

portions of toluene. The organics were combined, dried (Na_2SO_4), and chromatographed on silica gel with 1:9 methanol-dichloromethane as the developing solvent. The principal band at R_f 0.72 afforded after elution 1.22 g (4.45 mmol, 54.7%) of solid **1a** which recrystallized from heptane as pale yellow crystals: mp 144-145 °C (lit.² mp 141-143 °C); UV (EtOH) λ_{max} 276.5 nm (ϵ 1.2×10^4).

Anal. Calcd for $\text{C}_7\text{H}_7\text{N}_4\text{I}$: C, 30.6; H, 2.6; N, 20.4. Found: C, 30.6; H, 2.6; N, 20.2.

Another band at R_f 0.49 gave 0.24 g (0.88 mmol, 10.8%) of 6-iodo-7-ethylpurine which crystallized from heptane as fluffy, pale, lemon-colored crystals: mp 160-162 °C; UV (EtOH) λ_{max} 283.5 nm (ϵ 7.4×10^3); ^1H NMR (CDCl_3) δ 1.62 (t, 3 H), 4.62 (q, 2 H), 8.37 (s, 1 H), 8.79 (s, 1 H); mass spectrum, m/z (relative intensity) 275 (6.3), 274 (M^+ , 54.2), 149 (6.9), 148 (11.1), 147 (M^- , 100.0), 119 (41.7).

Anal. Calcd for $\text{C}_7\text{H}_7\text{N}_4\text{I}$: C, 30.6; H, 2.6; N, 20.4. Found: C, 30.3; H, 2.7; N, 20.6.

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Registry No. **1a**, 74465-49-9; **1b**, 5987-74-6; **2a**, 83026-89-5; **2b**, 83026-93-1; **3a**, 83026-90-8; **3b**, 83026-94-2; **4a**, 83026-91-9; **4b**, 83026-95-3; **5a**, 83026-92-0; **5b**, 83026-96-4; **6**, 83026-97-5; benzene, 71-43-2; *N*-methylpyrrole, 96-54-8; 2-methylfuran, 534-22-5; thiophene, 110-02-1; diphenyl disulfide, 882-33-7; 9-ethyladenine, 2715-68-6; 6-iodopurine, 2545-26-8.

Mechanistic Features of Allylic Hydrogen Abstraction by Alkoxy Radicals

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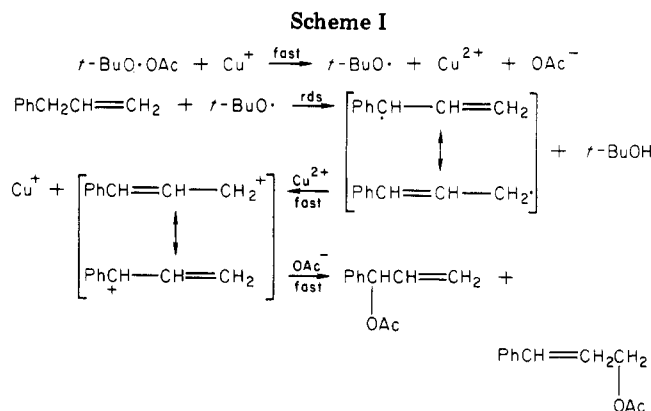
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A TS[‡] of angular H abstraction from allylbenzene in the course of the allylic acetoxylation reaction was previously invoked to explain a temperature-independent primary KIE; $k_{\text{H}}/k_{\text{D}} = 2.90$. This reaction geometry is now fully supported by the finding of inverse α -secondary deuterium isotope effects at both ends of the double bond in allylbenzene; $(k_{\text{H}}/k_{\text{D}})_{\alpha}^{\text{C}_1} = 0.977$ and $(k_{\text{H}}/k_{\text{D}})_{\alpha}^{\text{C}_2} = 0.985$. In keeping with these results an unsymmetrically structured, bridged radical intermediate, formed by the interaction of *t*-BuO• with the allylic double bond, steers the reaction course. Such a complex is recognized to be unusual since most of the verified cases of radical bridging involve heteroatom centers capable of octet expansion. A discussion is also given of the factors determining the relative influence of benzene and double bond participation in the H-abstraction reactions of allylbenzene, which possesses both of these activating functions.

