mg of Pr(fod)$_3$ in 400 μL of CHCl$_3$) δ -4.35 (17%, **12-OH**), -7.68 (83%, **13-OH**); ^{1}H NMR as expected.[17]

1-Methyl-2(a)-adamantanol-*4*(*a*)-*d* and -*4*(*e*)-*d* (14-OH/15-OH). A crude mixture of **10-OH/11-OH** + **12-OH/13-OH** (170 mg, 10 mmol) was isomerized to the corresponding 1-methyl-2(a)-adamantanols, **14-OH/15-OH**, in boiling 80% aqueous acetone containing 0.3% H$_2$SO$_4$ as employed for the unlabeled alcohols by Majerski et al.[8] mp 157-159 °C (lit.[8] 158-160 °C); ^{2}H NMR (15 mg of substrate + 75 mg of Pr(fod)$_3$ in 400 μL of CHCl$_3$) δ -10.0 (17%, **14-OH**[13]), -4.7 (83%, **15-OH**[13]); ^{1}H NMR as expected.[17] The binary nature of this product and the configurational assignments were confirmed by oxidation-reduction to produce the four-isomer mixture as follows.

Four Diastereomeric 1-Methyl-2-adamantanols-*4-d* (14-OH-17-OH). Labeled 1-methyl-2(a)-adamantanols **14-OH/15-OH** (170 mg, 10 mmol) were oxidized in 90% yield to the corresponding ketones by the method of Numan and Wynberg.[25] This product was in turn reduced in 85% yield with LiAlH$_4$ in ether[26] to the four diastereomeric 1-methyl-2-adamantanols-*4-d*, **14-OH-17-OH**. The shift-enhanced ^{2}H NMR spectrum of the mixture (15 mg of substrate + 75 mg of Pr(fod)$_3$ in 400 μL of CHCl$_3$) consisted of the expected[13] four signals at δ -2.7 (42%), -3.2 (9%), -4.7 (41%), and -10.0 (8%). The latter two peaks are those of **15-OH** and **14-OH**, respectively, by chemical shift identity with those of the precedent twofold mixture (above), while the former must be those of **17-OH** and **16-OH**, respectively, in consideration of their relative intensities as well as relative induced shifts.[13]

4-Methyl-*exo*-4-protoadamantyl-*exo-5-d* and -*endo-5-d* 3,5-Dinitrobenzoate (10-ODNB/11-ODNB) and 4-Methyl-*endo*-4-protoadamantyl-*exo-5-d* and -*endo-5-d* 3,5-Dinitrobenzoate (12-ODNB/13-ODNB). Epimeric alcohols **10-OH/11-OH** and **12-OH/13-OH** were each converted to the 3,5-dinitrobenzoate in 70% yield by using the procedure described by Majerski et al.[8] for the preparation of the undeuterated esters. For **10-ODNB/11-ODNB**: mp 110-112 °C (lit.[8] 113-114 °C); ^{1}H NMR as expected.[4] For **12-ODNB/13-ODNB**: mp 127-130 °C (lit.[8] 130-131 °C); ^{1}H NMR as expected.[4]

1-Methyl-2(a)-adamantyl-*4*(*a*)-*d* and -4(*e*)-*d* Tosylate (14-OTs/15-OTs). Alcohol **14-OH/15-OH** was converted to the tosylate in 60% yield using the procedure employed by Majerski[8] for the undeuterated ester: mp 113-114 °C (lit.[8] 113-114 °C); ^{1}H NMR as expected.[4]

