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Abstract: The isomerization of 2,4,6-tri-*tert*-butylphenyl, which occurs by quantum-mechanical tunneling of a hydrogen atom from an ortho *tert*-butyl group,⁵ occurs at the same rate in matrices as in solution. The rate of this process has been measured at temperatures down to 28 K. At such low temperatures the rate is virtually independent of temperature. Tri-*tert*-(perdeuter-iobutyl)phenyl decays by deuterium atom tunneling at the same rate in matrices as in solution. A number of less hindered aryls decay by intermolecular hydrogen abstraction from the surrounding medium. However, octamethyloctahydroanthracen-9-yl decays by intramolecular hydrogen tunneling, even though the corresponding deuterated radical decays by reaction with the solvent.

We have shown previously that quantum-mechanical tunneling plays an important role in the isomerization of the 2,4,6-tri-*tert*-butylphenyl radical (1) to 3,5-di-*tert*-butylneophyl (2).⁵ This reaction was examined in solution over the



maximum practicable range of temperatures, viz., -26 to -160 °C. It subsequently occurred to us that because this is a unimolecular reaction which involves a relatively inflexible and nonpolar species the rate might not be affected by changing from the liquid to the solid phase. If this were found to be the case, then the reaction could be studied at temperatures below -160 °C where the effects of quantum-mechanical tunneling should become even more pronounced.⁵⁻⁸ Experiments showed that the reaction rate was indeed independent of phase and we have now extended our kinetic measurements down to -245 °C. In this paper we also report kinetic studies on the decay of some other hindered aryl radicals.

Experimental Section

The kinetic technique and methods of generating the radicals have been described previously.⁵ For the deuterated aryls, measurements of the rate of reaction were made only after sufficient time had elapsed for any incompletely deuterated radical to have decayed completely.

Materials. The precursors of 1 (the bromide and tert-butylperbenzoate), of 2,4,6-tri-tert-(perdeuteriobutyl)phenyl, 1D (bromide), and of 2,4,6-tri(1'-adamantyl)phenyl, 3 (bromide) were available from our previous work.⁵ The new aryl radicals 4-7 were generated from the appropriate sterically hindered aryl bromides, 4-Br-7-Br, using photochemically produced tri-n-butyltin radicals to abstract the bromine.5 The unlabeled tricyclic hydrocarbons were prepared as previously described9 and were converted to aryl mono- and dibromides by silver-induced brominations ("neutral" conditions).¹⁰ Analyses of each reaction mixture by GLC eluted the compounds in the order starting hydrocarbon, monobromo derivative, dibromo derivative. Larger quantities of material were separated by preparative TLC on $20 \text{ cm} \times 20 \text{ cm} \times 0.5 \text{ mm}$ silica gel (Woelm TLC silica gel F) plates using pentane as the developer. This eluted the compounds in the order dibromo derivative, monobromo derivative, unreacted hydrocarbon. Yields of the monobromo derivatives varied between 25 and 40%. Analytical and spectroscopic results for the various bromo compounds

isolated were consistent with the assigned structures. These data are available as supplementary material.





In order to investigate deuterium kinetic isotope effects on the decay of 7 we required 9-bromooctaperdeuteriomethyloctahydroanthracene as the precursor of the corresponding radical **7D**. To prepare the hy-



7 D drocarbon, 1,1,4,4-perdeuteriotetramethyl-1,4-butanediol was synthesized from trideuteriomethylmagnesium iodide and diethyl succinate by a modification of the reported procedure¹¹ and was then converted to the corresponding dichloride by treatment with a solution of DCl in heavy water.¹² The dichloride showed a singlet in the NMR at δ 1.96 due to the -CH₂- and lacked -CH₃ absorption. The mass spectrum gave a peak at *m/e* 159, as expected for M – 35. This dichloride (1.51 g, 7.74 mmol) and benzene (0.301 g, 3.85 mmol) were treated in carbon disulfide (4 mL) under dry nitrogen with anhydrous aluminum chloride (0.1 g) for 2 h, after which time direct NMR observation indicated complete reaction. The product (1.10 g, 89%), mp 216–218 °C (lit.⁹ 220 °C), showed a methylene absorption (s, δ 1.69)

Results

Isomerization of Tri-tert-butylphenyl in the Solid State. The

and an aromatic singlet (δ 7.33) in a 4:1 ratio, as expected.