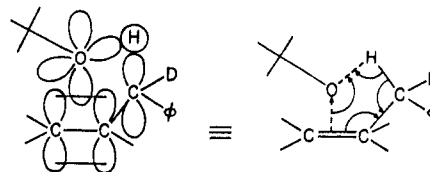
The unusual stability (through resonance) of allylic radicals compared to simple alkyl radicals is often treated as the cause of the high susceptibility of allylic or benzylic hydrogen to radical abstraction.¹ Moreover, polar resonance structures are widely invoked^{2,3} as the determining factors in the reactivity of benzylic and allylic hydrogen toward radical abstraction. Another reason for implicating the resonance participation of the double bond in the case of allylic H abstraction is that allylic rearrangements are common in such cases.^{4,5}

Allylic H abstraction is often the rate-determining step in many synthetically important reactions; (a) the hydroperoxidation of olefins by singlet oxygen,⁶ (b) the ene reaction,⁷ and (c) allylic and benzylic halogenation⁸ are three common examples.

The properties of the TS[‡] in H abstraction from various reaction centers has been the subject of several investi-



Scheme II. Bent TS[‡] of Allylic Hydrogen Abstraction



gations.^{2,3,9} Prior and Kniepp⁹ have tested for the symmetry of the TS[‡] of H abstraction from sulfur in reaction with a wide variety of free radicals by plotting the primary $k_{\text{H}}/k_{\text{D}}$ value at 25 °C vs. the heat of reaction. This work has produced cogent evidence suggesting that the mag-

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(5) Walling, C. In de Mayo, P. "Molecular Rearrangements"; Interscience: New York, 1967; pp 431-38.

(6) (a) For reviews of this reaction see: Foote, C. *Acc. Chem. Res.* 1968, 1, 104; *Pure Appl. Chem.* 1971, 27, 635. Stephenson, L. M.; Grdina, M. J.; Orphanopoulos, M. *Acc. Chem. Res.* 1980, 13, 419. See also: (b) Fenical, W.; Kearns, D. R.; Radlick, P. *J. Am. Chem. Soc.* 1969, 91, 3396, 7771. (c) Stephenson, L. M.; McClure, D. E.; Sysak, P. K. *Ibid.* 1973, 95, 7888. (d) Kellogg, R. M.; Kaiser, J. K. *J. Org. Chem.* 1975, 40, 2575.

(7) For a review of this reaction, see: Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* 1969, 8, 556.

(8) Larson, G. F.; Gilliom, R. D. *J. Am. Chem. Soc.* 1975, 97, 3444.

(9) Pryor, W. A.; Kniepp, K. G. *J. Am. Chem. Soc.* 1971, 93, 5584. See also: Lewis, E. S.; Butler, M. M. *Chem. Commun.* 1971, 941.

nitude of k_H/k_D bears the same relationship to the symmetry of the TS^* as does ΔH , the heat of reaction. It is the foundation of the argument that if the stability of the allylic radical to be formed were a factor in the ease of H abstraction, reaction with (for example) *t*-BuO \cdot radical would take place along a linear pathway representing the minimum energy requirement in an oriented, bimolecular approach. Indeed, Wiberg and Motell¹⁰ have provided the evidence for the linearity of H transfer and the symmetry of the TS^* in an H abstraction with formation of simple (nonallylic) alkyl radicals such as in the case of methane chlorination. This was achieved through measurement of k_H/k_D as a function of temperature with results ($[\Delta E_a]_D^H \approx 1.3$ kcal and $A_H/A_D \approx 1.1$) consonant with a symmetrical TS^* of linear H transfer and no tunnel correction.

More recently, measurements of the temperature dependence of k_H/k_D in allylic acetoxylation of $C_6H_5CHD-CH=CH_2$ ¹¹ gave a very different conclusion concerning the geometry and symmetry of the TS^* in a reaction involving rate-determining allylic H abstraction (see Scheme I).¹² The isotope effect activation parameters, $[\Delta E_a]_D^H \approx$ and $A_H/A_D \approx 2.9$, were deemed¹³ to be indicative of a bent TS^* of H abstraction, rather than the symmetrical, linear H-transfer TS^* anticipated on the basis of considerations discussed above.