Solvolyses of 10-ODNB/11-ODNB, 12-ODNB/13-ODNB, and 14-OTs/15-OTs in Aqueous Dioxane. The solvolysis procedure for the three substrates was as follows. Deuterated ester (250 mg, 0.69 mmol) was dissolved in 25 mL of 60% aqueous dioxane containing 82 mg (0.77 mmol) of 2,6-lutidine (Aldrich), and the resulting solution was stirred at 60 °C for >10 half-lives:[8] 12 h for **10-ODNB/11-ODNB**, 50 h for **12-ODNB/13-ODNB**, and 13 h for **14-OTs/15-OTs**. The mixture was then allowed to cool, poured into 200 mL of water, and extracted with five 50-mL portions of pentane. The combined pentane extracts were washed successively with water, 5% aqueous hydrochloric acid, saturated aqueous sodium bicarbonate, and saturated brine. After the mixture was dried (MgSO$_4$) the pentane was removed by rotary evaporation, leaving a yellow liquid from which 1-methyl-2-adamantanol and 4-methyl-*exo*-4-protoadamantanol were isolated by preparative TLC (silica gel with 3:7 ethyl acetate-hexane as eluant). From all three esters the ^{2}H NMR spectrum of the 1-methyl-2-adamantanol product (15 mg of substrate + 75 mg of Pr(fod)$_3$ in 400 μL of CHCl$_3$) showed only two peaks, corresponding to **14-OH** (δ -10.0, 17%) and **15-OH** (δ -4.7, 83%); no peaks corresponding to **16-OH** (δ -2.7) or **17-OH** (δ -3.2) could be detected (<3%). The ^{2}H NMR spectrum of the 4-methyl-*exo*-4-protoadamantanol product (15 mg of substrate + 70 mg of Pr(fod)$_3$ in 400 μL of CHCl$_3$) in each case showed only two peaks, corresponding to **10-OH** (δ -10.9, 17%) and **11-OH** (δ -5.8, 83%).

The similarly dispersed ^{1}H spectrum of undeuterated 4-methyl-*exo*-4-protoadamantanol (**1-OH**) (15 mg of substrate + 70 mg of Pr(fod)$_3$ in 400 μL of CDCl$_3$) provided positive evidence for the absence (<3%) of 2-deuterated 4-methyl-*exo*-4-protoadamantanol, **18-OH**, from the **10-OH/11-OH** solvolysis product. The exo- and endo-5-proton signals at δ -10.9 and -5.8, respectively, were integrated for 1 H each and were well separated (>0.75 ppm) from the other proton absorptions. Since ^{1}H and ^{2}H NMR chemical shifts are parallel,[23] the possible superimposition of 2-*d* and 5-*d* peaks in the ^{2}H spectrum was thus excluded.

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Studies of Free Radicals at High Pressures. 2. Kinetics for a Variety of Reactions[1]

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Abstract: Kinetic EPR studies of a variety of free-radical reactions have been carried out at high pressures. Volumes of activation were measured for the β-scission reactions of di-*tert*-butyliminyl (3.0 ± 1.0 cm^3 mol^{-1}) and triethoxy-*tert*-butoxyphosphoranyl (0.2 ± 1.9 cm^3 mol^{-1}), for the self-reaction of di-*tert*-butyliminyl (-18.0 ± 5.3 cm^3 mol^{-1}), and for the rearrangements of 2,4,6-tri-*tert*-butylphenyl (5.3 ± 1.7 cm^3 mol^{-1}) and 2,4,6-tris(perdeuterio-*tert*-butyl)phenyl (-1.2 ± 2.0 cm^3 mol^{-1}). These measurements improve the descriptions of the transition states for the various reactions and in the case of the phenyl rearrangements provide supporting evidence for a mechanism involving quantum mechanical tunneling.

The properties of the transition state for a chemical reaction are often inferred from measurements of the activation parameters for that reaction. The activation energy, $\Delta E^{\ddagger}$, is the parameter which is most easily, and hence most often, determined. However, the description of the transition state can be substantially improved if the volume of activation, $\Delta V^{\ddagger}$, is also measured.[2]

The volume of activation represents the change in volume which occurs when reactants pass to transition state. It is obtained from the pressure dependence of the rate constant,[3] and its magnitude is generally characteristic of the rate-determining pathway.[4-7]

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = \frac{-\Delta V^{\ddagger}}{RT} \qquad (1)$$

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(1) Issued as NRCC publication No. 19163. For Part 1, see ref 14b.

