopic study of the rearrangements of the primary alkyl radicals derived from **1** and 4-*tert*-butylpyridine (**4**), and from **2** and *tert*-butylbenzene (**3**), and from 2-*tert*-butylnaphthalene (**5**).


3


4


5

The rearrangement of the primary alkyl derived from **3** (3U) has been studied previously by EPR by Hamilton and Fischer.[8] These workers generated the radical by the same procedure we have used, i.e., photolysis of di-*tert*-butyl peroxide solutions of the hydrocarbon.[4,10] However, they estimated only the activation energy for the rearrangement and did not measure the actual rate constants for this reaction. Some assumptions were also made in estimating this activation energy.

We[11a,12] and others[13,14] have shown that rate constants for radical isomerizations[11a] and β-scissions[12-14] can be quite readily obtained by EPR. Measurements of the concentration of unrearranged (U) and rearranged (R) radicals under steady-state conditions can yield the rate constant for isomerization of U (k_i) provided the radicals react according to the following scheme.[11-14]

$$\begin{array}{l} \mathrm{U} \xrightarrow{k_i} \mathrm{R} \\ \left.\begin{array}{l} \mathrm{U} + \mathrm{U} \xrightarrow{k_t^{\mathrm{U}}} \\ \mathrm{U} + \mathrm{R} \xrightarrow{k_t^{\mathrm{UR}}} \\ \mathrm{R} + \mathrm{R} \xrightarrow{k_t^{\mathrm{R}}} \end{array}\right\} \text{nonradical products} \end{array}$$

The usual steady-state treatment yields[11b]

$$\frac{1}{[\mathrm{R}]} = \frac{2k_t^{\mathrm{R}}[\mathrm{R}]}{k_i[\mathrm{U}]} + \frac{2k_t^{\mathrm{UR}}}{k_i}$$

Provided U and R are relatively unhindered and are of equal (or near equal) molecular weight, it can be safely assumed[15-17] that $k_t^{\mathrm{U}} = k_t^{\mathrm{UR}} = k_t^{\mathrm{R}}$. Therefore

$$\frac{k_i}{2k_t^{\mathrm{R}}} = \frac{[\mathrm{R}]}{[\mathrm{U}]}([\mathrm{R}] + [\mathrm{U}]) \qquad (1)$$

and so k_i can be calculated provided k_t^{R} is measured.

Experimental Section

Commercially available materials were purified by normal procedures before use.

Solutions of the aromatic compounds in di-*tert*-butyl peroxide (2:3 v/v) were carefully degassed and were then photolyzed in the cavity of a Varian E-4 EPR spectrometer. After 15-20 min photolysis, the alkylpyridine solutions started to yellow and the radical concentrations decreased. Each measurement was therefore made on a fresh sample drawn from the same stock solution and using the same EPR tube. Relative concentrations of the U and R radicals were determined by double integration (by hand) of appropriate lines in the first derivative EPR spectrum. Overlap of U and R lines caused some problems, particularly with **5** and with **2** and **3** at low temperatures. However, some R lines never overlapped, and so U could be determined by difference from an overlapping region of the spectrum. Absolute radical concentrations were calibrated against DPPH.[18] The kinetic EPR technique has been described previously.[12,15,18]

Results

EPR Spectra. The EPR spectral parameters of the unrearranged and rearranged radicals derived from **1, 2, 3, 4,** and **5** are given in Table I.

Table I. EPR Parameters for the Primary and Tertiary Alkyl Radicals Derived from *tert*-Butyl Substituted Benzenes and Pyridines

Radical	Temp, °C	g	a^H, gauss
1U	−45	2.0024	21.58 (2 H); 0.80 (6 H)
1R	40	2.0028	16.83 (2 H); 22.92 (6 H)
2U	−20	2.0025	21.72 (2 H); 1.01 (6 H)
2R	90	2.0026	18.60 (2 H); 22.66 (6 H)
3U[a]	−36	2.0027	21.85 (2 H); 1.02 (6 H)
3R[a]	90	2.0027	18.80 (2 H); 22.87 (6 H)
4U	−45	2.0024	22.10 (2 H); 0.94 (6 H)
4R	40	2.0027	17.71 (2 H); 23.01 (6 H)
5U	−70	2.0025	21.71 (2 H); 1.02 (6 H)
5R	50	2.0031	18.44 (2 H); 22.75 (6 H)

[a] Reference 8.

