e.g., NO_2, CN, etc. In the case of the acids of the nucleophiles of the phenol type, on the other hand, a substantial contribution to the ionization constant is made by electrostatic interaction of the cationic site and the proton, a repulsion of the latter assisting in its removal by the water molecules. Hence the basicity of the "α" nucleophile possessing a cationic charge to a neutral species will be reflected in its basicity to a proton (pK_a) and the reactivity of a "charged α" nucleophile is predictable from its pK_a.

Finally, it appears desirable to point out the implications of these conclusions on the general factors affecting nucleophilicity[14,21,22] and especially on the high reactivity shown by "α" nucleophiles.[14] In the anions of phenols and hydrated aldehydes, it is thought that the site of high electron density is highly localized in the nucleophile's oxygen,[23] whereas in the "α" nucleophiles, it is felt that the electrons are highly mobile and distributed over several of the electronegative atoms.[24] The lack of mobility of the highly localized electrons is responsible for the relatively low slope (β) values[21] in the correlation equations of rate and pK_a of the "non-α" nucleophiles in their reactions with organophosphorus esters. (Higher slopes are obtained with such nucleophiles if other factors, such as H bonding, contribute to the formation of the transition state, *e.g.*, in catechol.) In contrast, the highly mobile electrons in the "α" nucleophile are much more available for transition-state bond formation and show generally higher slopes. It is interesting, too, in this connection that β for the anions of keto oximes, which it is postulated contain *some* "non-α" character, lies between that of the anions of phenols and those of hydroxamic acids.

---

(21) R. F. Hudson, *Chimia* (Aarau), **16**, 173 (1962).

(22) J. F. Bunnett, *Ann. Rev. Phys. Chem.*, **14**, 271 (1963).

(23) In apparent contradiction to the postulation that the electron density is localized on the phenolic oxygen, it is well known that phenols react with many electrophiles at ring positions rather than at the phenolate oxygen, indicating that there is a high electron density at the ring positions. It is our feeling, however, that the high ring electron density results from the approach of the electron-deficient reactant; that in the presence of a localized substrate the distribution of electrons in the phenolate anions will be localized on the phenolic oxygen.

(24) See ref 12.

Secondary Deuterium Isotope Effects on a Cyclic Allylic Rearrangement[1]

Kirk D. McMichael

Contribution from the Department of Chemistry, Washington State University, Pullman, Washington 99163. *Received November 12, 1966*

Abstract: Secondary α- and γ-deuterium isotope effects on the cyclic intramolecular rearrangement of allyl thionbenzoate to allyl thiolbenzoate have been measured. The α effect (1.06) is significantly smaller than that observed for (1.10–1.12) carbonium ion, carbanion, or radical pathways. With the γ effect (0.97), this result indicates that these effects are useful mechanistic criteria for allylic rearrangements. These results also indicate that the transition state structurally resembles reactant more than product, suggesting that this type of study will be useful in characterizing the position of a transition state along a reactant–product coordinate in such reactions.

Intramolecular allylic rearrangement reactions have occupied a position of considerable importance in the development of organic reaction mechanism theory.[2] Many of these reactions have been important in the study of carbonium ion processes[3] and others have been resistant enough to ordinary mechanistic probes to earn the sobriquet "no mechanism" reactions.[4]

It has long been recognized that a continuum of merging carbonium ion pair and cyclic mechanisms may connect these two classes of allylic rearrangements.[5] Since examples of carbanion and homolytic intramolecular allylic rearrangements are now known,[2,6] this mechanistic continuum may be generalized to include, at the noncyclic limit, reactions of all three charge types, carbonium ion, radical, and carbanion, each merging with a cyclic reaction scheme at the other end of the continuum.

No satisfactory method for characterizing the mechanism of an intramolecular allylic rearrangement in terms of such a general cyclic to noncyclic continuum is presently available. A mechanistic criterion suited to this purpose should be insensitive to medium effects to permit its use in a wide variety of environments including the gaseous state. Methods for qualitatively placing a particular reaction along a carbonium ion cyclic continuum have been developed[7] and depend primarily on estimation of the polarity of the kinetically important transition state by means of kinetic solvent or substituent effects; reactions which are sensitive to polar effects are considered to involve carbonium ion pair mechanisms, and those which are insensitive are assigned cyclic mechanisms. The interpretation of

---

(1) Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) For a recent review, see P. B. D. de la Mare, "Molecular Rearrangements," P. DeMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 2.