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Despite the significance of ΔV^*, high-pressure studies of free radical reactions have rarely been carried out. Among the few examples are the effects of pressure on polymerization,[8] on the combination vs. diffusion of geminate radical pairs,[9] and on the reaction of *N′,N′*-diphenyl-*N*-picrylhydrazyl (DPPH) with thiols[10] and phenols.[11]

EPR spectroscopy has been used to study the effects of pressure on spectral line widths,[12,13] hyperfine splittings,[14] and equilibria involving radical anions,[15,16] but it has not been used in kinetic studies. In many of these experiments the EPR cavity has been integrated into the design of the pressure bomb.[13,17,18] Although such cavities can withstand pressures of several thousand atmospheres, they are completely unsuitable for kinetic studies of transient organic radicals since these often need to be generated photolytically,[19] at low temperatures and from small quantities of precursor.

The purpose of this work was to develop a pressure cell for use in kinetic EPR spectroscopy[20] and to measure volumes of activation for some typical free radical processes. These included a bimolecular self-reaction, two β scissions, and a rearrangement involving quantum mechanical tunneling.

Experimental Section

Materials. Di-*tert*-butyl ketimine, 2,4,6-tri-*tert*-butylbromobenzene and 2,4,6-tris(perdeuterio-*tert*-butyl)bromobenzene were available from previous work.[21-24] Di-*tert*-butyl peroxide was commercially available and was purified by chromatography through alumina which removes traces of the hydroperoxide. All other materials were commercially available in high purity.

Radical Generation and Decay. Radicals were generated by photolysis of appropriate solutions contained in a quartz pressure cell (vide infra), which was positioned in the cavity of a Varian E4 spectrometer. The photolysis source was a 500-W mercury arc lamp, and its output was filtered by using an aqueous nickel/cobalt solution so as to remove most of the visible and infrared radiation. The light was deliberately defocused at the sample so as to ensure uniform radical distribution. Radical decay was followed by using the standard sectored disk arrangement; a procedure which has been described in detail elsewhere.[20]

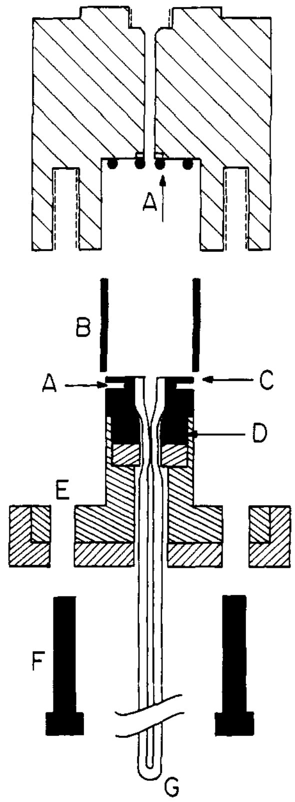

Figure 1. High-pressure cell and coupler: A, Viton O-ring; B, steel sleeve; C, steel washer; D, Teflon block; E, steel, male assembly; F, bolts; G, quartz pressure cell.

Pressure Cell. The high-pressure EPR cell and coupling was a scaled-up and somewhat modified[25] version of the design reported by LeNoble and Staub[15] (Figure 1). The cell was made from Spectrosil tubing, (o.d., 10 mm; i.d., 3 mm) which was drawn down in a glass-blowing lathe to the following dimensions (o.d. × i.d. × length): head, 10 × 3 × 7 mm; constriction, 5 × 0.5 × 11 mm; main body, 7 × 1.5 × 150 mm. The "flat" on top of the tube was made by cutting the drawn down tube using a diamong cutting wheel. The rough surface was then ground slightly. Polishing to an optical grade surface was not necessary. The heat drawing process actually improved the quality of the cells presumably because it removed surface scratches which lead to fracture under pressure. Cells were filled with solvent and were tested for 1 h at 300 atm before they were used in the spectrometer. Approximately 80% of cells survived testing and could then be repeatedly pressurized to 300 atm. The pressure cells invariably failed when they were operated at 500 atm.

The pressure coupling was made from stainless steel. The components which form the male section of the coupler were made in two halves so as to fit around the cell head and were secured with a stainless-steel collar.