Table II. Determination of $k_i/2k_t^R$ for *tert*-Butylpyridines 1 and 4 (Concentrations in M Units)

	1			4		
Temp, °K	[1U] $\times 10^7$	[1R] $\times 10^7$	$k_i/2k_t^R$ $\times 10^7$	[4U] $\times 10^7$	[4R] $\times 10^7$	$k_i/2k_t^R$ $\times 10^7$
235	5.26	0.06	0.06	0.97	0.18	0.21
246	1.82	0.22	0.42	0.77	0.25	0.33
254	2.72	0.34	0.38	0.70	0.45	0.74
273	2.32	0.70	0.91	0.65	0.90	2.15
284	1.12	0.57	0.86	0.37	0.74	2.22
291	0.92	0.92	1.9	0.41	1.02	3.56

Table III. Determination of $k_i/2k_t^R$ for *tert*-Butylbenzenes 2 and 3 (Concentrations in M Units)

	2			3		
Temp, °K	[2U] $\times 10^7$	[2R] $\times 10^7$	$k_i/2k_t^R$ $\times 10^7$	[3U] $\times 10^7$	[3R] $\times 10^7$	$k_i/2k_t^R$ $\times 10^7$
283	2.42	0.16	0.17	1.71	0.07	0.07
288	2.41	0.13	0.14	1.06	0.15	0.17
293	1.75	0.22	0.25	1.79	0.18	0.20
298	1.65	0.30	0.36	1.09	0.29	0.37
303	1.34	0.44	0.58	1.08	0.41	0.57
307	1.10	0.46	0.65	0.92	0.30	0.40

Table IV. Determination of $k_i/2k_t^R$ for 2-*tert*-Butylnaphthalene (Concentrations in M Units)

Temp, °K	[5U] $\times 10^7$	[5R] $\times 10^7$	$k_i/2k_t^R \times 10^7$
237	0.67	0.90	2.1
248	0.46	0.73	1.9
256	0.32	0.83	3.0

Table V. Rate Constants for the Bimolecular Self-Reaction of 2U

Temp, °K	$2k_t \times 10^{-8}$, M^{-1} s^{-1}
232	1.5
242	2.7
250	3.5
269	8.0
279	12
287	14
289	15
298	18

Steady-State Measurements. The experimental data used to determine $k_i/2k_t^R$ via eq 1 for the isomerization of **1U** and **4U** are given in Table II and for the isomerization of **2U** and **3U** in Table III. The variations of $k_i/2k_t^R$ with temperature can be represented by

$$\mathbf{1U}: \log (k_i/2k_t^R/M) = (1.4 \pm 0.8) - (6.8 \pm 1.0)/\theta \tag{2}$$

$$\mathbf{4U}: \log (k_i/2k_t^R/M) = (1.3 \pm 0.5) - (6.6 \pm 0.5)/\theta \tag{3}$$

$$\mathbf{2U}: \log (k_i/2k_t^R/M) = -(1.1 \pm 1.3) - (11.7 \pm 1.8)/\theta \tag{4}$$

$$\mathbf{3U}: \log (k_i/2k_t^R/M) = -(2.9 \pm 2.3) - (14.2 \pm 2.9)/\theta \tag{5}$$

where $\theta = 2.3RT$ kcal/mol, and the error limits are standard deviations which probably do not reflect our true errors. For **2U** and **3U**, the errors in the determination of the individual $k_i/2k_t^R$ values are rather greater than for **1U** and **4U**. This is a consequence of the greater overlap of the U and R radicals' spectra (see Experimental Section) and of the low [R]/[U] ratio produced by the necessity to eliminate potential problems arising from methyl radicals.[17] The errors in the Arrhenius parameters for the isomerization of **2U** and **3U** are also greater than for **1U** and **4U** because of the smaller range of temperatures that could be safely covered with these radicals. It was only possible to measure $k_i/2k_t$ for **5U** over a 20° temperature range because of the overlap of the **5U** and **5R** spectra (Table IV).

Kinetic Measurements. We chose to determine $2k_t^R$ using **2U**. Although this is an unrearranged radical, its mass and size are similar to those of the rearranged radicals that we are interested in. It is therefore safe to assume[15-17] that the rate constants for bimolecular decay of **2U** and all the rearranged radicals are similar. Values of $(2k_t)_{2U}$ were determined by kinetic EPR spectroscopy[12,15,18] under conditions identical with those of the steady-state measurements. Even at the highest temperatures employed, the corrections for the **2U** → **2R** isomerization and for the **2U** + **2R** reaction were probably less than the errors involved in determining $2k_t$, and so they were not applied. Values of $2k_t$ given in Table V can be represented by

$$\log (2k_t/M^{-1}\ \mathrm{s}^{-1})_{2U} = 13.1(\pm 0.3) - 5.2(\pm 0.3)/\theta \tag{6}$$

where the error limits are again standard deviations which do not reflect our real potential errors. The apparent activation energy for this reaction, which we presume is diffusion controlled, is about twice as large as the activation energy that would be calculated from the temperature coefficient of the solution's macroscopic viscosity. High (ca. 5 kcal) values for E_t have been reported previously for Me_2COH in Me_2CHOH[19] and for cyclopentylmethyl in a mixed solvent,[11a] but lower E_t values are more common[20] and more believable. While we do not understand (and therefore remain somewhat suspicious of) eq 6, we believe it is the most appropriate equation to combine with eq 2–5 in order to obtain Arrhenius parameters for the neophyl rearrangements.

