The additional compounds listed in Table VI are shown to illustrate the difficulties, not to advocate the usefulness of this scheme for the calculation of such quantities. The very large errors here (1-3 kcal/mol) are discouraging. We are unable to decide at present why these numbers are as poor as they are. The point we wish to make is that for simple compounds (containing one oxygen) the heat of formation calculations look to be nearly as reliable as they are for hydrocarbons, although the number and types of compounds investigated have been much less (because of a lack of experimental data for comparison). However, when there are two oxygens in the molecule, the results are best described as poor. Presumably they can be improved, although whether they can be really made adequate or not is not clear at this time. The reasons for the difficulty here are uncertain, but are likely to involve, at least in part, the electrostatics of the molecules. The reliability of the experimental data is also far from certain. For one thing, the heats of vaporization of the molecules are often estimated and the reliability of such estimates for these kinds of compounds is completely unknown.

References and Notes

(1) For paper 117, see N. L. Allinger, J. Kao, H, Chang, and D. B. Boyd, *Tetrahedron*, in press.
(2) This was supported in part by the grant AM-14042 from the National Institutes of Health, Institute of Arthritic and Metabolic Diseases.
(3) For reviews, see: (a) J. E. Williams, P. J. Stang, and P. v. R. Schleyer, *Annu. Rev. Phys. Chem.*, **19**, 531 (1968); (b) C. Altona and D. H. Faber, *Top. Curr. Chem.*, **45**, 1 (1974); (c) N. L. Allinger, *Advan. Phys. Org. Chem.*, **13**, 1 (1976).
(4) N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *J. Am. Chem. Soc.*, **91**, 337 (1969).
(5) D. H. Wertz and N. L. Allinger, *Tetrahedron*, **30**, 1579 (1974). The program used for the calculations herein (MMI) has been submitted to the QCPE, University of Indiana, Bloomington, Indiana.
(6) R. G. Snyder and G. Zerbi, *Spectrochim. Acta, Part A*, **23**, 391 (1967); P. Labarbe, M. T. Forel, and G. Bessis, *ibid.*, **24**, 2165 (1968).
(7) N. L. Allinger and M. J. Hickey, *J. Am. Chem. Soc.*, **97**, 5167 (1975).
(8) M. A. Robb, W. J. Haines, and I. G. Csizmadia, *J. Am. Chem. Soc.*, **95**, 42 (1973).
(9) A. L. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, Calif., 1963.
(10) J. Lehn and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1113 (1963).
(11) M. Wuesthoff and L. Dosen-Micovic, unpublished work.
(12) See, for example, R. J. Abraham and Z. L. Rossetti, *J. Chem. Soc., Perkin Trans. 2*, 582 (1973).
(13) U. Blukis, P. H. Kasai, and R. J. Myers, *J. Chem. Phys.*, **38**, 2753 (1963).
(14) L. Pierce and M. Hayashi, *Spectrochim. Acta*, **18**, 1370 (1962).
(15) (a) A. J. deKok and C. Romers, *Recl. Trav. Chim. Pays Bas*, **89**, 313 (1970); (b) G. Schultz and I. Hargittai, *Acta Chim. Acad. Sci. Hung.*, **83**, 331 (1974).
(16) R. M. Lees and J. G. Baker, *J. Chem. Phys.*, **48**, 5299 (1968).
(17) A. J. de Hoog, H. R. Buys, C. Altona, and E. Havinga, *tetrahedron*, **25**, 3365 (1969).
(18) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Wiley-Interscience, New York, N.Y., 1965, p 376.
(19) (a) N. L. Allinger, J. C. Tai, and M. A. Miller, *J. Am. Chem. Soc.*, **88** 4495 (1966); (b) C. C. Levin, R. Hoffmann, W. J. Hehre, and J. Hudec, *J. Chem. Soc., Perkin Trans. 2*, 210 (1973).
(20) Reference 18, p 253.
(20a) It has been concluded independently earlier from ab initio calculations (G. A. Jeffrey, J. A. Pople, and L. Radom, *Carbohydr. Res.*, **25**, 117 (1972)) that a twofold barrier with this approximate height and orientation exists in methanediol and related compounds such as here. Although the details of the interaction were cast in a different form, they in fact correspond closely to what has been deduced in the present work. We are grateful to Dr. W. F. Bailey for calling our attention to this work.
(21) H. Wieser, W. G. Laidlaw, R. J. Krueger, and H. Fuhrer, *Spectrochim. Acta*, **24**, 1055 (1968).
(22) K. Aoki, *J. Chem. Soc. Jpn.*, **74**, 110 (1953).
(23) E. E. Astrup, *Acta Chem. Scand.*, **25**, 1494 (1971).
(24) E. L. Eliel and E. C. Gilbert, *J. Am. Chem. Soc.*, **91**, 5487 (1969).
(25) R. M. Clay, G. M. Kellie, and F. G. Riddell, *J. Am. Chem. Soc.*, **95**, 4632 (1973).
(26) F. G. Riddell and M. J. T. Robinson, *Tetrahedron*, **23**, 3417 (1967).
(27) E. L. Eliel and M. C. Knoeber, *J. Am. Chem. Soc.*, **90**, 3444 (1968).
(28) K. Pihlaja and J. Heikkila, *Acta Chem. Scand.*, **21**, 2390, 2430 (1967).
(29) E. L. Eliel, *Acc. Chem. Res.*, **3**, 1 (1970).
(30) E. L. Eliel, W. F. Bailey, H. Connon, K. B. Wiberg, and F. W. Nader, *Justus Liebigs Ann. Chem.*, in press.
(31) G. M. Kellie and F. G. Riddell, *Top. Stereochem.*, **8**, 225 (1974).
(32) (a) A. Almenningen, H. M. Seip, and T. Willadsen, *Acta Chem., Scand.*, **23**, 2748 (1969); (b) C. W. N. Cumper and A. I. Vogel, *J. Chem. Soc.*, 3521 (1959); (c) J. A. Greenhouse and H. L. Strauss, *J. Chem. Phys.*, **50**, 124 (1969).
(33) R. M. Moriarty, *Top. Stereochem.*, **8**, 271 (1974).
(34) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970.

Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. 26. Quantum-Mechanical Tunneling in the Isomerization of Sterically Hindered Aryl Radicals[1]

G. Brunton,[2] D. Griller,[3] L. R. C. Barclay,[4] and K. U. Ingold*

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada.

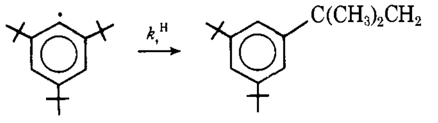
Received March 1, 1976

Abstract: Rate constants for the isomerization of 2,4,6-tri-*tert*-butylphenyl to 3,5-di-*tert*-butylneophyl have been measured from −26 to −160 °C, and for the corresponding isomerization of 2,4,6-tri-*tert*-(perdeuteriobutyl)phenyl from 20 to −150 °C. This pair of reactions has an exceptionally large deuterium kinetic isotope effect at all temperatures. Arrhenius plots for both reactions are nonlinear and over any range of temperature the activation energy and Arrhenius preexponential factor are much larger for deuterium than for hydrogen transfer. The experimental results can be quantitatively accounted for by quantum-mechanical tunneling through a potential barrier. The analogous isomerization of 2,4,6-tri(1′-adamantyl)phenyl, which was studied from −28 to −167 °C, also occurs by quantum-mechanical tunneling. Attempts to detect other aryl radicals by EPR spectroscopy are described.

Phenyl is a destabilized[5] σ radical[6-8] which is highly reactive both in atom abstractions and in additions to unsaturated molecules. It therefore has only a transitory existence under most conditions. For this reason, attempts to detect phenyl and other aryl radicals in solution by physical methods have not met with much success.[9] Prior to the preliminary account of the present work,[10] only two aryls had been detected in solution by EPR spectroscopy.[11] These two radicals [o-$CH_3OC(O)C_6H_4\cdot$ and o-$(CH_3)_2NC(O)C_6H_4\cdot$] were generated by rapid reduction of the appropriate arenediazonium ion with

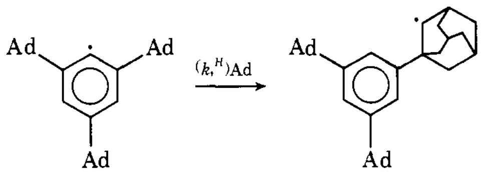
Ti^{III} in an aqueous flow system. More recently, a number of other aryls have been detected by EPR in aqueous media.[12] These radicals were generated either by reaction of radiolytically produced e_{aq}^- with aryl bromide or by reaction of photochemically produced $SO_4\cdot^-$ with arylcarboxylic acids.