In a typical experiment the reaction mixture was purged with nitrogen for ca. 10 min and was transferred to the coupler-cell assembly under a nitrogen atmosphere. The pressure cell was then sealed with a few drops of mercury which, because of the constriction, rarely entered the main body of the cell. Cell and coupler were connected via stainless-steel pressure tubing filled with mineral oil to a hand pump and Bourdon gauge. The cell was lowered into the variable-temperature insert of the spectrometer which had been modified to accept the 7-mm o.d. tube. It was then cooled to the appropriate temperature and was slowly (15 min) pressurized to 300 atm. Kinetic experiments were then carried out and were generally repeated several times at a given temperature, alternating between pressures of 300 and 1 atm.

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Table I. Rate Constants for the β Scission of Di-*tert*-butyliminyl in 2-Methylbutane

T, K	P, atm	$\log k_4$, s^{-1}
251	1	−0.390
251	295	−0.427
254	1	−0.0857
254	300	−0.109
255	1	−0.167
255	295	−0.192
260	1	0.0494
260	300	0.0285
260	1	0.169
260	295	0.139
264	1	0.214
264	285	0.231
265	1	0.319
265	300	0.321
266	1	0.417
266	290	0.410
268	1	0.450
268	300	0.424
270	1	0.565
270	300	0.504
272	1	0.689
272	295	0.696
274	1	0.780
274	305	0.748
276	1	0.790
276	290	0.770
283	1	1.059
283	295	1.058

The sample volume of the pressure cell is similar to that of normal EPR tubes, and therefore transient organic radicals could be generated photolytically to given spectra with good signal-to-noise levels. However, the upper operating limit of 300 atm for this cell design is a severe constraint since, for most normal volumes of activation, the change in rate constant over this pressure range is fairly small[6] and is therefore difficult to measure accurately.

Results and Discussion

Volumes of Activation for Reaction of Di-*tert*-butyliminyl. Di-*tert*-butyliminyl is an excellent subject for high-pressure studies since it undergoes a unimolecular β scission in the temperature range 248 to 283 K (reaction 4), while at lower temperatures it decays via bimolecular self-reaction (reaction 5).[21]

The radical was generated by photolysis of di-*tert*-butyl peroxide and di-*tert*-butyl ketimine in either 2-methylbutane or 2,2,4-trimethylpentane as solvent (reactions 2 and 3). The solution

$$t\text{-BuOO-}t\text{-Bu} \xrightarrow{h\nu} 2t\text{-BuO}\cdot \qquad (2)$$

$$t\text{-BuO}\cdot + (t\text{-Bu})_2\text{C}{=}\text{NH} \rightarrow t\text{-BuOH} + (t\text{-Bu})_2\text{C}{=}\dot{\text{N}} \qquad (3)$$

$$(t\text{-Bu})_2\ \text{C}{=}\dot{\text{N}} \xrightarrow{k_4} t\text{-Bu}\cdot + (t\text{-Bu})\text{C}{\equiv}\text{N} \qquad (4)$$

$$(t\text{-Bu})_2\text{C}{=}\dot{\text{N}} \xrightarrow{k_5} (t\text{-Bu})_2\text{C}{=}\text{N}{-}\text{N}{=}\text{C}(t\text{-Bu})_2 \qquad (5)$$

and coupler cell were rigorously degassed with nitrogen before use so that formation of di-*tert*-butyliminoxyl[21,28] was negligible.

Unimolecular Decay. Rate constants, k_4, for the β scission of di-*tert*-butyliminyl were measured at 1 atm over the temperature range 248–283 K so as to improve the precision of the previously reported data.[21] Radical decay was strictly first order, and the rate constants obtained were within experimental error of those reported earlier.[21] No contribution from the second-order process (reaction 5) could be detected in this temperature range. The results are listed in Table I and can be represented by[29]

$$\log k_4 = (12.3 \pm 0.3) - (14.5 \pm 0.4)/\theta$$

Table II. Relative Rate Constants for the Bimolecular Self-Reaction of Di-*tert*-butyliminyl at 194 K

P, atm	$\log (k_5^P/k_5^1)$	$\Delta V^{\ddagger}$, $\text{cm}^3\ \text{mol}^{-1}$
285	0.144	−18.6
280	0.100	−13.2
280	0.044	−5.5
280	0.241	−30.2
285	0.182	−23.4
285	0.005	−0.6
290	0.305	−38.5
295	0.110	−13.7

where $\theta = 2.30RT$ kcal mol^{-1}.