Discussion

Estimations of the rate constants for radical-molecule reactions can be greatly assisted by a knowledge of the rate constants for the irreversible isomerization of an appropriate radical.[21] This is the second[23] of a planned series of papers on the rates of irreversible isomerization of alkyl radicals. The radicals have been chosen to cover as wide a range of k_i values as possible in order to maximize their utility in other systems. The neophyl rearrangements reported herein are the slowest isomerizations that could be conveniently studied by EPR techniques.

The isomerization of **4U** may be somewhat faster than the isomerization of **1U**, but the difference is probably within our true experimental error. Combination of eq 2 and 6 yields

$$\log (k_i/\mathrm{s}^{-1}) = (11.7 \pm 1.1) - (12.0 \pm 1.3)/\theta$$

$$k_i = 8 \times 10^2\ \mathrm{s}^{-1} \text{ at } 25° \text{ for } \mathbf{1U}$$

Combination of eq 3 and 6 yields

$$\log (k_i/\mathrm{s}^{-1}) = (11.8 \pm 0.8) - (11.8 \pm 0.8)/\theta$$

$$k_i = 1.4 \times 10^3\ \mathrm{s}^{-1} \text{ at } 25° \text{ for } \mathbf{4U}$$

The isomerizations of **2U** and **3U** proceed at equal rates. Since the errors involved in determining $k_i/2k_t$ for these two radicals were larger than for **1U** and **4U** (see above), we have made the reasonable assumption that the preexponential factors for isomerization of **2U** and **3U** are equal to the mean of the values found for **1U** and **4U**. With this assumption, we obtain

$$\log (k_i/\mathrm{s}^{-1}) = (11.7_5 \pm 1.0) - (13.6 \pm 1.0)/\theta$$

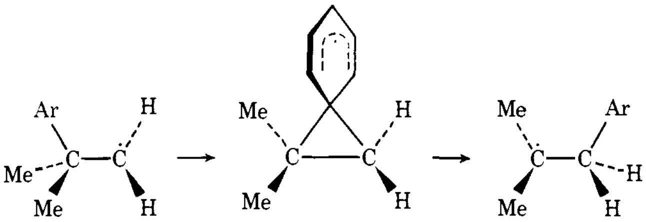
$$k_i = 59\ \mathrm{s}^{-1} \text{ at } 25° \text{ for } \mathbf{2U} \text{ and } \mathbf{3U}$$

For **5U** we again assume the preexponential factor for isomerization is $10^{11.75}$ and obtain

$$\log (k_i/\mathrm{s}^{-1}) = (11.7_5 \pm 1.0) - (11.3 \pm 1.0)/\theta$$

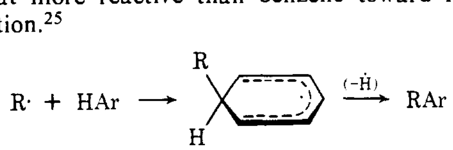
$$k_i = 2.9 \times 10^3\ \mathrm{s}^{-1} \text{ at } 25° \text{ for } \mathbf{5U}$$

The activation energy for isomerization of the "parent" neophyl radical, **3U**, is somewhat higher than the value of 10.3 ± 2.2 kcal/mol reported by Hamilton and Fischer.[8] However, all these isomerizations probably proceed via a cyclohexadienyl-like transition state.[9]



For such a process, we estimate[24] that, in the transition state, the radical will have lost about 8 gibbs/mol by the loss of two rotational degrees of freedom and will have gained about 2 gibbs/mol from changes in various vibrational frequencies. The calculated A factor for these isomerizations at the mean temperature of our experiments is, therefore, $10^{13.1} - 10^{6/4.6} = 10^{11.8}\ M^{-1}\ \mathrm{sec}^{-1}$. The agreement between this estimate and our experimental value (for the butylpyridines) implies that our rate constants and activation energies are reasonably reliable.

The higher rates of isomerization of the pyridines and the naphthalene can also be rationalized in terms of a cyclohexadienyl-like transition state since both compounds are somewhat more reactive than benzene toward homolytic substitution.[25]



Thus, the partial rate factors[26] for the phenylation of pyridine at the 2, 3, and 4 positions are 1.83, 1.0, and 1.18, respectively,[27] and those for methylation are about 3.1, 1.0, and 1.7.[28] The partial rate factor for the phenylation of naphthalene at the 2-position is 1.43.[29] In view of these rate factors, we were somewhat surprised that we could not detect any really significant difference in the rates of isomerization of **1U** and **4U**. However, the measured partial rate factors may not accurately reflect differences in the reactivities of the pyridine ring positions since the molecular products of substitution may be formed with varying efficiencies from the intermediate cyclohexadienyl radicals.