(3) H. L. Goering, *Record Chem. Progr.*, **21**, 109 (1960), and later papers in this series.

(4) For a recent review, see S. J. Rhoads, ref 2, Chapter 10.

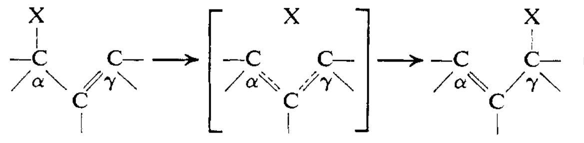
(5) S. Winstein, *Nature*, **173**, 898 (1954).

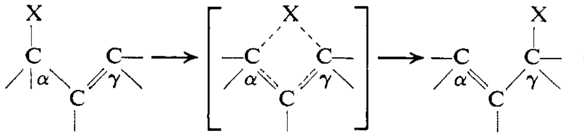
(6) G. S. Hammond and C. D. DeBoer, *J. Am. Chem. Soc.*, **86**, 899 (1964).

(7) S. G. Smith, *ibid.*, **83**, 4285 (1961).

these effects rests on a large body of empirical evidence concerning the magnitudes of polar solvent and substituent effects on carbonium ion reaction rates;[8] these methods are not directly applicable to the merging carbanion cyclic or homolytic cyclic continua.

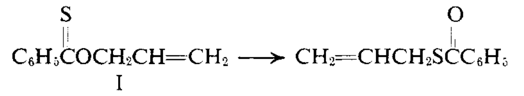
The fundamental difference between mechanisms for cyclic and noncyclic reactions is one of timing. In an extreme noncyclic reaction mechanism, the bond between the migrating group and carbon atom to which it was originally attached (α-carbon) is essentially completely broken before the onset of bonding between the migrating group and the migration terminus (γ-carbon), as indicated in eq 1. In contrast, the transition state for a cyclic reaction is characterized by significant bonding between the γ-carbon and the migrating group *before* completion of bond breaking between the α-carbon and the migrating group (eq 2). Thus a criterion capable of distinguishing between synchronous and stepwise bond-breaking and bond-making processes should be capable of distinguishing between cyclic and noncyclic mechanisms, or, more subtly, of placing a reaction on a general continuum between these extremes.


(1)


(2)

Recent investigations have shown that the study of secondary α-deuterium isotope effects ("effects of the first kind," in Halevi's terminology[9]) are valuable probes in studying the timing of bond-making and bond-breaking processes.[10] For our purposes, such effects have several valuable characteristics. First, Seltzer[11] has pointed out that the magnitude of the rate retardation associated with the substitution of one deuterium atom for a hydrogen atom α to the leaving group is remarkably constant at 10–12%, regardless of the charge type (carbanion, free radical, or carbonium ion) of the reaction. Second, inverse isotope effects have been observed upon substitution of deuterium for hydrogen at doubly bonded carbon atoms for a variety of reactions in which these carbons undergo a trigonal to tetrahedral conversion, similar to that envisioned for the γ-carbon in a cyclic allylic rearrangement transition state.[9] Third, since secondary deuterium isotope effects are basically substituent effects and appear to be unaffected by reaction medium effects, their use as mechanistic criteria in studying allylic rearrangement reactions should be restricted only by the availability of kinetic or other means of measuring the deuterium isotope effect with adequate precision and the ability to introduce deuterium atoms at the α- and γ-carbons of the appropriate allylic system. In this framework, cyclic allylic rearrangement transition states should exhibit smaller than normal rate retardations due to α-deuterium substitution and significant rate accelerations due to γ-deuterium substitution, in keeping with the synchyronous nature of bond-making and bond-breaking processes. In contrast, noncyclic rearrangements should exhibit normal α-deuterium isotope effects, since bond breaking at the transition state should be about as complete in their reactions as it is in the examples of carbonium ion, carbanion, and radical reactions for which deuterium isotope effects have been measured. The magnitude, even the direction, of γ-deuterium isotope effects in noncyclic reactions is less readily predicted, and a definite answer to this question awaits experimental evidence.