Rate constants (k_4) were also measured in this temperature range at 300 atm and were generally slightly smaller than corresponding 1-atm values (Table I), implying that reaction 4 has a small and positive volume of activation. Analysis of the data using eq 1 gives $\Delta V_4^{\ddagger} = 3.0 \pm 1.0$ $\text{cm}^3\ \text{mol}^{-1}$, where the quoted error represents one standard deviation.[33] The positive values of $\Delta V^{\ddagger}$ indicate an increase in volume in going from the ground-state radical to the transition state, suggesting that significant C–C bond stretching has occurred. Similar volumes of activation have been reported for homolytic single *or* multiple bond scission processes in molecules such as *N*-(1-cyanocyclohexyl)-pentamethylene ketimine and azocumene.[6]

Bimolecular Self-Reaction. Experiments in the temperature range 173–228 K confirmed the previous report[21] that di-*tert*-butyliminyl decays by a second-order process (reaction 5). Absolute rate constants, k_5, at 1 and 300 atm were *not* needed to determine $\Delta V_5^{\ddagger}$ since only the ratio of the rate constants at the two pressures is required (eq 1). As a result there was no need to measure the *absolute* radical concentration[34] and, consequently, an important source of experimental error was eliminated.

The *relative* radical concentrations at the two pressures were required in order to calculate the *relative* rate constants, $k^{1\ \text{atm}}/k^{300\ \text{atm}}$, and these were obtained via double integration of the EPR spectra by using the signal from a ruby disk located on the EPR cavity as a reference. Eight measurements of the relative rate constants at 194 K gave $\Delta V_5^{\ddagger} = -18.0 \pm 5.3$ $\text{cm}^3\ \text{mol}^{-1}$. The data are reported in detail in Table II.

The large and negative volume of activation for the self-reaction of di-*tert*-butyliminyl (reaction 5) is not dissimilar to those observed for bond-forming reactions and cycloadditions of neutral species.[5] This result seems reasonable since the coming together of two radicals to form a covalent bond should be accelerated by pressure. It contrasts with volumes of activation of ca. +16 $\text{cm}^3\ \text{mol}^{-1}$ found for radical–radical termination reactions in polymerizations.[8] However, as Walling pointed out,[8b] retardation of the termination process with increasing pressure is due to the fact that these radical–radical reactions are diffusion controlled.[35] Under such conditions, pressure affects the rate of radical–radical encounters and has little effect on the reaction of the caged radical pair.

Finally, no change could be detected in the hyperfine splittings of di-*tert*-butyliminyl when the pressure was increased to 300 atm, although at 194 K there was a small increase on line width with increasing pressure.

β Scission of *tert*-Butoxytriethoxyphosphoranyl. The chemistry of phosphoranyl radicals has been the subject of considerable

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[28] Mendenhall, G. D.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 2963.

[29] The earlier data[21] give $\log k_4 = (14.4 \pm 3.0) - (17.1 \pm 3.0)/\theta$.

[30] The temperature dependence of $\Delta V^{\ddagger}$ is negligible[3,31] in systems which do not require extensive solvation of the transition state.[32]

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[33] For a large sample, over two-thirds of the observations lie within plus or minus one standard deviation (σ) of the mean and 95% lie within $\pm 2\sigma$.

[34] For a description of the technique, see: Adamic, K.; Bowman, D. F.; Gillan, T.; Ingold, K. U. *J. Am. Chem. Soc.* **1971**, *93*, 902. Watts, G. B.; Ingold, K. U. *Ibid.* **1972**, *94*, 491.

[35] It has been suggested that it is artificial to assign values of $\Delta V^{\ddagger}$ to nonactivated processes like diffusion. See: Brower, K. R. *J. Org. Chem.* **1980**, *45*, 1004.