Figure 1. Arrhenius plot of the rate constants for the isomerization of 1 in matrices, open circles, and in solution, filled circles, and for the isomerization of 1D in matrices, open squares, and in solution, filled squares. The theoretical curves have been calculated using the parameters listed in Table II. Where several measurements were made at one temperature, bars are used to indicate the limits in log k_i .

principal feature in the EPR spectrum of tri-tert-butylphenyl in solution is a 1:2:1 triplet which arises from the splitting by the two meta hydrogen atoms.⁵ The lines that make up this triplet are broadened in the solid state but they can still be observed without much difficulty in frozen benzene or C_6D_6 at liquid nitrogen temperatures $(a^{\rm H}(2 {\rm H}) = {\rm ca.} 6.8 {\rm G}, \Delta H_{\rm pp})$ = ca. 3.3 G at 77 K). At temperatures above 100 K this triplet decayed when the light which generated 1 was cut off, and no new EPR signal appeared. This implies that 2 is sufficiently reactive or sufficiently mobile to decay rapidly at these temperatures. However, at temperatures below 100 K the spectrum due to 1 was replaced by a new, broad, 1:2:1 triplet $(a^{H}(2 H))$ = ca. 21.5 G) which can be assigned to 2.5 At these low temperatures, rate constants for the decay of 1 (which were found by monitoring the decay of the outer lines of the narrower triplet) were essentially identical with the rate constants for the formation of 2 (which were obtained by monitoring the growth of the outer lines of the broader triplet). An Arrhenius plot of these kinetic results is shown in Figure 1 together with old⁵ and new solution data.

At 28 K (the boiling point of liquid neon) neither 1 nor 2 could be observed as distinct triplets in a benzene matrix. Only a broad, structureless line was obtained. However, 1 and 2 could both be identified in a neopentane matrix though the line width was such (ca. 3.6 G) that the $1 \rightarrow 2$ isomerization could only be properly monitored by following the formation of 2. In view of the possibility that a radical, $(CH_3)_3CCH_2$, with hyperfine splittings similar to those for 2 might be formed from the neopentane matrix the kinetic measurements at 28 K were repeated in a $(CD_3)_4C$ matrix. The rate constants in neopentane and in perdeuterioneopentane were equal within experimental error.

The EPR spectrum of 2,4,6-tri-*tert*-(perdeuteriobutyl)phenyl (1D) is a 1:2:1 triplet virtually identical with that for the undeuterated radical. However, the corresponding neophyl radical, 2D, which is produced by isomerization of 1D will give an EPR spectrum that is only about one-third as wide as that of the undeuterated neophyl.¹³ This means that the EPR spectra of 1D and 2D are of similar overall width and hence the 1D \rightarrow 2D isomerization could only be monitored in the benzene matrices at temperatures above 100 K¹⁴ where the EPR signal decays completely. The results obtained at temperatures from 233 to 123 K in this matrix are, however, in satisfactory agreement with kinetic data obtained previously in solution (see Figure 1). The measured rate constants for



Figure 2. Arrhenius plot of the rate constants for the isomerization of 7 in solution. The theoretical curves have been calculated using the parameters listed in Table II.

decay of 1 and 1D in the matrices are available as supplementary material.