Conceivably, there are a number of ways in which a bent TS^* of H abstraction could be realized. In an earlier communication,¹¹ in which a bent TS^* was deduced for the Scheme I reaction, the explanation was advanced that the allylic double bond was involved through formation of a preliminary complex with the *tert*-butoxy radical (see Scheme II). The TS^* of reaction arises from the decomposition of this complex, wherein the structure of the complex readily accommodates an angular H abstraction resulting in the allylic radical.

The problem addressed in the study on which we are reporting here could be titled as a search for evidence that an allylic double bond-*tert*-butoxy radical complex does indeed intervene in the course of allylic H abstraction. Conventionally, the addition of an electron-seeking reagent to the double bond, such as is presumed to occur in forming the complex with *t*-BuO \cdot , can be tested by means of α -secondary deuterium isotope effects.

This approach is illustrated in the early "qualitative" study of Denny and Tunkel¹⁴ and more recently in the extensive studies conducted by Wilkins and Regulski¹⁵ on polar electrophilic additions to styrenes in which various familiar reagents of the double bond were characterized by small, inverse, α -secondary deuterium isotope effects. The greater (inverse) magnitudes of $(k_H/k_D)_\alpha$ found were associated with those reagents which gave ancillary evidence of a bridging interaction with the double bond. For example, the 2,4-dinitrobenzenesulfonyl halides, which exhibited $(k_H/k_D)_\alpha$ values in the range of 0.94–0.95, are reagents for which Kharasch and co-workers¹⁶ have ad-

vocated episulfonium ion bridging in reaction with styrene. On the other hand, $(k_H/k_D)_\alpha = 0.97$ for the addition of Br₂ to styrene, for which reaction Yates¹⁷ has found evidence that only weak bridging occurs.

Similar inverse α -secondary deuterium isotope effects have been observed during radical additions to the double bond. For example, Pryor and co-workers¹⁸ have demonstrated such inverse isotope effects in styrene polymerization, suggesting the possible existence of an intermediate in the radical chain propagation event, one involving the chain-carrying radical in a bridging complex with styrene monomer. The addition of methyl or trifluoromethyl radicals to deuterated olefins is yet another clear example where an inverse $(k_H/k_D)_\alpha$ value (about 5% per D) is found.¹⁹ Moreover, α -secondary deuterium isotope effects are exerted at both ends of the styrene double bond, with the greater effect per deuterium at the phenyl-substituted carbon. On the basis of such precedence we undertook the evaluation of $(k_H/k_D)_\alpha$ at both the substituted and unsubstituted carbons in allylbenzene undergoing the allylic acetoxylation reaction outlined in Scheme I.

Experimental Section

Preparation of 3-Phenylpropionic-2,2-*d*₂ Acid. Sodium hydrocinnamate (0.1 mol) was charged in an autoclave along with 0.1 mol of sodium methylate and 0.6 mol of D₂O. The autoclave was rapidly sealed and heated at 200 °C for 24 h (approximately 200 psig of pressure was developed). When the cooled autoclave was opened and the contents transferred to a large beaker, 6 N HCl was cautiously added along with ice to keep the mixture cool while neutralization was achieved. The strongly acidic mixture was repeatedly extracted with ether, the ether extracts were dried, and the solvent was stripped. The crude residue was used as such in converting it to the 3-phenylpropanol stage.