Table III. Rate Constants for the β Scission of Triethoxy-*tert*-butoxyphosphoranyl in 2-Methylbutane

T, K	P, atm	$\log k_7$, s^{-1}
181	1	1.945
181	300	1.935
185	1	2.090
185	300	2.095
188	1	2.260
188	295	2.205
191	1	2.450
191	285	2.445
195	1	2.455
195	290	2.490
198	1	2.555
198	290	2.595
205	1	2.870
205	305	2.845

interest over the past decade.[36] In particular, kinetics for the β scissions of tetraalkoxyphosphoranyls have been extensively studied. We decided to measure the volume of activation for the β scission of $t\text{-BuO}\dot{\text{P}}(\text{OEt})_3$, which gives *tert*-butyl and triethyl phosphate as products. Since this is a highly exothermic reaction,[37] it might, on the basis of Hammond's postulate, be expected to have an "early" transition state and, hence, a very small volume of activation.

The phosphoranyl radical was generated by photolysis of di-*tert*-butyl peroxide and triethyl phosphite in 2-methylbutane solvent (reactions 6 and 7). Radical decay, (reaction 8) was

$$t\text{-BuOO-}t\text{-Bu} \xrightarrow{h\nu} 2t\text{-BuO}\cdot \quad (6)$$

$$t\text{-BuO}\cdot + (\text{EtO})_3\text{P} \rightarrow t\text{-BuO}\dot{\text{P}}(\text{OEt})_3 \quad (7)$$

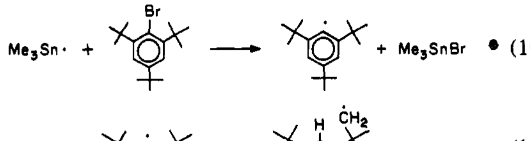
$$t\text{-BuO}\dot{\text{P}}(\text{OEt})_3 \xrightarrow{k_8} t\text{-Bu}\cdot + \text{OP}(\text{OEt})_3 \quad (8)$$

cleanly first order in the temperature range 181–205 K, and the rate constants measured at 1 atm were in excellent agreement with previously reported data.[37]

Seven measurements of k_8 were made at 1 and 300 atm of pressure between 181 and 205 K and gave $\Delta V_8^\ddagger = 0.2 \pm 1.9$ cm^3 mol^{-1}, where the stated error represents one standard deviation.[33] The data are given in detail in Table III. This volume of activation is much smaller than those normally obtained for homolytic bond fission reactions[6] (see di-*tert*-butyliminyl) and supports the view that this highly exothermic reaction has an "early" transition state.

Pressure Effects in Quantum Mechanical Tunneling. The isomerizations of 2,4,6-tri-*tert*-butylphenyl and 2,4,6-tris(perdeuterio-*tert*-butyl)phenyl to the corresponding 3,5-di-*tert*-butylneophyl (reaction 11) are thought to proceed by quantum mechanical tunneling.[22-24] This assessment is based mainly on the observation that the isomerization shows an H/D kinetic isotope effect much greater than that allowed by classical theory and that Arrhenius plots for H and D transfer are curved, with the curvature being for greater in the case of H transfer.[24] The existence of tunneling in a reaction is difficult to prove unequivocally and so it is important to bring the maximum weight of evidence to bear in any given case.[38]

$$\text{Me}_6\text{Sn}_2 \xrightarrow{h\nu} 2\text{Me}_3\text{Sn}\cdot \quad (9)$$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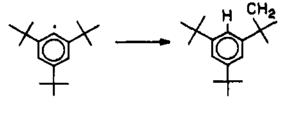
(11)

Table IV. Rate Constants for Isomerization of 2,4,6-Tri-*tert*-butylphenyl in 2-Methylbutane

T, K	P, atm	$\log k_{11}$, s^{-1}
144	1	−0.967
144	295	−1.047
153	1	−0.814
153	285	−0.888
171	1	−0.237
171	275	−0.270
172	1	−0.346
172	290	−0.350
173	1	−0.332
173	280	−0.353
185	1	0.452
185	280	0.445
194	1	0.208
194	280	0.202
210	1	0.717
210	290	0.646

Isaacs, Javaid, and Rannala have shown that the effect of pressure on the H/D isotope effect for a reaction can be used as evidence for tunneling.[39] In a reaction which does not involve tunneling $\Delta V_H^\ddagger$ is essentially equal to $\Delta V_D^\ddagger$. However, when tunneling is a contributing factor, $\Delta V_H^\ddagger \neq \Delta V_D^\ddagger$. We have therefore measured $\Delta V_H^\ddagger$ and $\Delta V_D^\ddagger$ for reaction 11.