Recent work from this laboratory has shown that the lifetimes of many types of free radicals can be dramatically increased by surrounding the radical center with bulky substituents.[1,5] Phenyl is no exception. In this paper we present the results of detailed kinetic studies of the intramolecular rearrangement of 2,4,6-tri-*tert*-butylphenyl (**1**) to 3,5-di-*tert*-butylneophyl (**2**) and of the corresponding isomerization of 2,4,6-tri(1′-adamantyl)phenyl)**3**). We also discuss our attempts to detect other aryl radicals.



(1)

1 **2**



(2)

3 **4**

Experimental Section

The techniques of kinetic EPR spectroscopy have been described in previous papers in this series.[1]

Materials. 1,3,5-Tri-*tert*-(perdeuteriobutyl)benzene was prepared from benzene and perdeuterio-*tert*-butyl chloride (Merck Sharpe and Dohme, Ltd.) by a modification of the direct alkylation procedure.[13] The deuterium content of the *tert*-butyl groups was estimated to be somewhat greater than 99% by comparison of the integrals of the proton NMR signals in the *tert*-butyl region (δ 1.34) and in the aryl region (δ 7.37). This hydrocarbon and its undeuterated counterpart were converted to the corresponding 2,4,6-tri-*tert*-butylbromobenzenes by the silver-induced ("neutral" conditions) method of Myhre, Owen, and James.[14]

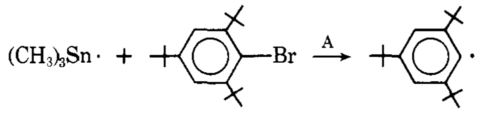
2,5-Di-*tert*-butylbromobenzene was prepared as previously described.[15]

1,3,5-Tri(1′-adamantyl)benzene was prepared by Friedel-Crafts alkylation of benzene with 1-adamantyl bromide in liquid sulfur dioxide and isolated by the procedure of Rundel.[16a] The hydrocarbon was brominated as previously described[16b] and was separated by repetitive thin layer chromatography on silica gel using cyclohexane eluant. The bromo compound showed the characteristic two peaks for parent ions at *m/e* 558 and 560, as expected for $C_{36}H_{47}Br$.

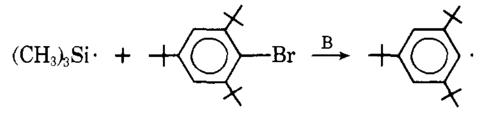
tert-Butyl-2,4,6-tri-*tert*-butyl perbenzoate and *tert*-butyl-2,4,6-trimethyl perbenzoate were gifts from Professor T. T. Tidwell. 1-Bromo-, 1-iodo-, and 1,3,5-tribromo-2,4,6-trineopentylbenzenes were originally prepared by Dr. K. Olsson.[17] They were a gift to us from Dr. R. E. Carter. All other compounds were commercially available materials which were used as received.

Results

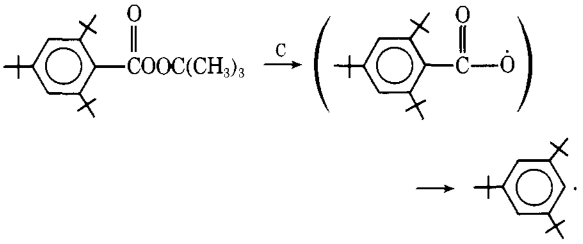
EPR Spectral Parameters of 1 and 2. As previously reported,[10] an EPR spectrum which we assign to 2,4,6-tri-*tert*-butylphenyl (**1**) is produced by in situ photolysis of 2,4,6-tri-*tert*-butylbromobenzene in cyclopropane at temperatures ≤0 °C in the presence of hexamethylditin (method A) or of a mixture of trimethylsilane and di-*tert*-butyl peroxide (method B). This radical is also produced by photolysis of *tert*-butyl 2,4,6-tri-*tert*-butylperbenzoate (method C).[18]



(3)



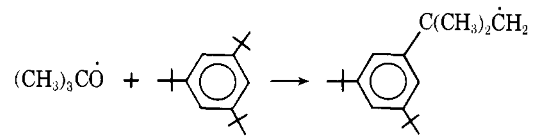
(4)



(5)

For optimum resolution, the spectrum of **1** is best measured at low microwave power (≤0.2 mW) and low modulation amplitude (ca. 0.1 G). Its spectrum consists principally of a 1:2:1 triplet (a^H(meta) = 7.31 G, g = 2.002 38 at −40 °C) with further hyperfine splittings (hfs) from the ortho *tert*-butyl protons (a^H(18 H) = 0.298 G). The spectrum is sufficiently intense to resolve hfs due to ^{13}C in natural abundance at the α (122.5 G), ortho (6.16 G), and meta (14.52 G) positions. These ^{13}C hfs are in good agreement with those calculated for the unsubstituted phenyl radical.[10,19] A similar spectrum with a^D = 0.047 G is obtained for the radical with the fully deuterated *tert*-butyl groups. For this radical the ^{13}C hfs due to the methyl carbons of the ortho-tertiary groups (2.02 G) could also be resolved.

At higher microwave power levels a second radical becomes visible at ambient and lower temperatures. The EPR spectral parameters for this radical (a^H(2 H) = 21.70 G, a^H(6 H) = 1.02 G, g = 2.002 48 at 0 °C) indicate that it is 3,5-di-*tert*-butylneophyl (**2**).[20,21] The same radical can be produced by photolysis of a di-*tert*-butyl peroxide solution of 2,4,6-tri-*tert*-butylbenzene.[10,21]



(6)

2

Kinetics of the 2,4,6-Tri-*tert*-butylphenyl Isomerization. The decay of **1** was monitored directly by kinetic EPR spectroscopy. Decay occurs with "clean" first-order kinetics under all conditions. In solvents such as propane, cyclopropane, isopentane, and toluene, the rates of decay were identical for **1** generated from aryl bromide and $Me_3Sn\cdot$ radicals (method A), from the *tert*-butyl perester (method C), and from aryl bromide and $Me_3Si\cdot$ radicals (method B) at high but not at low temperatures. The 2,4,6-tri-*tert*-(perdeuteriobutyl)phenyl radical generated by methods A and B also decays with clean first-order kinetics in cyclopropane and in isopentane. However, with method B, the rate of decay was significantly faster at low temperatures than with method A. We presume the reaction being monitored using **1** generated by methods A and C is the isomerization to the neophyl radical, **2**, and that the analogous isomerization is being monitored when deuterated **1** is generated by method A. However, when the phenyl or deuterated phenyl are generated by method B, the abstraction of hydrogen from the silane by the phenyl radical can become competitive with the isomerization. The measured rate constants for these two reactions, k_r^H and k_r^D, are listed in Table I.

Strong evidence in support of our presumption that the reaction being monitored is, in fact, the isomerization comes from studies under steady-state conditions. Under steady illumination, the concentration ratio [**2**]/[**1**] decreases with decreasing temperature and with increasing light intensity. At

Table I. Rate Constants for the Isomerization of 2,4,6-Tri-*tert*-butylphenyl and 2,4,6-Tri-*tert*-(perdeuteriobutyl)phenyl

T, °K[a]	log k_i^{H}, s^{-1}	T, °K[b]	log k_i^{D}, s^{-1}
247 (A)	1.28	293	1.00
247 (A)	1.23	290	0.43
245 (B)	1.29[c]	289	0.58
245 (C)	1.25	278	0.20
227 (A)	1.03	278	0.15
226 (C)	0.79	274	0.05
207 (A)	0.33	268	0.02
206 (C)	0.32	258	−0.34
187 (A)	0.08	257	−0.42
187 (A)	−0.03	253	−0.36
186 (C)	−0.17	237	−1.00
183 (C)	−0.21	233	−0.99
173 (C)	−0.46	214	−1.94
173 (C)	−0.49	194	−2.85
165 (B)	0.26[c]	175	−3.49
163 (C)	−0.64	156	−4.23
153 (C)	−0.70	143[d]	−3.5[c]
143 (C)	−0.92	143	−4.65
133 (C)	−1.00	123	−5.30
123 (C)	−1.20		
118 (C)	−1.20		
113 (C)	−1.38		

[a] Method of radical generation is in parentheses. [b] Radicals generated by method A unless otherwise noted. [c] Data not plotted in Figures 5, 6, and 7. [d] Method B.