Preparation of 3-Phenylpropanol-2,2-*d*₂. The crude 3-phenylpropionic-2,2-*d*₂ acid (ca. 0.1 mol) prepared above was reduced with lithium aluminum hydride in ether which had been freshly distilled from LiAlH₄. Under a dry nitrogen atmosphere, 5 g of LiAlH₄ was charged into a stirred reaction flask and covered with 400 mL of the dry ether. The deuterated acid dissolved in 100 mL of ether was slowly (over a period of 0.5 h) added to the stirred LiAlH₄ suspension. After the addition was completed, the stirred reaction was brought to reflux and held there overnight (ca. 13 h). The reaction mixture, cooled in an ice bath, was now quenched through addition of 6 mL of H₂O, 6 mL of 15% NaOH, and finally an additional 6 mL of H₂O to precipitate the white lithium and aluminum hydroxides. The ether solution was then filtered on a coarse, sintered-glass funnel, washed with saturated salt solution, dried over Mg SO₄, and stripped of the solvent on a rotary evaporator. The residue was vacuum distilled, and the fraction boiling at 100–105 °C (10 mm; 12.1 g) was identified by NMR to be the desired product: ¹H NMR (CCl₄) δ 7.13 (m, 5 H, aromatic), 3.58 (s, 3 H, CH₂OH), 2.61 (s, 2 H, benzylic), with no visible peaks at δ 1.77 where the central CH₂ absorption multiplet of an authentic sample of undeuterated 3-phenylpropanol normally occurs. This was taken to indicate almost complete deuteration at C₂, and the product was therefore utilized in the ensuing steps for preparation of the deuterated allylbenzene.

General Preparation of 3-Phenylpropanol Tosylate Derivatives.²⁰ The alcohol was added slowly to an ice bath cooled solution of 27.6 g (ca. 0.145 mol) of *p*-toluenesulfonyl chloride in 20 g of triethylamine and 200 mL of methylene chloride. The solution was allowed to come to room temperature and remain there under stirring for 20 h. The reaction mixture was then

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(13) For a discussion and the references cited therein, see: Kwart, H.; Brechbiel, M. *J. Am. Chem. Soc.* 1981, 103, 4650.

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(19) Feld, M.; Stefani, A. P.; Szwarc, M. *J. Am. Chem. Soc.* 1962, 84, 4451.

(20) The following procedure was used: Tipson, R. S. *J. Org. Chem.* 1944, 9, 235.

poured into excess water, stirred vigorously, and extracted with ethyl ether. The combined extracts were washed to neutrality with salt solution and dried over magnesium sulfate. The solvent was then stripped on the rotary evaporator. The residual yellow oil was used directly, without further purification, in several of the reaction steps described below.

Preparation of 3-Phenylpropene-2-*d*.²¹ Diphenyl diselenide (1.56 g, 5.0 mmol in EtOH (25 mL) was treated with NaBH₄ (0.375 g, 10 mmol) in small portions during which procedure the solution became colorless. The stirred solution was then cooled in an ice bath, and 2.85 g (9.8 mmol) of the tosylate of 3-phenylpropanol-2,2-*d*₂ dissolved in 20 mL of dry THF was added over a period of 0.5 h. The mixture was stirred at room temperature for 4 h and then poured into 5% Na₂CO₃. After extraction with ether, drying of the ether extracts, and stripping of the solvent, the crude selenide (2.8 g) remained as a yellowish oil. This oil was taken up in chloroform and treated with ozone at about -20 to -30 °C until the solution acquired the light blue coloration of excess ozone. This solution was refluxed for ca. 8 h, and the chloroform solvent was then stripped by distillation at ambient pressures in a jacketed Vigreux column. The reddish residue was then subjected to high-vacuum distillation with the distillate trapped in a receiver kept at -78 °C. This product was chromatographed on 100 mL of silica gel to remove any traces of selenium-containing contaminants and subjected to a final high-vacuum distillation before use; yield 1.2 g. It showed a ¹H NMR spectrum which indicated almost entirely allylbenzene-2-*d* by the unbroadened singularity of the peak representing aliphatic methylene hydrogens, the simplified (compared to authentic allylbenzene) vinyl-methylene region, and the total absence of vinyl methine signals. This preparation was used in composing the reaction mixture for estimating the (*k*_H/*k*_D)_α in allylic acetylation.

Preparation of 3-Phenylpropanol-1,1-*d*₂.²² Ethyl cinnamate (16 g, 9.44 mmol) was added to a stirring solution of lithium aluminum deuteride (2 g, 4.77 mmol) in 100 mL of dry ethyl ether at a rate which maintained reflux. When the addition was completed, the solution was heated at reflux under stirring for an additional 12 h. After the mixture cooled, 2 mL of water, 2 mL of 10% aqueous NaOH, and then 6 mL of water were added successively. The resulting precipitate was removed on a coarse glass filter, and the filtrate was washed with water to neutrality, dried over magnesium sulfate, and stripped of the solvent by rotary evaporation. The residue was used without further purification to prepare the appropriate tosylate ester derivative as described above.