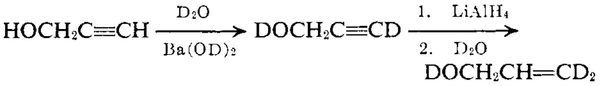
With this background, we have initiated a program to evaluate these effects as mechanistic criteria for intramolecular allylic rearrangements by measuring the kinetic effect of α- and γ-deuterium substitution on a reaction of known cyclic character. We chose to study the rearrangement of allyl thionbenzoate (I) to allyl thiolbenzoate (eq 3). Smith, who discovered this reaction, showed that it was extremely insensitive to polar, solvent, and substituent effects and must, therefore, involve a cyclic rather than a carbonium ion mechanism.[7] Other considerations render carbanion or free radical reactions unlikely. For our purposes, this reaction also offered ready synthetic accessibility and a convenient method for kinetic determinations.



$$\underset{\text{I}}{C_6H_5\overset{\overset{\text{S}}{\|}}{C}OCH_2CH{=}CH_2} \longrightarrow CH_2{=}CHCH_2S\overset{\overset{\text{O}}{\|}}{C}C_6H_5 \qquad (3)$$

Results

The required allyl-1,1-d_2 alcohol was prepared from acrylyl chloride and lithium aluminum deuteride according to the method of Schuetz and Millard.[12] After some exploratory experiments, the following route (eq 4) was worked out for the preparation of allyl-3,3-d_2 alcohol. The lithium aluminum hydride reduction of propargylic alcohols to allylic alcohols has been studied in some detail by Bates, Jones, and Whiting,[13] but this appears to be the first report of its use in the simplest case, propargyl alcohol itself. The deuterated allylic alcohols thus obtained were better than 99.2% homogeneous to capillary gas chromatography and had retention times undistinguishable from that of pure allyl alcohol. Their structures were further confirmed by infrared and nmr spectra. In particular in the infrared spectrum of the allyl-1,1-d_2 alcohol the α-CH_2 stretching bands at 3.41 and 3.49 μ appear as CD absorptions at 4.55 and 4.78 μ and the CH_2 deformation at 6.89 μ[14] is replaced by a new band at 8.70 μ which is probably the CD_2 deformation. In addition, the nmr spectrum of this compound differs from that of allyl alcohol in that



$$HOCH_2C{\equiv}CH \xrightarrow[\text{Ba(OD)}_2]{D_2O} DOCH_2C{\equiv}CD \xrightarrow[\text{2. } D_2O]{\text{1. LiAlH}_4} DOCH_2CH{=}CD_2 \qquad (4)$$

---

(8) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, Book Co., Inc., New York, N. Y., 1962, pp 42–49.

(9) E. H. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963).

(10) S. Seltzer and F. T. Dunne, *J. Am. Chem. Soc.*, **87**, 2628 (1965); S. Seltzer, *ibid.*, **87**, 1534 (1965).

(11) S. Seltzer, *ibid.*, **83**, 2625 (1961).

(12) R. D. Schuetz and F. W. Millard, *J. Org. Chem.*, **24**, 297 (1959).

(13) E. B. Bates, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1854 (1954).

(14) H. W. Thompson and P. Torkington, *Trans. Faraday Soc.*, **42**, 432 (1946).

the doublet at τ 6.00 of the α-methylene[15] proton is absent and the ten-line pattern of the β-vinyl proton is simplified to the four-line X portion of an ABX spectrum with J_{AX} (*trans*) = 16 Hz and J_{BX} (*cis*) = 10 Hz. Allyl-3,3-d_2 alcohol similarly exhibits a shift of the terminal methylene absorptions at 3.25, 3.35, 7.10, and 10.90 μ (CH) to 4.31, 4.51, 9.63, and 13.70 μ (CD) in the infrared. The nmr spectrum of this compound showed the absence of the 4.67–5.10 multiplet of the terminal methylene in allyl alcohol; the weak perturbations of the α-CH_2 doublet at τ 6.00 (long-range coupling) were gone and the β-vinyl resonance appeared as a broad hump at τ 4.12, presumably a triplet broadened by coupling to the deuterons on the γ carbon.