any particular temperature below 0 °C the concentration of **1** is proportional to the first power of the light intensity and the concentration of **2** is proportional to the square root of the light intensity. These results indicate that **1** isomerizes to **2** and that **2** decays by dimerization.[22]

$$\mathbf{1} \xrightarrow{k_i^{\mathrm{H}}} \mathbf{2}$$

$$\mathbf{22} \xrightarrow{2k_t} (\mathbf{2})_2$$

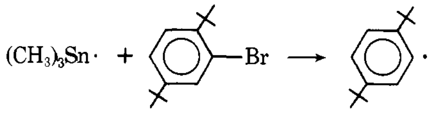
For such a simple set of reactions the usual steady-state treatment yields the relation[21,23-26]

$$1/[\mathbf{2}] = 2k_t[\mathbf{2}]/k_i^{\mathrm{H}}[\mathbf{1}]$$

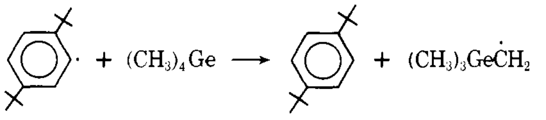
The absolute concentrations of **1** and **2** can be measured over a limited range of temperatures. This allows k_i^{H} to be determined in terms of $2k_t$ at the temperature (−30 °C) where the concentrations of **1** and **2** can be measured most accurately. Similarly k_i^{D} can be determined in terms of $2k_t$ at the optimum temperature (20 °C) for measuring the concentrations of the two deuterated radicals. We have previously measured $2k_t$ for the bimolecular coupling of 3-*tert*-butylneophyl radicals.[21] Since this radical and **2**, as well as deuterated **2**, are all expected to dimerize at essentially the same rate, we can determine k_i^{H} and k_i^{D} by this indirect procedure. The results given in Table II are in excellent agreement with the values of k_i^{H} and k_i^{D} measured directly. The direct measurements *must*, therefore, refer to the intramolecular hydrogen or deuterium transfer.

Attempts to Detect Other Aryl Radicals. Reaction of 2,4,6-tri(1′-adamantyl)bromobenzene with $\mathrm{Me_3Sn\cdot}$ or $\mathrm{Me_3Si\cdot}$ radicals gave the desired 2,4,6-tri(1′-adamantyl)phenyl (**3**), g = 2.002 27, a^{H}(2 H) = 7.1 G at −120 °C, with no additional fine structure being resolvable (ΔH_{pp} = 1.2 G, optimum microwave power ca. 1.0 mW). This radical decayed with clean first-order kinetics in the temperature range −28 to −167 °C. Rate constants, $(k_i^{\mathrm{H}})_{\mathrm{Ad}}$, for decay of **3** generated by method A are given in Table III. We presume the reaction being monitored is the intramolecular hydrogen transfer from the 2′ position of an ortho adamantyl group, i.e., reaction 2. The expected isomerized radical, **4**, could not be detected at any temperature, probably because it would have a very large number of individual EPR lines which would make its detection extremely difficult. To our surprise, radical **3** is more persistent than **1** at all temperatures studied.

No radicals could be detected when trimethyltin radicals were reacted with 2,5-di-*tert*-butylbromobenzene in cyclopropane at temperatures from 20 to −90 °C. Since there was no reason to suppose that the bromine would not be abstracted, it appeared likely that the 2,5-di-*tert*-butylphenyl, which is relatively unhindered, was being destroyed by rapid intermolecular reactions with the reagents and solvent. This was confirmed by adding tetramethylgermane[27] (1:1 v/v relative to the bromobenzene) to the reaction system. Upon photolysis at 20 °C the trimethylgermylmethyl radical was readily detected. It can only have been formed by the reaction sequence:



(7)



(8)

Our failure to detect any radicals in the absence of the germane can probably be attributed to the formation of several different radicals, none of which had sufficiently sharp lines for them to be observed at low concentrations.

The reaction of trimethyltin with 1-bromo-, 1-iodo-, and 1,3,5-tribromo-2,4,6-trineopentylbenzene at temperatures from 20 to −160 °C gave, in each case, only a neopentyl-type radical (a^{H}(2 H) = 21.5 G, a^{H}(multiplet of ≥7 lines) = 1.00 G at 20 °C). The addition of tetramethylgermane[27] to these reactions did not affect the intensity of the neopentyl-type radicals, nor were any $\mathrm{(CH_3)_3Ge\dot{C}H_2}$ radicals detectable. This implies that the initially formed phenyl radicals undergo an intramolecular isomerization via a six-membered cyclic transition state, i.e.

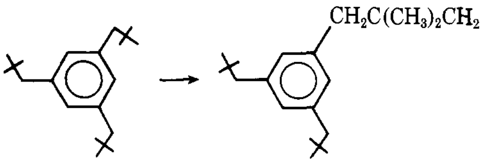
Table II. Comparison of Direct Decay and Steady Illumination Methods for Determining k_i^{H} and k_i^{D} for 2,4,6-Tri-*tert*-butylphenyl

1	T, °C	[**1**] × 10^7, M	[**2**] × 10^7, M	$2k_t$ × 10^{-8}, M^{-1} s^{-1} [a]	log k_i
Steady state (A)[b]	−30	8.4	2.1	2.6	1.14
Steady state (C)[b]	−30	4.7	1.9	2.6	1.30
Direct decay (C)[b]	−28				1.25
Deuterio-1					
Steady state (A)[b]	20	44.0	1.5_3	17.0	0.96
Direct decay (A)[b]	20				1.00

[a] From ref 21. [b] Method of radical formation.

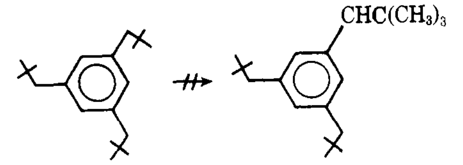
Table III. Rate Constants for the Isomerization of 2,4,6-Tri(1′-adamantyl)phenyl

T, °K	$\log (k_i^{H})_{Ad}$, s^{-1}	T, °K	$\log (k_i^{H})_{Ad}$, s^{-1}
245	0.05	166	−2.03
225	−0.76	147	−2.16
205	−1.15	147	−2.37
205	−1.28	136	−2.70
195	−1.24	126	−2.82
186	−1.45	116	−2.91
176	−1.58	106	−3.20



(9)

Since the trineopentylphenyl radical could not be detected even at −160 °C we must conclude that this intramolecular hydrogen transfer is very much faster than that which proceeds via a five-membered cyclic transition state in tri-*tert*-butylphenyl and triadamantylphenyl. Presumably ring strain effects are responsible for this difference, as well as for the fact that the trineopentylphenyls do not appear to undergo the more exothermic isomerization *via* a four-membered cyclic transition state to form a benzylic radical, i.e.,



(10)

No radicals could be detected when trimethyltin was allowed to react with 2,4,6-trimethylbromobenzene (20 to −160 °C) even in the presence of tetramethylgermane. The corresponding *tert*-butyl perester also gave no detectable concentration of radicals (20 to −160 °C) *unless* tetramethylgermane was added. (Of course, in this last experiment the $(CH_3)_3Ge\dot{C}H_2$ radicals may have been produced entirely via *tert*-butoxy attack on the germane.) Since we see no reason to suppose that trimethylphenyls were not produced in these reactions we can only suppose that our failure to detect radicals is, at least in part, a kinetic phenomenon. That is, EPR spectroscopy is not very sensitive toward benzylic radicals because these radicals have many lines and saturate at quite low levels of microwave power. In addition, unhindered benzylic radicals cannot reach high steady-state concentrations because they dimerize at the diffusion-controlled rate.[28] Therefore, if phenyls are produced slowly and are rapidly converted to benzyls we would be unable to detect any radicals. The phenyl to benzyl reaction might occur by an intramolecular process[29] or by an intermolecular process which is not intercepted by tetramethylgermane because of the greater reactivity of the benzylic hydrogens in the starting trimethylbromobenzene.

Attempts to Detect Benzoyloxy Radicals. The thermal decomposition of *tert*-butyl perbenzoate, *tert*-butyl 2,4,6-trimethylperbenzoate, and *tert*-butyl 2,4,6-tri-*tert*-butylperbenzoate all proceed through a rate-determining scission of the O-O bond.[18] Despite steric crowding in the last two compounds, the rates of decarboxylation of all three benzoyloxy radicals are similar.[18] It is, therefore, not unreasonable to suppose that all three benzoyloxys might be detectable by EPR spectroscopy at sufficiently low temperatures. However, it should first be noted that Edge and Kochi[30] could not detect benzoyloxy during the photolysis of *tert*-butyl perbenzoate in cyclopropane at −120 °C, though in the presence of ethylene the $C_6H_5CO_2CH_2\dot{C}H_2$ adduct radical was observed at this temperature (a^{H}(2 H) = 28.19, a^{H}(2 H) = 22.20 G, g = 2.002 57).