Decay of Other Hindered Aryl Radicals. In our previous work⁵ we found that 2,4,6-tri(1'-adamantyl)phenyl (3) decayed more slowly than 1 despite the fact that a secondary hydrogen rather than a primary is transferred to the aromatic ring. We attributed the increased persistence of triadamantylphenyl to the fact that in this radical the hydrogen had to jump (tunnel) a greater distance (1.84 Å, assuming normal bond lengths and angles) than was necessary in 1 (1.34 Å). We therefore prepared precursors of some other hindered aryls in which the two ortho tert-butyls of 1 had been "tied back" by incorporation into five- or six-membered rings. If the aryls derived from these compounds, i.e., radicals 4-7 in Table I, were to decay intramolecularly, a primary hydrogen would have to jump more than 1.34 Å and so these aryls should be more persistent than 1. Unfortunately, this prediction proved to be correct only with radical 7. The less hindered aryls, 4, 5, and 6, were much less persistent than 1. When generated from their parent bromides with tri-n-butyltin radicals in solvents such as cyclopropane or isooctane they decayed with first-order kinetics. However, this decay actually involved an intermolecular hydrogen atom abstraction from the hexa-n-butylditin since its rate was directly proportional to the concentration of ditin. Rate constants for attack of these aryls on the ditin at 168 K are included in Table I. When 4 was generated in cyclopropane by direct photolysis of the bromide its half-life increased by about a factor of 10 and upon the addition of tetramethylgermane⁵ the spectrum due to 4 was replaced by that due to $(CH_3)_3$ Ge $\dot{C}H_2$. It is clear that radicals 4-6 have too "open" a structure for intramolecular hydrogen tunneling to occur under our experimental conditions. An attempt was made to inhibit the intermolecular decay of 4-6 by generating these radicals in a C_6D_6 matrix at temperatures in the range 250-100 K. Unfortunately, the EPR spectra which were obtained could not be unequivocally interpreted.

In contrast to the aryls 4–6, radical 7, octamethyloctahydroanthracen-9-yl was quite persistent. The rate constants for its decay (available as supplementary material) did not depend upon the solvent or upon the presence or absence of hexa-nbutylditin. An Arrhenius plot of these data is strongly curved (see Figure 2) which implies that 7 decays by intramolecular hydrogen atom tunneling. For this reason, the aryl fully deuterated in the eight methyl groups, 7D, was studied. It was found to be appreciably more persistent than 7. However, under optimum experimental conditions the magnitude of the kinetic isotope effect increased only from ca. 20 to ca. 50 over a temperature range from 50 to -100 °C. Moreover, the first-order rate constants for decay¹⁵ were dependent upon the experimental conditions. [For example, at -50 °C using a minimum¹⁶ of hexa-n-butyditin (ca. 0.1 M) to generate 7D, $k_i \approx 0.003$ and 0.01 s⁻¹ in cyclopropane^{15,17} and isopentane,

Table I. Hindered Aryl Radicals in Cyclopropane at 168 K	

Radical	H "jump distance", Å	$a({}^{13}C_{\alpha}), G$	a(H _{para}),	$k, M^{-1} s^{-1}$ Ar' + $(n-Bu_3Sn)_2$
	1.34	122.5		0
3 Ad Ad Ad	1.84	122.0		0
	2.25	а	1.73	1.5
5	b	144.5	1.75	0.6
	Ь	116.0		0.4
7 202	1.45 ^{c.d} 1.88 ^e	113.85	0.60 <i>s</i>	0

^a Too weak to measure. ^b As for 4 and 7. ^c Less stable half-boat conformation. ^d The two extreme conformers probably interconvert freely on the time scale of a radical decay since a ¹H NMR study of 7-Br in CS₂ shows that the signals due to the pairs of methyls adjacent to the bromine (at -110 °C: a 6-Hz doublet at 1.53 ppm) coalesce at -80 °C (ΔG^{\ddagger} = 9.9 kcal/mol). The parent hydrocarbon did not show nonequivalent methyls even at -115 °C. ^e More stable half-chair conformation. ^f Also, $a({}^{13}C_{ortho}) = 6.00$ G; $a({}^{13}C_{meta}) = 15.00$ G. ^g Splitting observed only in 7D. It is a 1:3:3:1 quartet attributed to 1 para and 2 equatorial H in the 2 and 7 CH₂ groups. The line width in 7 (ca. 1.5 G) precludes detection of this splitting.