These alcohols, together with unlabeled allyl alcohol, were converted to the corresponding thionbenzoate esters by treatment with sodium hydride followed by thiobenzoyl chloride.[7] The latter compound was prepared by the method of Staudinger and Siegmant[16] and purified by repeated distillation to constant nmr and infrared spectra.

The allyl-1,1-d_2 thionbenzoate (II) thus obtained contained 1.98 D atoms per molecule and the isomeric allyl-3,3-d_2 thionbenzoate (III) has 1.85 D atoms per molecule.[17] The infrared spectrum of allyl thionbenzoate (I) was in agreement with that reported by Smith,[7] and its nmr spectrum supported the assigned structure. It is perhaps worthy to note that the aromatic protons *ortho* to the thiocarbonyl group in this series of compounds are deshielded relative to their counterparts in similar benzoyl compounds by about 0.3 ppm. The spectra of the deuterium-substituted allyl thionbenzoates are also consistent with their assigned structures, exhibiting spectral features similar to those observed for the corresponding alcohols.

The kinetic data recorded in Table I were obtained by the ampoule technique, following the disappearance of the thionbenzoate absorption at 410 μ in acetonitrile. Rate constants were calculated by the method of DeTar for the best least-squares fit to the exponential form of the first-order rate equation (see Experimental Section[18]). Standard errors in almost all cases were less than 0.8%, so that the 95% confidence limits for the individual rate constants are less than ±1.7%. Isotope effects (rate ratios) are calculated for simultaneous determinations on the three allyl thionbenzoates I–III. Isotope effects calculated for one deuterium atom at 100° are: α, 0.059 ± 0.007 and γ, 0.97 ± 0.007. Activation parameters calculated for the rearrangement of the unlabeled compound, allyl thionbenzoate, are $\Delta H^{\ddagger}$ 25.7 ± 0.6 kcal/mole and $\Delta S^{\ddagger}$ -10 cal/mole deg.

The effect of temperature on the deuterium isotope effects is so small that it is within the experimental error of our determinations. The slight increase in the magnitude of the γ-isotope effect is consistent with Seltzer's results on thiocyanate ion catalyzed isomerization of maleic to fumaric acid but is not of itself statistically significant. Attempts to calculate $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ from these data by the method of Leffek, Robertson, and Sugamori[19] give values which are not statistically significant.

Table I. First-Order Rate Constants and Deuterium Isotope Effects for Allyl Thionbenzoate–Allyl Thiolbenzoate Rearrangement in Acetonitrile

Temp, °C	$k_I \times 10^5$, sec^{-1}	$k_{II} \times 10^5$, sec^{-1}	$k_{III} \times 10^5$, sec^{-1}	$\alpha k_H/k_D$ (k_I/k_{II})	$\gamma k_H/k_D$ (k_I/k_{III})
100.0	4.29		4.50		0.945
	4.17	3.81	4.48	1.117	0.932
	4.22	3.73	4.44	1.131	0.950
	4.16	3.77	4.41	1.102	0.941
85.0	0.938	0.828	1.031	1.136	0.936
	0.909	0.841	0.977	1.128	0.937
70.0	0.186	0.168	0.201	1.111	0.926
	0.192	0.170	0.206	1.131	0.932

Samples of the reaction products, allyl thiolbenzoates, were obtained by treating samples of the allyl thionbenzoates I–III for 200 hr at 100° in sealed tubes.[7] Allyl thiolbenzoate was obtained from I, as indicated by the correspondence of its infrared spectrum with that reported by Smith and the agreement of its nmr spectrum with the assigned structure. Allyl-1,1-d_2 thionbenzoate (II) afforded the product of clean allylic rearrangement, allyl-3,3-d_2 thiolbenzoate, most clearly indicated by the absence of the τ 4.40–5.08 terminal methylene absorption in the nmr. Similarly allyl-3,3-d_2 thionbenzoate (III) gave allyl-1,1-d_2 thiolbenzoate as indicated by the absence of the τ 4.37 doublet (α-methylene). We estimate that no more than 3–4% of unrearranged allyl moiety could have gone undetected in these experiments. These results agree with the conclusion of Smith that clean arrangement of the allyl moiety accompanies conversion of the thion to the thiol ester.