References and Notes

(1) Issued as NRCC No. 15171. Part XXIII: R. A. Kaba and K. U. Ingold, *J. Am. Chem. Soc.*, in press.

(2) NATO Fellow 1974–1975. Permanent address: Laboratoire de Chimie Appliquée, Université de Bordeaux I, 33405 Talence, France.

(3) D. Griller, K. Dimroth, T. M. Fyles, and K. U. Ingold, *J. Am. Chem. Soc.*, **97**, 5526 (1975).

(4) A. Hudson and H. A. Hussain, *J. Chem. Soc. B*, 793 (1969).

(5) J. K. Kochi and P. J. Krusic, *J. Am. Chem. Soc.*, **91**, 3940 (1969).

(6) A. Ohno, N. Kito, and Y. Ohnishi, *Bull. Chem. Soc. Jpn.*, **44**, 470 (1971).

(7) D. J. Edge and J. K. Kochi, *J. Am. Chem. Soc.*, **94**, 7695 (1972).

(8) E. J. Hamilton, Jr., and H. Fischer, *Helv. Chim. Acta*, **56**, 795 (1973).

(9) J. W. Wilt in "Free Radicals", Vol. I., J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, pp 346–356.

(10) P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, **90**, 7155 (1968).

(11) (a) D. Lal, D. Griller, S. Husband, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 6355 (1974). (b) In this equation, $2k_t^{\mathrm{R}}$ appears because two R's are destroyed in each R + R reaction; $2k_t^{\mathrm{UR}}$ appears because the cross reaction is, for statistical reasons, twice as likely to occur as either self-reaction.

(12) G. B. Watts, D. Griller, and K. U. Ingold, *J. Am. Chem. Soc.*, **94**, 8784 (1972).

(13) D. Griller and B. P. Roberts, *Chem. Commun.*, 1035 (1971); *J. Chem. Soc., Perkin Trans. 2*, 747 (1972).

(14) A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 993 (1972).

(15) G. B. Watts and K. U. Ingold, *J. Am. Chem. Soc.*, **94**, 491 (1972).

(16) D. Griller and K. U. Ingold, *Int. J. Chem. Kinet.*, **6**, 453 (1974).

(17) This assumption is not valid for radicals of grossly different molecular weight.[15] The present work was therefore carried out at temperatures where methyl radical production (via the β-scission of $\mathrm{Me_3CO\cdot}$) was negligible. Since Hamilton and Fischer[8] worked at generally higher temperatures, part of the difference between their and our data on **3** may be due to problems arising from the greater rate of radical–radical reactions when one of the radicals is methyl.

(18) K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Am. Chem. Soc.*, **93**, 903 (1971).

(19) G. S. Hammond, E. J. Hamilton, Jr., S. A. Weiner, H. J. Hefter, and A. Gupta, *Proc. XXIII Int. Congr. Pure Appl. Chem., Spec. Lect.*, **4**, 257 (1971).

(20) H. J. Hefter, C. H. S. Wu, and G. S. Hammond, *J. Am. Chem. Soc.*, **95**, 851 (1973); H. Schuh and H. Fischer, private communication.

(21) The normal procedure[22] for determining k_a would involve analysis of the products UA and RA in a reaction system for which k_i was known and which was sufficiently simple to be represented by

$$\mathrm{U\cdot} \longrightarrow \mathrm{R\cdot} \qquad (k_i)$$

$$\mathrm{U\cdot} + \mathrm{AB} \rightarrow \mathrm{UA} + \mathrm{B\cdot} \qquad (k_a)$$

$$\mathrm{R\cdot} + \mathrm{AB} \rightarrow \mathrm{RA} + \mathrm{B\cdot}$$

(22) See, e.g., K. U. Ingold in "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 2.

(23) The first is ref 11a.

(24) See, S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968.

(25) See e.g., G. H. Williams, "Homolytic Aromatic Substitution", Pergamon, Oxford, 1960; D. C. Nonhebel and J. C. Walton "Free Radical Chemistry", Cambridge University Press, New York, N.Y., 1974, Chapter 11.

(26) Statistically corrected reactivities relative to benzene.

(27) G. Vernin, H. J. M. Dou, L. Bouscasse, and J. Metzger, *Bull. Soc. Chim. Fr.*, 3387 (1967).

(28) R. A. Abramovitch and K. Kenashuk, *Can. J. Chem.*, **45**, 509 (1967).

(29) See M. J. Perkins in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, p 245.