Preparation of Dimethyl(3-phenylpropyl-1,1-*d*₂)amine.²³ The crude tosylate precursor (24 g) dissolved in dry ethyl ether (50 mL) was cooled in an ice bath under stirring. To this solution 15.4 g (335 mmol) of dry dimethylamine was added rapidly; the flask was tightly stoppered and allowed to stand at room temperature for 3 days. The solution was then poured into excess water and extracted with ethyl ether. The combined extracts were washed to neutrality and dried over magnesium sulfate before the solvent was stripped off on a rotary evaporator. The residual amine was vacuum distilled; the useful fraction at 80-85 °C (35 mm) comprised 5.48 g (40.4%).

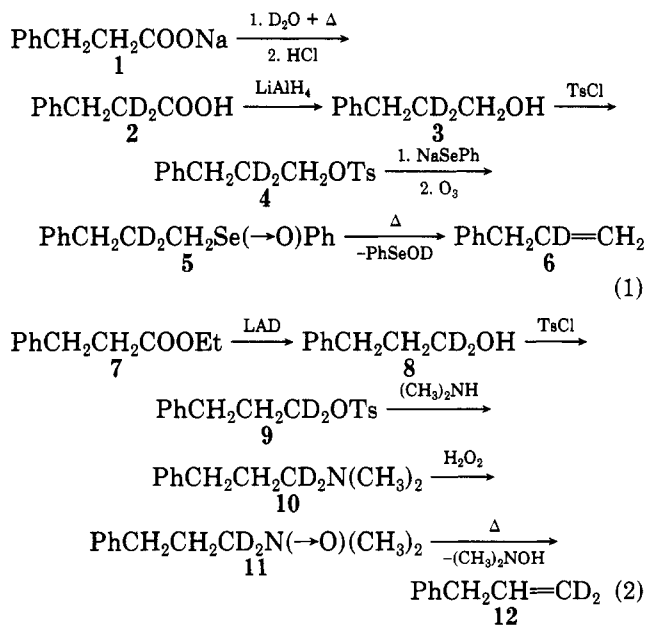
Preparation of 3-Phenylpropene-1,1-*d*₂ via Pyrolysis of the Amine Oxide.²⁴ A solution of 5.48 g of the amine prepared above in 5 mL of methanol was cooled in an ice bath, and an equimolar amount of 50% H₂O₂ was added under stirring. A second equimolar amount of the 50% H₂O₂ was added 80 min later. This solution was allowed to stir at ambient temperatures for 4 days, after which the remaining H₂O₂ was decomposed by cautious addition of 0.1 g of platinum oxide (Adams catalyst). This catalyst was recovered by filtration on a sintered-glass funnel, and the methanol and water were stripped from the filtrate by

vacuum distillation with minimal heat. The residual, viscous oil was then placed in a short-column distilling apparatus, with the distillation pot in a heated oil bath and the receiver immersed in a dry ice-acetone cooling bath. A vacuum of 10 mm was applied while the contents of the pot were stirred (magnetically) and heated slowly (over a period of 2.5 h) to a temperature of 160 °C. When volatile product was no longer perceptible, the contents of the receiver were transferred to a separatory funnel. The top layer was separated and redistilled under a 10-mm vacuum to give 2.21 g of the desired allylbenzene (55.4% yield overall).

Kinetic Procedures. A mixture of the appropriately deuterated and undeuterated allylbenzene was prepared in ca. 7.5 mL of acetonitrile solution and loaded into Pyrex pyrolysis tubes. The solution in each tube containing about 100 mg of the allylbenzene mixture was then saturated with cuprous bromide (about 0.1% based on the allylbenzene). To each tube was then added 1 g of a 70% *tert*-butyl peracetate solution in benzene. Each of the tubes was now subjected to a degassing procedure consisting of three cycles of freezing-pumping at high vacuum and thawing before sealing and immersion in an oil bath at 85.5 °C. The tubes were removed from this bath at appropriate times and worked up by reaction with a solution of sodium borohydride in 10 g of 25% aqueous NaOH. The organic phase was separated, dried over magnesium sulfate, and subjected to both analytical (to determine the extent of reaction) and preparative GLC procedures. The components of the reaction mixture separated from each tube were trapped in a cold capillary, sealed, and stored at -20 °C. The seal was broken only before use in the high-precision mass spectrometric procedure^{10f} by means of which we determined the ratio of deuterated and of undeuterated unreacted allylbenzene (as a function of extent of reaction).