Photolysis of *tert*-butyl 2,4,6-tri-*tert*-butylperbenzoate in ethylene at −160 °C gave two radicals, one a fairly broad singlet (g = 2.0155) and the other a triplet of triplets (a^{H}(2 H) = 31.5, a^{H}(2 H) = 21.0 G, g = 2.0027). The singlet decayed when the light was cut off, but it could be regenerated in the dark by warming the sample to −120 °C. Cooling and warming the sample decreased and increased this signal in a reversible manner. However, it was permanently destroyed by a few minutes of continuous photolysis. This signal is almost certainly due to *tert*-butylperoxy[31-33] formed from *tert*-butoxy and residual traces of oxygen.

The other radical was not destroyed by prolonged photolysis. Its EPR parameters are characteristic of an adduct to ethylene,[30,34] $ArCH_2\dot{C}H_2$ (Ar = 2,4,6-tri-*tert*-butylbenzoyloxy or 2,4,6-tri-*tert*-butylphenyl), in which the Ar group lies in, or close to, the C_α $2p_z$ nodal plane.[35] Similar experiments in propane gave only the 2,4,6-tri-*tert*-butylphenyl radical (see above). Photolysis of the trimethylperbenzoate in ethylene at −160 °C also gave an adduct to ethylene (a^{H}(2 H) = 22.00, a^{H}(2 H) = 27.00 G, g = 2.0025) and $(CH_3)_3COO\cdot$, no radical being detected in propane at this temperature.

Recent CIDNP studies[36,37] have indicated that the rate constant for decarboxylation of benzoyloxy is much faster than was first estimated[38] (i.e., $\geq 10^8$ s^{-1} at 130 °C[36] and ca. 2.5×10^7 s^{-1} at room temperature[37]). Our failure to detect benzoyloxy radicals, even at −160 °C, may be due to rapid decarboxylation. However, it is worth noting that if this is the case, it implies that the preexponential factor for decarboxylation is less than the "normal" [39] value for a unimolecular bond scission (ca. 10^{13} s^{-1}). Alternatively, benzoyloxy radicals may not be readily detectable by EPR in solution[40] because of excessive line broadening.[41]

Discussion

The 2,4,6-Tri-*tert*-butylphenyl Isomerization. Evidence for Quantum-Mechanical Tunneling. There can be little doubt that tunneling is often involved in hydrogen atom and proton transfer reactions.[42] Unfortunately, kineticists have embraced the concept of tunneling so enthusiastically that it is frequently invoked on somewhat flimsy experimental evidence. Much of the evidence is capable of other interpretations[43] and relatively few "tunneling" reactions have received a rigorous examination.[44] If there is appreciable tunneling in a reaction, this will be indicated by the four kinetic phenomena listed below. The rearrangement of the 2,4,6-tri-*tert*-butylphenyl radical exhibits all of these phenomena, and so the reaction must involve hydrogen tunneling.

(1) Large Kinetic Isotope Effect. In the absence of tunneling, the kinetic isotope effect, k^{H}/k^{D}, arises from differences in the zero-point energies of the H and D containing reactants and their transition states.[42] The isotope effect will be maximized if all zero-point energy is lost in the transition state. In such a case, the difference in the zero-point energies of the H and D containing reactants will equal the difference in the activation energies for the two reactions, $E^{D} - E^{H}$. For the breaking of a C-H/C-D bond this activation energy difference is ≤1354 cal/mol provided the zero-point energies of *both* stretching *and* bending vibrations are lost in the transition state.[42e,50] Thus, for the simple rupture of a C-H/C-D bond the *maximum* possible values for k^{H}/k^{D} are 17, 53, and 260 at −30, −100, and −150 °C, respectively. Of course, in the 2,4,6-tri-*tert*-butylphenyl rearrangement there *could* be an additional contribution to k^{H}/k^{D} because of secondary deuterium isotope effects. However, these are always small, and we doubt if they could amount to more than a factor of 2 at −30 °C and 6 at −150 °C.[51]

If tunneling is allowed, then k^H/k^D values much greater than the "maximum possible" values estimated above are also allowed.[53] This is because the lighter hydrogen atom can tunnel (i.e., react) much more readily than a deuterium. The experimentally determined k^H/k^D ratios rise from 80 at −30 °C to 1400 at −100 °C and to 13 000 at −150 °C (see Figure 1). It is clear that these values are significantly larger than the "maximum possible" values. We therefore conclude that hydrogen atom tunneling is important in this reaction at all temperatures where measurements were made.

(2) Nonlinear Arrhenius Plots. Tunneling should become *relatively* more important as the reaction temperature is decreased. This should lead to positively curved Arrhenius plots, the curvature being more pronounced for H transfer than for D transfer. While curved Arrhenius plots are by no means uncommon in hydrogen atom transfers, the unbiased observer is more likely to attribute the curvature to experimental errors, or to a change in reaction mechanism, than to tunneling. In the present case, Arrhenius plots of the data in Table I show very distinct positive curvature for both the H and D transfers (see, e.g., Figures 5, 6, or 7). We believe that this curvature cannot be due to experimental error since the measured rate constants are highly reproducible. Furthermore, it seems unlikely that the curvature could be due to a change in mechanism since the rate constants do not depend on the solvent nor on the reaction used to generate the phenyl radical. In addition, there is satisfactory agreement between rate constants determined directly (by following phenyl radical decay) and indirectly (by steady-state measurements of the concentration of the phenyl and neophyl radical, see Results section). For these reasons, we believe that our curved Arrhenius plots indicate tunneling.

(3) Large Difference in the Activation Energies for H and for D Transfer. In the absence of tunneling, the maximum difference in the activation energy for H and for D transfer will be equal to the difference in the zero-point energy of the H and D containing reactants.[42] Appreciable tunneling should manifest itself as a larger difference in activation energies, i.e., $E^D - E^H > 1354$ cal/mol in this case (see 1 above). Because of curvature in our Arrhenius plots it is uncertain how $E^D - E^H$ should be measured. Thus, the "least-squares" straight line through all the H data gives $E^H = 2.5$ kcal/mol and that through all the D data gives $E^D = 6.4$ kcal/mol, while the tangent to curves through the experimental points at −30 °C (the highest temperature at which measurements were made on the undeuterated phenyl) gives $E^H = 6.2$ kcal/mol and $E^D = 9.4$ kcal/mol. It is clear that $E^D - E^H \gg 1.3$ kcal/mol, which again implicates tunneling in this reaction.

(4) Large Difference in the Preexponential Factors for H and for D Transfer. The limiting high temperature rate constants for H and D transfer at $T^{-1} = 0$ (which will equal the Arrhenius preexponential factors for linear Arrhenius plots) should be identical,[42b] or nearly so.[54] For our reaction, we can estimate by the usual methods[39] that this limiting rate constant should be $10^{11.5\pm0.5}$ s^{-1}. If we again draw the least-squares straight lines we obtain $A^H = 10^{3.1}$ s^{-1} and $A^D = 10^{5.1}$ s^{-1}, while the tangents at −30 °C give $A^H = 10^{6.5}$ s^{-1} and $A^D = 10^{7.5}$ s^{-1}. These low A factors and the small magnitude of A^H relative to A^D provide the final experimental evidence in favor of tunneling in this reaction.

Calculation of Tunneling Factors. In our opinion, some of the most dramatic (and hence some of the most convincing) demonstrations of tunneling are provided by Williams' studies of hydrogen atom abstractions by methyl radicals from acetonitrile,[55] methyl isocyanide,[56] and methanol[57] at low temperatures in the solid phase. The large isotope effects,[58] curved Arrhenius plot for methyl isocyanide, and low apparent activation energies and preexponential factors are all indicative of tunneling.[59] For the methyl radical–acetonitrile reaction, LeRoy, Sprague, and Williams[61] have shown that the experimental observations can be completely accounted for by a quantitative "tunneling" treatment. We have applied their methodology and their actual programs[61,62] for calculating tunneling "correction" factors to our own reactions with equally satisfactory results. The procedure, which is outlined briefly below, assumes that the passage of the system through the transition state can be described by the motion of a particle of constant mass along a single, separable, coordinate. That is, the multidimensional reaction surface is treated as a one-dimensional problem.

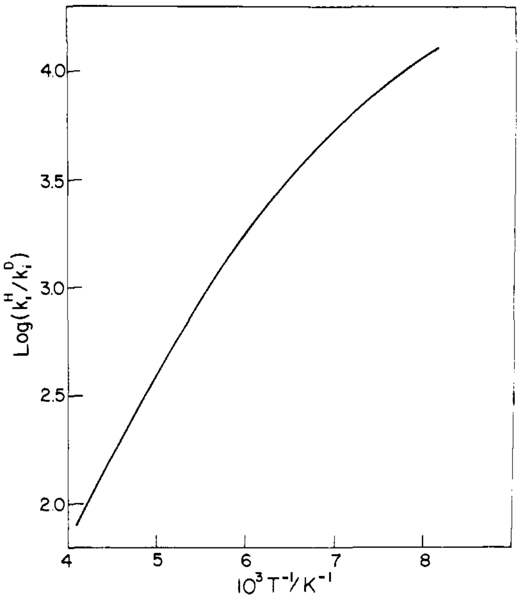


Figure 1. Deuterium kinetic isotope effect for the isomerization of 2,4,6-tri-*tert*-butylphenyl as a function of temperature.