Table II. Results of Tunneling Calculations for Intramolecular H and D Transfer in Hindered Aryl Radicals

Barrier	Eckart ^a	Gaussian ^b	Lorentzian ^c	Parabolic ^d
	1	and 1D		
$Log(A/s^{-1})$	10.0	11.5	8.2	12.0
$V_0(H)$, kcal/mol	13.8	14.4	16.5	12.3
$V_0(D)$, kcal/mol	13.9	14.9	16.5	13.7
a, Å	0.309	0.393	0.154	0.634
Error (H) ^e	0.77	0.22	2.46	1.42
		3		
$Log(A/s^{-1})$	11.7	12.6	8.6	12.4
V_0 (H), kcal/mol	18.4	17.4	18.5	14.0
a, Å	0.337	0.425	0.180	0.673
Error (H) ^e	0.05	0.01	1.2	0.3
		7		
$Log(A/s^{-1})$	12.7	13.1	11.0	12.8
$V_0(H)$, kcal/mol	21.0	19.9	23.5	17.0
a, Å	0.339	0.409	0.197	0.617
Error (H) ^e	0.03	0.35	0.66	5.20

 ${}^{a}V(x) = V_0 / \cosh^2(x/a)$. ${}^{b}V(x) = V_0 e^{-(x/a)^2}$. ${}^{c}V(x) = V_0 / 1 + (x/a)^2$. ${}^{d}V(x) = V_0 [1 - (x/a)^2]$ for |x| < a. e Experimental points were fitted to the curve $y = \alpha + \beta \gamma^x$, where x > 0 and 0 < y < 1, and the error sum of squares for the best fit for H transfer is defined by: Error (H) = $\sum_{i=1}^{n} [y - x - \beta \gamma^{xi}]^2$, where x and y are the n in number of experimental points data (see ref 21).

respectively, and with 0.2 M ditin in cyclopropane $k_i = 0.005$ s⁻¹. For comparison, at this temperature 7 has $k_i = 0.08$ s⁻¹ at all ditin concentrations (0–0.5 M) and in all solvents examined (cyclopropane, propane, isopentane, and isooctane).] For these reasons, it seems certain that 7D does not decay by intramolecular deuterium atom tunneling. Instead it must decay by intermolecular hydrogen atom abstractions from the surrounding medium, just like the other insufficiently hindered aryls, 4–6. However, since 7 is so much shorter lived than 7D it cannot be reacting with the surrounding medium to any significant extent. We conclude, therefore, that 7 decays by intramolecular hydrogen tunneling. An attempt to detect the

radical produced by decay of 7 by examining the reaction in a C_6D_6 matrix was frustrated by broad spectra that could not be identified with certainty.

Treatment of Experimental Data. We have previously shown that the kinetic data for the rearrangement of 2,4,6-tri-*tert*butylphenyl in solution can be nicely accounted for by using the one-dimensional, quantitative, "tunneling" treatment developed by LeRoy, Sprague, and Williams.^{19,20} Various types of potential barrier were arbitrarily selected (Eckart, Gaussian, etc.). For each type, the best fit between computed and measured rates for hydrogen atom transfer was obtained by adjustment of the barrier height, V_0 (which corresponds to the classical activation energy), the barrier width, a (the scaling factor in the equation used to define the barrier), and the temperature-independent "collision frequency", A (which corresponds to the Arrhenius preexponential factor). The kinetic data for deuterium atom transfer were then fitted to the same type of barrier using identical values for a and A but allowing V_0 to increase by up to 1.4 kcal/mol because of the difference in zero-point energies of C-H and C-D bonds. In this earlier work, "best fits" for both H and D transfer were obtained by eye. In the present work, a nonlinear least-squares treatment²¹ of the data provided a more objective estimation of the "quality of fit" for H-transfer provided by various barriers. The 1D transfer rate constants were again fitted by eye. The results of these computations are summarized in Table II and are illustrated for 1 and 1D in Figure 1 and for 7 in Figure 2. Our previous results⁵ with 3 have also been recomputed (see Table II). It should be noted that the lowest temperature (28) K) rate constants for the rearrangement of 1 were not employed in the barrier computations. Instead of having an unduly large effect on the barrier shape and dimensions these 28 K rate constants serve as an internal check on the predictive ability of the barriers computed from measurements at higher temperatures.

Discussion

The conclusions that can be drawn from our studies (old⁵ and new) of hindered aryl radicals are summarized below.