Results and Discussion

The appropriately deuterated allylbenzenes, 6 and 12, which were used as substrates in the allylic acetoxylation reactions for which the (*k*_H/*k*_D)_α values of interest were to be estimated, were prepared by the different routes outlined, respectively, in eq 1 and 2.



The procedure described in the Experimental section for carrying out the competition in the allylic acetoxylation afforded all the data listed in Tables I and II. The values of the respective isotope effects computed from these data are seen to be both inverse and position dependent. In the light of previously reported, reliable magnitudes of α -secondary deuterium isotope effects in the addition reactions of styrene,¹⁵ the values for the C₁ effect, (*k*_H/*k*_D)_α = 0.977 per deuterium, and that of the C₂ effect, (*k*_H/*k*_D)_α = 0.985 per deuterium, must be regarded as significantly different.

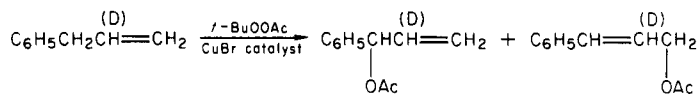
(21) This procedure is analogous to that developed by: Clark, R. D.; Heathcock, C. H. *J. Org. Chem.* 1976, 41, 1396.

(22) The procedure used here is analogous to that described by: Gannon, W. H.; House, H. O. *Org. Synth.* 1960, 40, 14.

(23) The procedure used here is based on one discussed by: Cope, A. C.; Pike, R. A.; Spencer, C. F. *J. Am. Chem. Soc.* 1953, 75, 3212.

(24) This procedure is analogous to one employed by: Cope, A. C.; Baumgardner, C. L. *J. Am. Chem. Soc.* 1957, 79, 960.

Table I. Kinetic Isotope Effect at 85.5 °C for the Reaction Below through Mass Ratio Determinations on the Composition of Starting Material Recovered at Various Stages of Reaction



f^c	M_{118}/M_{119}^a	$M_{\text{H}}/M_{\text{D}}^b$ (cor)	$M_{\text{D}}/M_{\text{H}} = R_{\text{A}_f}^c$	$k_{\text{H}}/k_{\text{D}}^{c,d}$
0	2.129 ± 0.002	0.603 ± 0.001	1.656 ± 0.001	
0.663	2.147 ± 0.001	0.616 ± 0.001	1.622 ± 0.001	0.979 ± 0.001
0.737	2.152 ± 0.002	0.620 ± 0.001	1.613 ± 0.001	0.979 ± 0.001
0.813	2.161 ± 0.006	0.626 ± 0.003	1.597 ± 0.002	0.977 ± 0.003
0.893	2.179 ± 0.002	0.639 ± 0.001	1.565 ± 0.001	0.974 ± 0.001

^a The molecular ions of allylbenzene and 2-deuterioallylbenzene were measured at 118 and 119 amu, respectively, with an ionizing potential of 70 eV. ^b $M_{\text{H}}/M_{\text{D}}$ was derived from M_{118}/M_{119} by correcting for the contribution of the $M_{\text{D}-1}$ peak and the $M_{\text{H}+1}$ peak. Analyses of pure allylbenzene and 2-deuterioallylbenzene gave $M_{\text{H}+1}/M_{\text{H}} = 0.0923 \pm 0.002$ and $M_{\text{D}-1}/M_{\text{D}} = 1.167 \pm 0.001$. The correction factor applied was