According to the one-dimensional model,[61] the temperature dependence of the rate constant $k_i(T)$ may be represented by,

$$k_i(T) = A\Gamma(T)e^{-V_0/RT} \tag{I}$$

where V_0 is the height of the potential barrier, R is the gas constant, and A is the approximately temperature-independent frequency of mass-point collisions with the barrier. The tunneling factor, $\Gamma(T)$, which is the ratio of the quantum mechanical to the classical barrier transmission rates for a Boltzmann distribution of incident mass-point kinetic energies, approaches unity at high temperatures[63] and hence the apparent activation energy approaches V_0.

Model Potential Barriers. Three different types of barriers were examined: Eckart barriers,[64]

$$V_E(x) = V_0/\cosh^2(x/a) \tag{II}$$

Gaussian barriers,

$$V_G(x) = V_0 e^{-(x/a)^2} \tag{III}$$

and Truncated Parabolic Barriers,[65]

$$\begin{aligned} V_P(x) &= V_0[1 - (x/a)^2] \text{ for } |x| < a \\ &= 0 \text{ for } |x| > a \end{aligned} \tag{IV}$$

For a given V_0 and a all three barriers have the same height and curvature at the maximum but their widths below the maximum increase from Parabolic, to Gaussian, to Eckart (see Figure 2). The size and width of the barriers are characterized by V_0 and the dimensionless parameter,

$$\beta = \pi a(2\mu V_0)^{1/2}/\hbar = 14.30946a(\mu V_0)^{1/2} \tag{V}$$

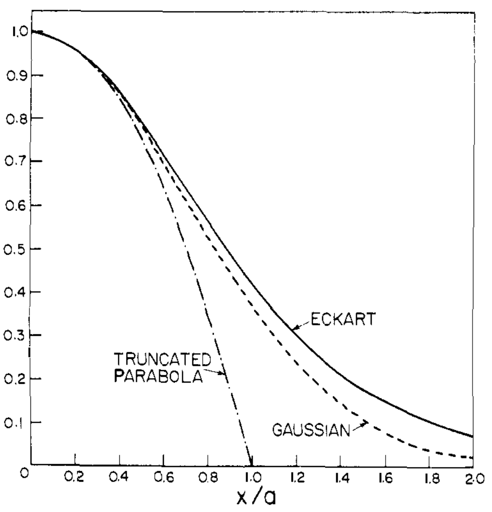


Figure 2. Shapes of the barriers used in the calculations.

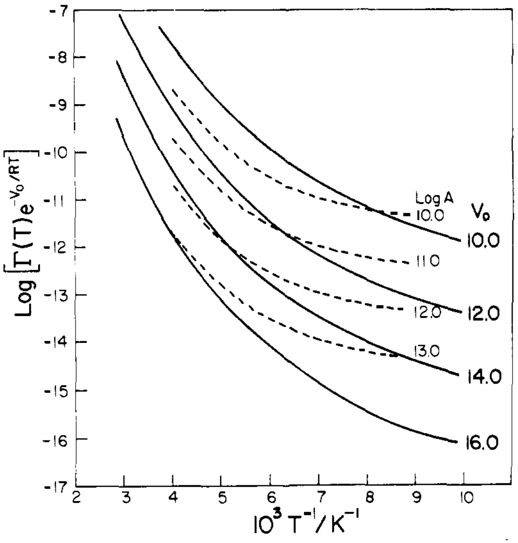


Figure 3. Effect of changing V_0 (kcal/mol) on log [$\Gamma(T)e^{-V_0/RT}$] calculated for an Eckart barrier having a = 0.40 Å (full lines). The dashed lines correspond to curves drawn through experimental values of log k_i^H s^{-1} and scaled for different values of A, i.e., they are plots of log k_i^H/A for different A values.

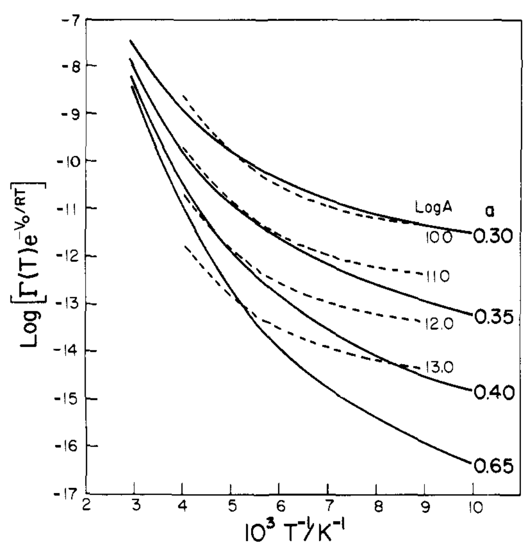


Figure 4. Effect of changing a (Å) on log [$\Gamma(T)e^{-V_0/RT}$] calculated for an Eckart barrier having V_0 = 14.0 kcal/mol (solid lines). The dashed lines are the same as those in Figure 3.

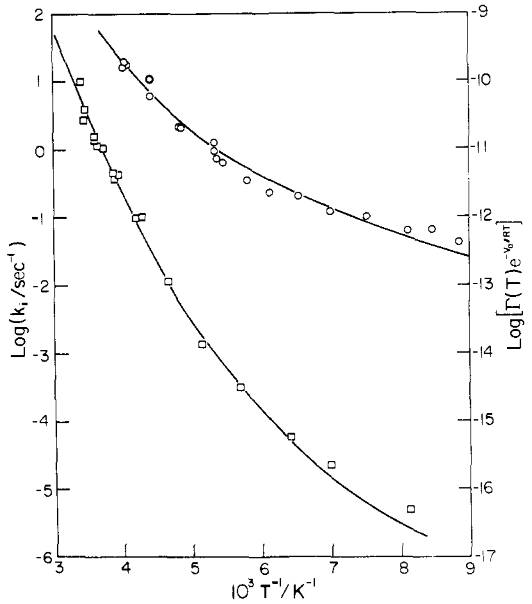


Figure 5. Isomerization of 2,4,6-tri-*tert*-butylphenyl using an Eckart barrier. The circles represent experimental values of log k_i^H s^{-1} and the squares experimental values of log k_i^D s^{-1}, the data being taken from Table I. The full curves were calculated using Eckart barriers having the parameters given in Table IV.

where μ is the mass of the hydrogen atom being abstracted in amu, a is the length in Å of the scaling factor appearing in the above equations, and V_0 is in kcal/mol. No attempt was made to allow for any asymmetry in the barrier shape which might arise because the reaction is not thermoneutral.

Determination of Barrier Heights and Widths. The computer program used to calculate tunneling factors has been described previously.[61] It was obtained from Professor R. J. LeRoy.

Equation I can be rearranged to,

$$\log [\Gamma(T)e^{-V_0/RT}] = \log [k_i(T)/A] \qquad \text{(VI)}$$

In the earlier work,[61] the paucity of experimental data required that A be independently estimated. This was unnecessary in the present instance. For each particular barrier shape, the left-hand side of eq VI was calculated exactly for hydrogen atom transfer and was then compared with the experimental data from Table I (data using method B were not used for the reasons outlined in the Results section). That is, it was compared with the measured values of log [$k_i^H(T)/A$], where A was arbitrarily selected to lie in the range 10^{10} to 10^{13} s^{-1}.[66] The comparison was made by plotting a set of curves for log [$k_i^H(T)/A$] against T^{-1} at various A values (i.e., the dotted lines in Figures 3 and 4) and a set of curves for log [$\Gamma(T)e^{-V_0/RT}$] against T^{-1} using various V_0 and a values (i.e., the solid lines in Figures 3 and 4, which have been calculated using the Eckart barrier). This procedure was carried out for each of the three barrier types. The optimum fit between the experimental and theoretical curves yields the best values of A, V_0^H, and a for each barrier. These values have been listed in Table IV. The fit between the actual experimental data (log k_i^H, s^{-1}) and log [$\Gamma(T)e^{-V_0/RT}$] is shown in Figure 5 for the Eckart barrier, in Figure 6 for the Gaussian barrier, and in Figure 7 for the Truncated Parabola.