Rate constants, k_{11}^H, for the isomerization of tri-*tert*-butylphenyl were measured in the temperature range 144–219 K at 1 atm. The radical was generated by photolysis of mixtures of hexa-*n*-butylditin and 2,4,6-tri-*tert*-butylbromobenzene in 2-methylbutane solvent (reactions 9 and 10). The data obtained were in excellent agreement with those previously reported[23] when cyclopropane was used as solvent. However, below these temperatures the previously reported data[23] could not be reproduced with the precision required for measurements of $\Delta V^\ddagger$, even when cyclopropane or propane was used as solvent. Nevertheless, we see no major reason to doubt the conclusions of the previous work[23,24] since the data obtained in the temperature range 144–219 K meet a number of the necessary criteria[23] for a reaction involving tunneling.

As a precautionary measure, rate constants for the isomerization of 2,4,6-tris(perdeuterio-*tert*-butyl)phenyl were measured in cyclopropane solvent over the temperature range 215–295 K and were in excellent agreement with the earlier results.[23,24] These new data are available as supplementary material. Since cyclopropane is unsuitable for use in the pressure cell, *tert*-butylbenzene and 2-methylbutane were tested for use as solvents. Rate constants measured in 2-methylbutane were slightly higher than those obtained in cyclopropane. This suggests that, at the higher temperatures required to follow the decay of the perdeuterated radical, some attack at the solvent was taking place. However, when *tert*-butylbenzene was used the measured rate constants were again in excellent agreement with the earlier cyclopropane data.[23,24] It should be noted that the necessity of using different temperature ranges to follow the decay of the deuterated and nondeuterated radicals dictates the use of different solvents and thus leads to experimental conditions which are somewhat less than optimal.

Values of k_{11}^H measured at 300 atm for the isomerization of 2,4,6-tri-*tert*-butylphenyl were consistently lower than their 1-atm counterparts and gave $\Delta V_{11(\text{H})}^\ddagger = 5.3 \pm 1.7$ cm^3 mol^{-1}. Similarly, experiments on 2,4,6-tris(perdeuterio-*tert*-butyl)phenyl in the temperature range 250–290 K gave $\Delta V_{11(\text{D})}^\ddagger = -1.2 \pm 2.0$ cm^3 mol^{-1}, where the stated errors represent one standard deviation. The data are reported in detail in Tables IV and V. Statistical

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[36] Roberts, B. P. *Adv. Free-Radical Chem.* **1980**, *6*, 225–289.

[37] Davies, A. G.; Griller, D.; Roberts, B. P. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 738. *J. Chem. Soc., Perkin Trans. 2* **1972**, 993, 2224. Watts, G. B.; Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1972**, *94*, 8784.

[38] For a detailed discussion of these problems see ref 23.

[39] Isaacs, N. S.; Javaid, K.; Rannala, E. *Nature (London)* **1977**, *268*, 372. *J. Chem. Soc., Perkin Trans. 2* **1978**, 709. Isaacs, N. S.; Javaid, K. *Ibid.* **1979**, 1583.

Table V. Rate Constants for Isomerization of 2,4,6-Tris(perdeuterio-*tert*-butyl)phenyl in *tert*-Butylbenzene

T, K	P, atm	$\log k_{11}$, s^{-1}
251	1	−0.352
251	290	−0.392
253	1	−0.340
253	300	−0.306
258	1	−0.094
258	295	−0.099
263	1	0.004
263	300	0.009
269	1	0.255
269	295	0.262
280	1	0.549
280	300	0.587
289	1	0.865
289	290	0.873

testing of the relationship between $\Delta V_{11(H)}^{*}$ and $\Delta V_{11(D)}^{*}$ shows that the probability that these volumes of activation are different is >99%. We take this to be further evidence supporting the hypothesis that the isomerization of 2,4,6-tri-*tert*-butylphenyl proceeds by quantum mechanical tunneling.