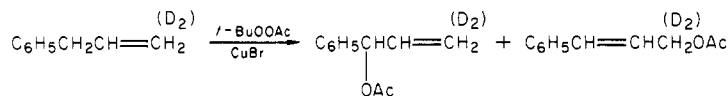
$$(M_{\text{D}}/M_{\text{H}})_{\text{cor}} = 0.183 \left[\frac{10.834 - \frac{M_{118}}{M_{119}}}{\frac{M_{118}}{M_{119}} - 1.167} \right]$$

^c Calculated by application of the equation

$$1/(k_{\text{H}}/k_{\text{D}}) = \frac{\ln(R_{\text{A}_f}/R_{\text{A}_0})}{\ln[(1-f)(1+R_{\text{A}_0})/(1+R_{\text{A}_f})]} + 1$$

where R_{A_0} is the ratio of heavy to light isotope at $t = 0$ and R_{A_f} is the heavy to light isotope ratio after a fraction f of reaction is completed. A linear regression of $\ln R_{\text{A}_f}$ vs. $\ln(1-f)$ yields $\ln R_{\text{A}_0}$ according to the derived relationship $\ln R_{\text{A}_f} = (k_{\text{D}}/k_{\text{H}} - 1) \ln(1-f) + \ln R_{\text{A}_0}$. Thus, R_{A_0} was found to be 0.8491. ^d Mean $k_{\text{H}}/k_{\text{D}} = 0.977 \pm 0.002$.

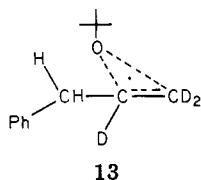
Table II. Kinetic Isotope Effect at 85.5 °C for the Reaction Below through Mass Ratio Determinations on the Composition of Starting Material Recovered at Various Stages of Reaction



f^c	M_{118}/M_{120}^a	M_{118}/M_{120}^b (cor)	M_{120}/M_{118} (R_{A_f} or R_{A_0})	$(k_{\text{H}}/k_{\text{D}})^c_{\text{det}}$	$k_{\text{H}}/k_{\text{D}}$ per D ^d
0	55.081 ± 0.001	47.304 ± 0.002	0.0211 ± 0.002		
0.530	56.128 ± 0.001	48.205 ± 0.003	0.0207 ± 0.001	0.975 ± 0.003	0.983 ± 0.002
0.663	56.719 ± 0.001	48.714 ± 0.012	0.0205 ± 0.002	0.969 ± 0.008	0.984 ± 0.004
0.737	57.249 ± 0.001	49.171 ± 0.004	0.0203 ± 0.002	0.968 ± 0.003	0.984 ± 0.002

^a The molecular ions of allylbenzene and allyl-1,1-*d*₂-benzene were measured at 118 and 120 amu, respectively, at an ionizing voltage of 70 eV. ^b See Table I, footnote b; here, however, the value M_{120}/M_{118} (for allyl-1,1-*d*₂-benzene) = 6.2200 ± 0.0005. Thus, $(M_{118}/M_{120})_{\text{cor}} = 0.861(M_{118}/M_{120} - 0.161)$. ^c The isotope effect was computed by applying the equation given in footnote c of Table I. ^d $(k_{\text{H}}/k_{\text{D}})_{\text{per D}} = (k_{\text{H}}/k_{\text{D}})_{\text{det}}^{1/2}$. Mean value of $k_{\text{H}}/k_{\text{D}}$ per D = 0.984 ± 0.001.

The most reasonable conclusion to be drawn from these results is that bridging of the double bond by the *t*-BuO· is taking place with formation of an intermediate like 13



whose structure closely resembles that of the allylic acetoxylation TS[†]. The requirement established by the earlier primary deuterium isotope effect studies¹¹ that the rate-determining H abstraction occurs with angular geometry is readily accommodated by an intermediate complex like 13. Moreover, the finding of a significant difference in the magnitudes of the $(k_{\text{H}}/k_{\text{D}})_\alpha$ values at C₁ and C₂ appears to support the unsymmetrical bridging structure assigned to 13. Therein, the greater degree of bonding (more sp³ character) depicted at C₁ is to be correlated with an inverse isotope effect (~2.5%) which is nearly twice as great as that at C₂ (1.5%).