Discussion

The strongly negative entropy of activation provides strong support for the conclusion, reached earlier by Smith[7] on the basis of polar solvent and substituent effects, that this reaction proceeds by way of a cyclic transition state. Similar values of $\Delta S^{\ddagger}$ have been observed for the Claisen and Cope rearrangements.[4,6] An alternate interpretation of large negative entropies of activation, electrostriction of solvent in a polar transition state, seems inapplicable here in view of the insensitivity of this reaction to solvent polarity.

The α-deuterium isotope effect (6–7% rate retardation) for this cyclic reaction is about one-half that observed at similar temperatures for the effect of similar deuterium substitution on reactions involving carbonium ion, carbanion, or radical pathways.[9,11] This difference in magnitude is well beyond the experimental uncertainty involved. Since allylic rearrangements of noncyclic character can be expected to show normal α-deuterium isotope effects (many of the "normal" reactions involve benzylic systems, electronically very similar to those involved in allylic noncyclic rearrangements), this result supports the hypothesis that α-deuterium isotope effects are of real value in distinguishing between cyclic and noncyclic pathways for these rearrangements.

---

(15) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 34.

(16) H. Staudinger and J. Siegmant, *Helv. Chim. Acta*, **3**, 824 (1920).

(17) Deuterium analysis by J. Nemeth, Urbana, Ill.

(18) D. F. DeTar, *J. Am. Chem. Soc.*, **78**, 3911 (1956). We are indebted to a referee for calling this method to our attention and to the staff of the Washington State University Computing Center for invaluable assistance.

(19) K. T. Leffek, R. E. Robertson, and S. Sugamori, *Can. J. Chem.*, **39**, 1989 (1961).

Similarly the rate acceleration (*ca.* 3% per deuterium) produced by deuterium substitution of the migration terminus is similar in magnitude and direction with several reactions in which some conversion of the trigonal carbon to tetrahedral has occurred at the transition state.[9]

This result may be compared to the γ-deuterium isotope effect of 1.00 (k_H/k_D) reported by Belanić-Lipovac, Borčić, and Sunko[20] for the solvolysis of α,α-dimethylallyl chloride. The small, but real, difference in γ-deuterium isotope effect between the cyclic reaction studied here and this carbonium ion solvolysis supports the hypothesis that this type of effect also can be useful as a mechanistic criterion in such systems, provided that further experimental work supports the generality of these effects. From an empirical point of view, these conclusions must be regarded as tentative until supported by further experimental work with both cyclic and noncyclic rearrangements.

Viewed in a more theoretical light, these conclusions do not rest on particular assumptions used with Bigeleisen's fundamental equation for deuterium isotope effects.[21] If we adopt Streitwieser's assumptions, application of eq 5 from his early paper[22] on this subject indicates that a change of -65 cm^{-1} in the bending frequencies of the allyl thionbenzoate is responsible for the γ-deuterium effect upon going to the transition state. Similarly a change of 135 cm^{-1} is associated with the α-deuterium effect. Again, adopting Streitwieser's analysis of the important isotope vibrational frequencies,[23] the terminal methylene group in allylic compounds has been assigned frequencies of 3080, 2990, 1410, and 920 cm^{-1}. Upon rearrangement these become, respectively, 2940, 2840, 1455, and 1385 cm^{-1} in the α-methylene compound, resulting in a total change of -325 cm^{-1} for the complete allyl thionbenzoate to allyl thiolbenzoate conversion. A similar change of $+325$ cm^{-1} is obtained for the deuterium-sensitive frequencies of the α-methylene group. Insofar as these changes in vibrational frequencies reflect the structure of the transition state, the situation at both the α- and γ-carbons resembles reactants more than products, with the change in frequencies somewhat more pronounced at the α- than the γ-carbon. It is worth noting that this conclusion does not rest on a detailed correlation between vibration frequencies and bond order of the reacting bond at the transition state, but rather on the assumption that changes in bond strength are reflected in roughly proportionate changes in vibration frequency for the α-CH bending modes.