The validity of the foregoing procedure was checked by comparing log k_i^D s^{-1} with log [$\Gamma(T)e^{-V_0/RT}$] for deuterium transfer. In these calculations, exactly the same values were used for A and a that gave the best fit for hydrogen transfer,[67] but μ was increased from 1.0 to 2.0, and V_0^D was allowed to increase above V_0^H by up to 1.4 kcal/mol to allow for differ-

Table IV. Results of Tunneling Calculations for the Isomerization of 2,4,6-Tri-*tert*-butylphenyl and 2,4,6-Tri-*tert*-(perdeuteriobutyl)phenyl

Barrier type	$\log A$, s^{-1}	V_0^{H} [a]	V_0^{D} [a]	$V_0^{D} - V_0^{H}$ [a]	a, Å
Eckart	11.0	14.5	14.9	0.4	0.330
Gaussian	11.5	14.0	15.0	1.0	0.395
Parabolic	12.0	12.0	13.4	1.4	0.635

[a] kcal/mol.

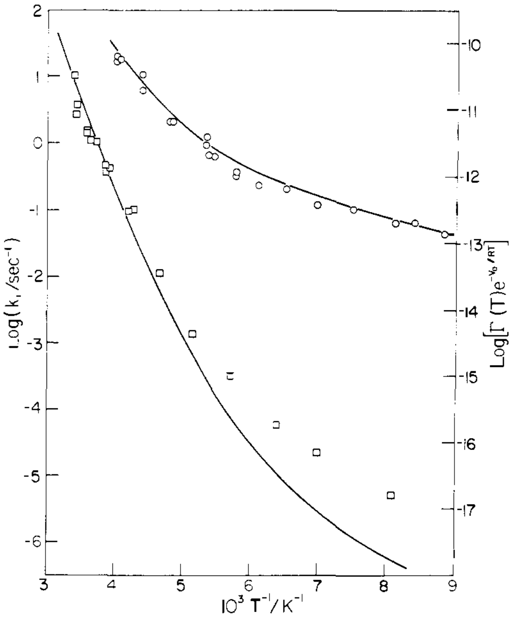


Figure 6. Isomerization of 2,4,6-tri-*tert*-butylphenyl using a Gaussian barrier. The points have the same and the lines a similar significance to those in Figure 5.

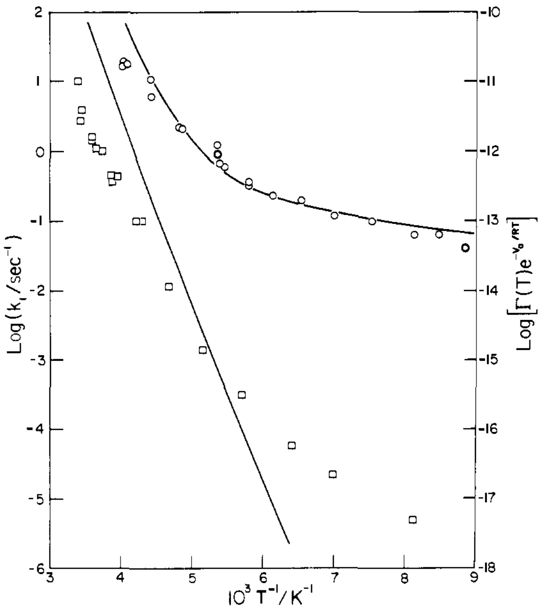


Figure 7. Isomerization of 2,4,6-tri-*tert*-butylphenyl using a truncated parabolic barrier. The points have the same and the lines a similar significance to those in Figure 5.

ences in zero-point energies for C–H and C–D bond rupture (see above). For each barrier, the fit between experiment and theory was optimized for values of $\log k_i^{D}\ s^{-1} > -2.0$. This was done because the measurement of k_i is less accurate with very slow reactions and because alternative pseudounimolecular processes (e.g., reaction with the hexamethylditin) might contribute to the overall decay. The optimum theoretical curves for deuterium transfer are included in Figures 5, 6, and 7, and the best values of V_0^{D} are included in Table IV. In connection with the last, the calculated values of $\log [\Gamma(T)e^{-V_0/RT}]$ for deuterium transfer are influenced mainly by the change in μ, changes in V_0 having only a relatively minor effect, e.g., an increase of 0.1 kcal/mol in V_0 decreases $\log [\Gamma(T)e^{-V_0/RT}]$ by only ca. 0.08 unit. For this reason, the estimated *differences* in the barrier heights for deuterium and for hydrogen transfer, i.e., $V_0^{D} - V_0^{H}$ (Table IV), are rather imprecise.

The theoretical curves and experimental rate constants are in excellent agreement for the Eckart barrier (Figure 5). The agreement is only slightly less good for the Gaussian barrier (Figure 6), which gave the best fit for the methyl radical acetonitrile reaction.[61] As is usually found, the truncated parabola gives only a poor fit with the experimental data, presumably because it has a rather unrealistic shape.

The numerical values of A, V_0^{H}, V_0^{D}, and a are within acceptable limits for all three barriers. Specifically, the A values (i.e., $(k_i)_{T^{-1}\to 0}$) lie in the expected[39,66] range of $10^{11.5\pm0.5}\ s^{-1}$. The barrier heights (i.e., classical activation energies) seem not unreasonable[71] and the fit to the deuterium data for the Eckart and Gaussian barriers is excellent with $V_0^{D} - V_0^{H}$ less than the 1.4 kcal/mol limit. The overall widths of the barriers also seem not unreasonable. Thus, using normal bond lengths and angles, we calculate that when the C–H bond which is to be broken is coplanar with the aromatic ring, the angle between this bond and the bond which is to be formed is 81°, and the hydrogen atom must be transferred through a linear distance of 1.34 Å. From Figure 2 we can see that an Eckart barrier with $a = 0.33$ Å is of this width at $V/V_0 = 0.065$ ($x/a = 2.03$), and a Gaussian barrier with $a = 0.395$ Å is of this width at $V/V_0 = 0.055$ ($x/a = 1.7$). A truncated parabola with $a = 0.635$ Å is everywhere narrower than 1.34 Å.

We believe that we have successfully interpreted our rate data for the isomerization of the 2,4,6-tri-*tert*-butylphenyl radical in terms of quantum mechanical tunneling. We do not see how our results could be explained in any other way. It is, we think, worth noting the magnitude of the tunneling "correction" under conditions where it is particularly large. For example, hydrogen transfer by a classical "over the top of the barrier" approach would, using the Eckart parameters (viz. $E^{H} = 14.5$ kcal/mol, $A = 10^{11}\ s^{-1}$), give $k_i^{H} = 10^{-14.8}\ s^{-1}$ at -150 °C (i.e., $\tau_{1/2} \sim 14$ million years). The experimental rate constant is $10^{-1.2}\ s^{-1}$, which corresponds to a staggering $10^{13.6}$ for the tunneling "correction".[72] For all practical purposes the isomerization proceeds entirely by tunneling at these temperatures. This reaction provides, therefore, an interesting illustration of the uncertainty principle, and there can be no doubt that the hydrogen atom which is transferred must be described by the wave model of quantum mechanics rather than by the particle model of classical mechanics.

The 2,4,6-Tri-(1′-adamantyl)phenyl Isomerization. An Arrhenius plot of the rate constants listed in Table III shows distinct curvature. A "least-squares" treatment of the data gives $E = 2.5$ kcal/mol and $A = 10^{1.5}\ s^{-1}$. Since both these

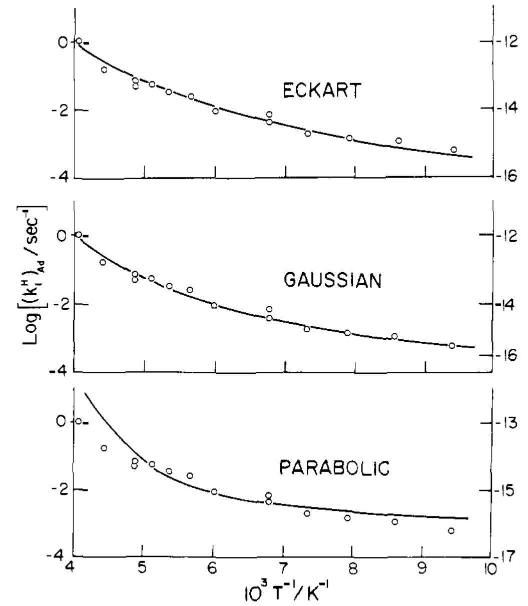


Figure 8. Isomerization of 2,4,6-tri(1′-adamantylphenyl). The experimental points are taken from Table III and the lines have been calculated using the parameters listed in Table V.

quantities are very much smaller than would be predicted, we conclude that quantum-mechanical tunneling also plays an important role in the isomerization of **3**.

Theoretical calculations were carried out using the method and barrier shapes outlined in the previous section. The results of these calculations are summarized in Table V and the calculated curves are shown in Figure 8. The Eckart and Gaussian barriers again gave excellent agreement with experiment, but the agreement is less good with the parabolic barrier.