We believe that these experiments were probably more difficult to carry out than would be the case for most reactions purported to involve tunneling. That is, most purported examples of reactions which involve tunneling take place on reasonably long time scales (minutes or more) and do not require that the reagents be photogenerated within an EPR cavity. Instead, these reactions can usually be monitored with existing apparatus up to pressures of several kilobars. Since volumes of activation can provide additional evidence supporting or denying the involvement of tunneling, we strongly advocate their measurement whenever possible.

Acknowledgment. We would like to thank W. J. LeNoble and P. Staub for providing us with detailed drawings of their pressure apparatus, J. Vandenhoff for patient and skillful glass blowing, and G. O. Grummett and C. Pink for their help in the design and construction of the coupler.

Supplementary Material Available: Rate constants for the isomerization of tris(perdeuterio-*tert*-butyl)phenyl in cyclopropane solvent (1 page). Ordering information is given on any current masthead page.

The Decomposition of β-Phenethylsulfonyl Azides. Solution Chemistry and Flash Vacuum Pyrolysis[1]

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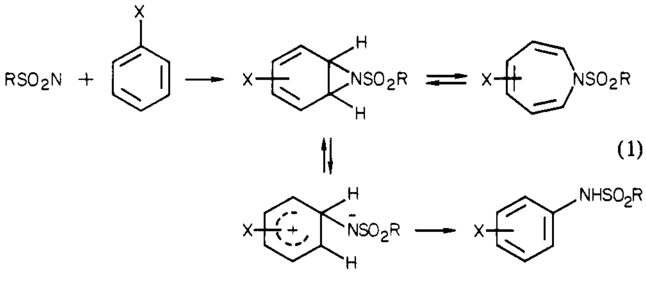
Abstract: The intramolecular cyclization of the parent title compound and a number of para-substituted derivatives (**1**) in solution was found to take place in low yield and to be accompanied by products of intermolecular reactions, namely, C–H insertion (**4**) and hydrogen abstraction (**3**). The use of an excess of a relatively inert solvent Freon 113 led to a better yield of the desired 3,4-dihydro-2,1-benzothiazine 2,2-dioxides (**2**). Flash vacuum pyrolysis (FVP) of **1** at 250–300 °C also gave some **2**, but the use of higher temperatures led to the formation of styrenes (**8**), indolines (**9**), indoles (**10**), sulfur dioxide, and the remarkable transformation products, the 4-substituted 6,7-dihydro-5*H*-1-pyrindines (**7**), in good yield. The styrenes result from the elimination of HN_3 and SO_2 from the azides, and indolines are formed in good yield by FVP of **2** at 650 °C. The dihydropyrindines are not obtained from **2**, and β-phenethylnitrene is not a source of any of the above observed products. A mechanism is proposed for the formation of **7** from β-arylethylsulfonylnitrenes. Consistent with this mechanism is the observation that both 1- and 2-phenylpropanesulfonyl azide give a mixture of 6- and 7-methyl-6,7-dihydro-5*H*-1-pyrindines in the same ratio on FVP at 650 °C. Thermolysis of **1a** in benzene at 100 °C gives an *N*-sulfonylazepine derivative. The FVP of **1** and **2** at 650 °C are preparative routes to **7** and **9**, respectively.

For a number of years we have been studying the reactions of sulfonylnitrenes, generated thermally from the corresponding azides,[3] with aromatic substrates.[4] Thus, it was established that, in the rate-determining step of the substitution process, singlet sulfonylnitrenes added to an aromatic nucleus to give a benzaziridine intermediate which underwent ring opening in a fast, product-determining step to give the *N*-sulfonanilides (thermodynamic control) or the *N*-sulfonylazepines (kinetic control) (eq 1). This reaction was then extended to the synthesis of heterocyclic compounds by intramolecular cyclization of sulfonylnitrenes.[5] Thus, cyclizations of 2-biarylsulfonyl azides[6a] and



(1)

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(1) For a preliminary communication on part of this work, see: Abramovitch, R. A.; Holcomb, W. D. *J. Am. Chem. Soc.* **1975**, *97*, 676.

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