The formation of bridged radical intermediates is not unprecedented.²⁵ A good deal of the evidence for the intermediacy of such cyclic radicals rests upon the observation of configurational retention in the course of radical substitution (bromination) in optically active bromobutanes,^{26,27} as well as a number of other cases based on stereochemical evidence^{28,29} for bridging following or concomitant with H abstraction. Evidence for halogen-bridged radicals also is to be found in ESR spectra which show that bridging can be unsymmetrical.^{30,31} Isotope effect³² and other kinetic studies³³ have also produced

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evidence for halogen-bridged radicals, and CIDNP evidence³⁴ has revealed the likelihood of unsymmetrical bridging in bromoethyl radicals. Finally, neighboring-group participation by RS groups, shown to be involved in the homolysis of *tert*-butyl peresters,³⁵ is yet another example of bridging by heteroatoms capable of octet expansion. The present case, wherein strong indications have been found for bridging by oxygen radicals, must be recognized as an unusual case of such activity by a heteroatom which does *not* possess octet expansion ability.

The evidence of $(k_H/k_D)_\alpha$ measurements considered above clearly specifies the double bond as the seat of bridging-complexation by the *t*-BuO· and consequently steers the course of reaction even though the flanking benzene ring is also capable of complexing such radicals. An example of complexing of the benzene ring by *t*-BuO· may be found in studies of the kinetic isotope effect associated with benzylic H abstraction.^{8,36} The work of Larson and Gilliom⁸ shows that when toluene reacts with *tert*-butyl hypochlorite, under conditions which exclude chlorine atoms as the chain carrier, linear H transfer involving tunneling is observed. The result is to be compared to the symmetrical, linear-H-transfer TS[‡] for methane chlorination, noted earlier to occur without evidence for tunneling.^{10a} Thus, the participation of the benzene ring in the H abstraction step as the seat of complexation for *t*-BuO· in organizing the ultimate H transfer from the nearby benzylic carbon is to be regarded as analogous to the role of the double bond in allylic H abstraction.

From this, we may conclude that if the benzene ring had been involved in the H-abstraction step, instead of the double bond in allylbenzene, we should have observed the pattern of steep temperature dependence of k_H/k_D , which is characteristic of the occurrence of tunneling, instead of

the temperature independent $k_H/k_D = 2.90$ that was observed.¹¹ On the other hand, if resonance stabilization of the resulting free radical was the driving force for H abstraction, one would have predicted that the greater benzylic resonance stabilization would dominate the course of the reaction and control the ease of reaction, contrary to the present experience.

A related concern is why a nucleophilic radical like *t*-BuO· leads predominantly to abstraction whereas electrophilic radicals like ROO· lead to addition.³⁷ Bertrand and Surzur³⁷ and Houk³⁸ have argued on the basis of frontier MO considerations that both nucleophilic and electrophilic radicals should attack the double bond and attain maximum stabilization interactions upon overlap with *p*-orbital centers. The present verification based on the identical experimental criteria^{15,17-19} that such a bridging interaction occurs both in the case of allylic H abstraction and in radical addition to the double bond is heartening. In other words, from both the experimental and frontier orbital viewpoints the ready formation of a bridged radical intermediate is an acceptable basis for interpretation of the course of subsequent events in the allylic H-abstraction process.

The question then arises as to the nature of the TS mobilized in a structure resembling that of the complex 13. We propose that this is a pseudopericyclic³⁹ TS (Scheme II) in which the *n* electrons on the oxygen abstracting the adjacent allylic H and the electrons bonding this oxygen to the π electron centers in the complex exchange roles as shown in Scheme II.

Registry No. 1, 114-84-1; 2, 83025-96-1; 3, 17428-98-7; 4, 60468-24-8; 5, 83025-98-3; 6, 83025-97-2; 7, 2021-28-5; 8, 17428-96-5; 9, 83025-99-4; 10, 83026-00-0; 11, 83026-01-1; 12, 83026-02-2; PhCH₂CD₂CH₂SePh, 83026-03-3; H₂, 1333-74-0; D₂, 7782-39-0; C₆H₅CH₂CH=CH₂, 300-57-2; *t*-BuOOAc, 107-71-1; CuBr, 7787-70-4; Me₃CO·, 3141-58-0; PhSeSePh, 1666-13-3.

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