For all three barriers, the barrier width, a, is predicted to be larger for the isomerization of **3** than for the isomerization of **1**. At first sight, this result is surprising since the former reaction is more exothermic and so might be expected to have the narrower barrier. However, in **3** the hydrogen atom which is to be transferred cannot approach the radical center as closely as in **1**. This is because closest approach will be achieved when the hydrogen is in the plane of the aromatic ring *but* in this position the 1′C-2′C bond in the adamantyl group is twisted 21° out of the aromatic plane and the 2′C-H bond makes an angle of 31° with this plane. Using normal bond lengths and angles, we calculate that in **3** the hydrogen must be transferred through a linear distance of 1.84 Å, which is considerably greater than the 1.34 Å for **1**.

The isomerization of **1** requires that rotation about the phenyl-*tert*-butyl bond and rotation about the quaternary carbon-methyl bond be "frozen-out" in the transition state, whereas the rearrangement of **3** requires that only the rotation about the phenyl-adamantyl bond be frozen-out. There should, therefore, be a larger negative entropy of activation for the former reaction. It is gratifying to find that, for each type of barrier, the calculated A factor for the isomerization of **3** is larger (by ca. one order of magnitude) than the calculated A factor for the isomerization of **1**. The barrier height, V_0, for the isomerization of **3** is greater than for the isomerization of **1**.

At all experimental temperatures, **3** is more persistent than **1**, but the tunneling correction to $(k_i^H)_{Ad}$ is greater than to k_i^H; for example, at −150 °C the experimental value for $(k_i^H)_{Ad}$ is $10^{-2.8}$ s^{-1} but the rate constant calculated from the Eckart barrier data using the classical Arrhenius equation is 10^{-20} s^{-1}, while for **1** the corresponding values are $10^{-1.2}$ and $10^{-14.8}$ s^{-1}.

Table V. Results of Tunneling Calculations for the Isomerization of 2,4,6-Tri(1′-adamantyl)phenyl

Barrier type	log A, s^{-1}	V_0^H kcal/mol	a, Å
Eckart	12.0	18.0	0.352
Gaussian	12.5	17.0	0.430
Parabolic	13.0	14.0	0.695

Finally, we note that if we had had 2,4,6-tri(1′-perdeuterioadamantyl)phenyl it would have been found to be extremely persistent at low temperatures. From the data in Table V, if we assume $V_0^D - V_0^H = 0.5$ kcal/mol, we predict that the half-life of this radical at −150 °C would be ca. 3 years using the Eckart barrier and an astonishing 8 years using the Gaussian barrier.

Conclusion

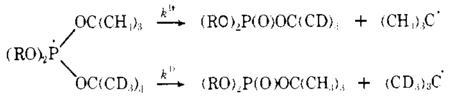
The isomerizations of the 2,4,6-tri-*tert*-butylphenyl radical and of the 2,4,6-tri(1′-adamantyl)phenyl radical occur by quantum-mechanical tunneling. The question remains as to whether these reactions represent unusual examples of tunneling or whether tunneling is common in intramolecular hydrogen atom transfers, but suitable experimental precision is uncommon.[73] Although no firm answer is possible, we consider it not unlikely that tunneling is enhanced when the reactants are prevented from achieving their optimum separation and orientation in the transition state.[74] This would suggest that tunneling should be *relatively* less important in the (unfortunately not measurable, see Results) isomerization of trineopentylphenyl, which occurs via a six-membered cyclic transition state in which the optimum spatial arrangement could be achieved without a large amount of steric strain.

Acknowledgements. We are deeply indebted to Professor R. J. LeRoy (University of Waterloo) for making available to us his computer program for calculating tunneling factors, for many helpful discussions regarding necessary modifications to the program, and for furnishing us with trial data to check the operation of the program. We also wish to thank Dr. D. N. Mitchell (N.R.C.C.) for his help with the computations. We are extremely grateful to Professor T. T. Tidwell (University of Toronto) and to Dr. R. E. Carter (Lund Institute of Technology, Sweden) for their generous gifts of the two *tert*-butyl peresters and the three neopentyl halobenzenes.

References and Notes

(1) Issued as N.R.C.C. No. 15536. Part XXV: J. C. Scaiano and K. U. Ingold, *J. Am. Chem. Soc.*, **98**, 4727 (1976).
(2) N.R.C.C. Postdoctoral Fellow, 1974–1976.
(3) N.R.C.C. Postdoctoral Fellow, 1972–1974.
(4) Department of Chemistry, Mount Allison University, Sackville, New Brunswick, Canada.
(5) D. Griller and K. U. Ingold, *Acc. Chem. Res.*, **9**, 13 (1976).
(6) G. Porter and B. Ward, *Proc. R. Soc. London, Ser. A*, **287**, 457 (1965).
(7) J. E. Bennett, B. Mile, and A. Thomas, *Chem. Commun.*, 265 (1965); *Proc. R. Soc. London, Ser. A*, **293**, 246 (1966); J. E. Bennett, B. Mile, A. Thomas, and B. Ward, *Adv. Phys. Org. Chem.*, **8**, 1 (1970).
(8) P. H. Kasai, E. Hedaya, and E. B. Whipple, *J. Am. Chem. Soc.*, **91**, 4364 (1969).
(9) A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc. B*, 403 (1968).
(10) L. R. C. Barclay, D. Griller, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 3011 (1974).
(11) A. L. J. Beckwith, *Intra-Sci. Chem. Rep.*, **4**, 127 (1970).
(12) H. Zemel and R. W. Fessenden, *J. Phys. Chem.*, **79**, 1419 (1975).
(13) L. R. C. Barclay, J. R. Mercer, and P. J. MacAuley, *Can. J. Chem.*, **53**, 3171 (1975).
(14) P. C. Myhre, G. S. Owen, and L. L. James, *J. Am. Chem. Soc.*, **90**, 2115 (1968).
(15) E. E. Betts and L. R. C. Barclay, *Can. J. Chem.*, **33**, 1768 (1955).
(16) (a) W. Rundel, *Chem. Ber.*, **99**, 2707 (1966); (b) **102**, 1649 (1969).
(17) K. Olsson, *Acta Chem. Scand.*, **26**, 3555 (1972).
(18) S. Icli, K. A. Kandil, C. Thankachan, and T. T. Tidwell, *Can. J. Chem.*, **53**, 979 (1975).
(19) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Am. Chem. Soc.*, **90**, 4201 (1968).