1. Highly hindered aryls (1, 3, and 7) are quite persistent and can be readily detected by EPR spectroscopy. They decay by an intramolecular hydrogen atom transfer which involves quantum-mechanical tunneling and a five-center cyclic transition state. Somewhat less hindered aryls (4, 5, and 6) can also be detected by EPR but they are less persistent because they decay by hydrogen abstraction from the surrounding medium. This is also the fate of **7D**, though under optimum conditions this is the most persistent aryl radical we have been able to obtain. Much less hindered aryls are too reactive under our conditions to be detected by EPR. Such radicals may decay either by rapid intramolecular processes (e.g., 2,4,6-trineopentylphenyl⁵) or by attack upon the solvent.

2. The rates of intramolecular H-transfer in 1 and D-transfer in 1D are the same in solid matrices as in solution. This provides further support for the view that many of the intermolecular hydrogen atom transfers that have been observed in matrices at low temperatures should be interpreted in terms of quantum-mechanical tunneling.^{7,8,19,22,23} rather than by invoking any special "matrix effect".24

3. The rate constants for the isomerization of 1 become virtually independent of the temperature below ca. 40 K (see Figure 1). That is, the activation energy for this intramolecular hydrogen atom transfer has decreased almost to zero below ca. 40 K, as has also been observed for intermolecular hydrogen abstractions by methyl radicals in methanol glasses⁷ and by iminoxy radicals in dimethylglyoxime crystals.8

4. Because H-tunneling occurs so much more readily than D-tunneling the isomerization of the 1/1D pair of radicals exhibits an enormous kinetic isotope effect at low temperatures. Even larger isotope effects have been reported in certain intermolecular hydrogen abstractions.²²

5. The decay of 1, 3, and 7 can be treated quantitatively in terms of quantum-mechanical tunneling of a hydrogen atom through a one-dimensional potential energy barrier. The experimental kinetic data for these three radicals can best be fitted by an Eckart or Gaussian barrier. The Lorentzian and truncated parabolic²⁵ barriers do not give such good fits (see Table II and figures). In view of simplicity of the model employed in our calculations we prefer not to speculate on the physical significance of the computed preexponential factors, barrier heights, and scaling factors listed in Table II.

6. Rate constants for the isomerization of 1D can be fairly well fitted by deuterium tunneling through the "best" barriers found for the isomerization of 1. It is necessary to make an appreciable correction for the difference in zero-point energies of C-H and C-D bonds for the Gaussian and parabolic barriers, but this is unnecessary for the Eckart and Lorentzian barriers.²⁷

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Supplementary Material Available: Tables containing analytical and spectroscopic data for the bromo compounds 4-Br-7-Br and rate constants for the isomerization of 1 and 1D in various matrices and for the isomerization of 7 in solution (6 pages). Ordering information is given on any current masthead page.

References and Notes

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- (13) Magnetogyric ratio for H:D = 6.5; $I_{\rm H} = \frac{1}{2}$, $I_{\rm D} = 1$
- The EPR signal of 1D in a benzene matrix at 77 K did not change significantly (14)after storage for 3 months. If there was any isomerization to 2D it was not apparent.
- (15) Decay of 7D occurs with "impure" first-order kinetics. The calculated rate constants actually decrease by about a factor of 2 as the radical concen tration decreases by a factor of 100.
- (16) Low concentrations of 7 and 7D can be generated by direct photolysis of the bromides. The rate of decay of 7 is not affected but 7D decays more rapidly in the absence than in the presence of the ditin which presumably is needed to scavenge the bromine atoms.
- (17) Similar rate constants were obtained during the later stages in the decay of the analogous radical having fully deuterated side rings, viz., octaperdeuteriomethyloctadeuterioanthracen-9-yl. The parent hydrocarbon was prepared from 1,3,5-tri-tert-(perdeuteriobutyl)benzene and tert-perdeuteriobutyl chloride by the electrophilic cycloalkylation route used for the unlabeled compound.¹⁸ This route led to some deuterium scrambling which was most readily observed by allowing the aryl to react with oxygen. The EPR spectrum of the corresponding phenoxy revealed that there was 64% D in the para position. The phenoxy from 7D showed no trace of D in this position
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