(20) E. J. Hamilton, Jr., and H. Fischer, *Helv. Chim. Acta*, **56**, 795 (1973).
(21) B. Maillard and K. U. Ingold, *J. Am. Chem. Soc.*, **98**, 1224 (1976).
(22) At higher temperatures **2** isomerizes to the 2-(3′,5′-di-*tert*-butylbenzyl)propyl-2 radical.[20,21]
(23) D. Griller and B. P. Roberts, *Chem. Commun.*, 1035 (1971); *J. Chem. Soc., Perkin Trans. 2*, 747 (1972).
(24) A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 993 (1972).
(25) G. B. Watts, D. Griller, and K. U. Ingold, *J. Am. Chem. Soc.*, **94**, 8784 (1972).
(26) D. Lal, D. Griller, S. Husband, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 6355 (1974).
(27) Tetramethylgermane was chosen for this experiment because the $(CH_3)_3Ge\dot{C}H_2$ radical gives a sharper (i.e., narrower EPR lines) 1:2:1 triplet than any other primary alkyl of which we are aware. For this reason, $(CH_3)_3Ge\dot{C}H_2$ can be detected at lower concentrations than any other transient carbon-centered radical.
(28) K. U. Ingold, "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 2.
(29) B. C. Childress, A. C. Rice, and P. B. Shevlin, *J. Org. Chem.*, **39**, 3056 (1974).
(30) D. J. Edge and J. K. Kochi, *J. Am. Chem. Soc.*, **95**, 2635, (1973).
(31) P. D. Bartlett and G. Guaraldi, *J. Am. Chem. Soc.*, **89**, 4799 (1967).
(32) J. E. Bennett, D. M. Brown, and B. Mile, *Chem. Commun.*, 504 (1969).
(33) K. Adamic, J. A. Howard, and K. U. Ingold, *Chem. Commun.*, 505 (1969); *Can. J. Chem.*, **47**, 3803 (1969).
(34) I. H. Elson, S. W. Mao, and J. K. Kochi, *J. Am. Chem. Soc.*, **97**, 335 (1975).
(35) P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, **93**, 846 (1971).
(36) R. E. Schwerzel, R. G. Lawler, and G. T. Evans, *Chem. Phys. Lett.*, **29**, 106 (1974).
(37) C. F. Poranski, Jr., W. B. Moniz, and S. A. Sojka, *J. Am. Chem. Soc.*, **97**, 4275 (1975).
(38) D. F. DeTar, *J. Am. Chem. Soc.*, **89**, 4058 (1967).
(39) S. W. Benson "Thermochemical Kinetics", Wiley, New York, N.Y., 1968.
(40) However, it would appear that benzoyloxy and other acyloxy radicals can be detected by EPR in solids. See, e.g., T. Komatsu, T. Seguchi, H. Kashwabara, and J. Sohma, *J. Polym. Sci., Part C*, 535 (1967); M. Iwasaki, B. Eda, and K. Toriyama, *J. Am. Chem. Soc.*, **92**, 3211 (1970); B. Eda and M. Iwasaki, *J. Chem. Phys.*, **55**, 3442 (1971); K. Toriyama, M. Iwasaki, S. Noda, and B. Eda, *J. Am. Chem. Soc.*, **93**, 6415 (1971); H. C. Box, H. G. Freund, K. T. Lilga, and E. E. Budzinski, *J. Phys. Chem.*, **74**, 40 (1970); N. J. Karch, E. T. Koh, B. L. Whitsel, and J. M. McBride, *J. Am. Chem. Soc.*, **97**, 6729 (1975). See also, J. Pacansky and J. Bargon, *ibid.*, **97**, 6896 (1975).
(41) Cf. alkoxy radicals: M. C. R. Symons, *J. Am. Chem. Soc.*, **91**, 5924 (1969).
(42) There are several excellent reviews of quantum-mechanical tunneling in chemical reactions, see, e.g., (a) H. S. Johnston, *Adv. Chem. Phys.*, **3**, 131 (1960); (b) E. F. Caldin, *Chem. Rev.*, **69**, 135 (1969); (c) M. D. Harmony, *Chem. Soc. Rev.*, **1**, 211 (1972); (d) R. P. Bell, "The Proton in Chemistry", Chapman and Hall, London, 1973, Chapter 12; (e) R. P. Bell, *Chem. Soc. Rev.*, **3**, 513 (1974). For a recent example of proton tunneling see: E. F. Caldin and S. Mateo, *J. Chem. Soc., Faraday Trans. 1*, **71**, 1876 (1975); **72**, 112 (1976). For an interesting example of tunneling in a physical process see: J. Williams, E. Shohamy, S. Reich, and A. Eisenberg, *Phys. Rev. Lett.*, **35**, 951 (1975).
(43) See, e.g., M. Salomon, *Can. J. Chem.*, **42**, 610 (1964).
(44) "Tunneling" in the simplest atom transfer reactions ($H\cdot + H_2$, $H\cdot + D_2$, etc.) has been studied the most thoroughly.[45-49]
(45) W. R. Schulz and D. J. LeRoy, *J. Chem. Phys.*, **42**, 3869 (1965); B. A. Ridley, W. R. Schulz, and D. J. LeRoy, *ibid.*, **44**, 3344 (1966).
(46) D. J. LeRoy, B. A. Ridley, and K. A. Quickert, *Discuss. Faraday Soc.*, **44**, 92 (1967).
(47) K. J. Laidler, *Discuss. Faraday Soc.*, **44**, 172 (1967).
(48) A. A. Westenberg and N. de Haas, *J. Chem. Phys.*, **47**, 1393 (1967).
(49) D. N. Mitchell and D. J. LeRoy, *J. Chem. Phys.*, **58**, 3449 (1973); D. N. Mitchell, Thesis, University of Toronto, 1973.
(50) If only stretching vibrations are considered, $E^D - E^H = 1080$ cal/mol[42e] which yields $k^H/k^D = 9.4$ at -30 °C.
(51) Although few secondary deuterium isotope effects on radical reactions have been measured with precision over a wide range of temperature, we may note that the reactions, $2(CH_3)_3C\cdot \rightarrow (CH_3)_3CH + (CH_3)_2C{=}CH_2$ (k^H) and $2(CD_3)_3C\cdot \rightarrow (CD_3)_3CD + (CD_3)_2C{=}CD_2$ (k^D) have $k^H/k^D = 1.4 \pm 0.2$ from 80 to -20 °C[52] and that the reactions



have $k^H/k^D = 1.8$ at -30 °C and extrapolation gives values of 2.9 at -100 °C and 5.6 at -150 °C.[52]
(52) D. Griller and K. U. Ingold, *J. Am. Chem. Soc.*, **97**, 1813 (1975).
(53) For an interesting example of large k^H/k^D values see: A. Bromberg and K. A. Muszkat, *J. Am. Chem. Soc.*, **91**, 2860 (1969); A. Bromberg, K. A. Muszkat, and E. Fischer, *Chem. Commun.*, 1352 (1968); A. Warshel and A. Bromberg, *J. Chem. Phys.*, **52**, 1262 (1970); A. Bromberg, K. A. Muszkat, and A. Warshel, *ibid.*, **52**, 5952 (1970); A. Bromberg, K. A. Muszkat, E. Fischer, and F. S. Klein, *J. Chem. Soc., Perkin Trans. 2*, 588 (1972).
(54) J. Bigeleisen, *Pure Appl. Chem.*, **8**, 217 (1964).
(55) (a) E. D. Sprague and F. Williams, *J. Am. Chem. Soc.*, **93**, 787 (1971); (b) K. Takeda, J.-T. Wang, and F. Williams, *Can. J. Chem.*, **52**, 2840 (1974).
(56) J.-T. Wang and F. Williams, *J. Am. Chem. Soc.*, **94**, 2930 (1972).
(57) A. Campion and F. Williams, *J. Am. Chem. Soc.*, **94**, 7633 (1972).
(58) For example, $k^H/k^D > 2 \times 10^3$ for acetonitrile at 87 K and $> 1 \times 10^3$ for methyl isocyanide at 110 K. In both cases, the abstraction of deuterium was too slow to be measured, which led to the term[56] "all-or-nothing" isotope effects.
(59) Alternative explanations have been suggested[60] and rejected.[55b]
(60) F. P. Sargent, M. G. Bailey, and E. M. Gardy, *Can. J. Chem.*, **52**, 2171 (1974).
(61) R. J. LeRoy, E. D. Sprague, and f. Williams, *J. Phys. Chem.*, **76**, 546 (1972).
(62) R. J. LeRoy, K. A. Quickert, and D. J. LeRoy, *Trans. Faraday Soc.*, **66**, 2997 (1970); University of Wisconsin Theoretical Chemistry Institute Report, WIS-TCI-384 (1970).
(63) H. S. Johnston, "Gas Phase Reaction Rate Theory", Ronald Press, New York, N.Y., 1966, Chapter 10.
(64) C. Eckart, *Phys. Rev.*, **35**, 1303 (1930).
(65) R. P. Bell, *Trans. Faraday Soc.*, **54**, 1 (1959).
(66) The lower limit for A was chosen to be slightly greater than the value obtained by a linear extrapolation of the log k_i^D vs. T^{-1} plot to $T^{-1} = 0$. The upper limit was chosen to be 10^{13} s^{-1} since this is the magnitude of the A factor for a unimolecular reaction in which there is no entropy of activation.[39]
(67) It is possible that a for deuterium transfer should be slightly greater than for hydrogen transfer because of the smaller amplitude of vibration of deuterium atoms.[68] This same factor may make a contribution to secondary deuterium isotope effects[69] though the evidence is conflicting.[70]
(68) *See*, e.g., P. J. Mitchell and L. Phillips, *Chem. Commun.*, 908 (1975).
(69) L. S. Bartell, *Tetrahedron Lett.*, 13 (1960); *J. Am. Chem. Soc.*, **83**, 3567 (1961).
(70) See, e.g., L. R. C. Barclay, J. R. Mercer, and P. J. MacAuley, *Can. J. Chem.*, **53**, 3171 (1975); and J. L. Fry and R. C. Badger, *J. Am. Chem. Soc.*, **97**, 6276 (1975).
(71) For example, the bond energy–bond order (BEBO) method[83] gives 7.1 kcal/mol for hydrogen abstraction from neopentane by phenyl, to which should be added ca. 6.3 kcal/mol of strain energy for a five-membered cyclic transition state.[39]
(72) Alternatively, passage over a classical barrier would have a rate constant of $10^{-1.2}$ s^{-1} if $E = 6.9$ kcal/mol ($A = 10^{11}$ s^{-1}).
(73) As we have noted previously,[52] the advantage of the kinetic EPR technique is its high accuracy over a wide range of reaction rates (or temperatures).
(74) Steric enhancement of hydrogen kinetic isotope effects and hence of tunneling has been suggested previously[75] but there is little supporting evidence.[76]
(75) E. Baciocchi, G. Illuminati, and G. Sleiter, *Tetrahedron Lett.*, L23, 30 (1960).
(76) See, e.g., J. A. Howard and E. Furimsky, *Can. J. Chem.*, **51**, 3738 (1973).