Alternatively, if one adopts the formulation of Wolfsberg and Stern[24] in which bending force constants rather than vibrational frequencies are used as primary structural parameters, the same conclusion may be reached. In this way, one interprets the γ effect as reflecting a small alteration of the carbon–hydrogen bending force constants at the transition state and the α effect as involving a smaller alteration at this site than those commonly encountered or treated in Wolfsberg's model calculations. Insofar as bending force constants reflect structure, then, the same conclusion regarding placement of the transition state along the reaction coordinate is reached. The validity of this argument also does not rest on a relationship between force constants and bond order in the "reacting" bonds, although it seems reasonable to believe that the length of this bond in the transition state will influence the steric environment of the neighboring carbon–hydrogen bonds enough to alter the bending force constants.

Further, the transition state for this reaction may be described as "looser" than completely concerted in that bond breaking at the α-carbon appears to be more advanced than bond formation at the γ-carbon. This involves the assumption, reasonable but not firmly established, that the functional relationships between bond order in the bond-breaking process and the α-deuterium isotope effects are the same as those operating between the bond-making process and the γ-deuterium isotope effect. In this light, the fact that the γ-deuterium isotope effect is smaller than the α effect implies that bond making at the γ-carbon is lagging behind bond breaking at the transition state. *A posteriori*, this is reasonable since the conversion of reactant to transition state is an endothermic process and in a unimolecular reaction devoid of strong solvation effects it must involve a decrease in total bond order. This takes no account, of course, of over-all bond order changes internal to the allyl and thiocarboxyl moieties, which may well play a significant role in the activation process.

The pattern of deuterium isotope effects observed here is consistent with a transition state which more closely resembles reactant (allyl thionbenzoate) than product (allyl thiolbenzoate). This interpretation, which is consistent with Hammond's postulate[25] for a one-step exothermic reaction, does not depend on a particular set of approximations used in interpreting deuterium isotope effects, as discussed above, and raises the intriguing possibility that measurement of these effects in reactions of known cyclic character can lead to placement of their transition states along a reactant–product reaction coordinate. We are presently testing this hypothesis on such cyclic allylic rearrangements.

Experimental Section

Thiobenzyl Chloride. This material was prepared by the method of Staudinger.[16] Repeated distillation removed impurities exhibiting absorptions at τ 2.17–2.40 in the nmr and 12.6 and 14.2 μ in the infrared. The purified material was deep purple in color and had bp 53–55° (0.2 mm); λ_{max}^{film} 8.07 (s), 9.56 (s), 11.93 (s), 13.18 (s), 14.81 (s), and 15.70 (s) μ; nmr multiplets at τ 1.86–2.08 (2 H, *ortho*) and τ 2.48–3.08 (3 H, *meta* and *para*); λ_{max}^{ether} 527 mμ (ϵ 68).

Allyl-1,1-d_2 Alcohol. This material was prepared by the method of Schuetz and Millard,[12] bp 92–95° (690 mm); λ_{max}^{film} 3.00 (broad, s), 4.55 (m), 4.78 (s), 7.09 (s), 8.38 (s), 9.10 (s), 10.04 (s), 10.40 (s), and 10.80 (s) μ; nmr absorptions at τ 3.86–4.31 (1 H, quadruplet, $J_{AX} = 16$ Hz, $J_{BX} = 10$ Hz), τ 4.67–5.10 (2 H, two overlapping AB quadruplets, J_{AX} and J_{BX} as above, $J_{AB} = -2$ Hz), and τ 5.30 (1 H, singlet); no detectable absorption at τ 6.0 (α-CH$_2$).

---

(20) V. Belanić-Lipovac, S. Borcic, and D. E. Sunko, *Croat. Chem. Acta*, **37**, 61 (1965).

(21) J. Bigeleisen, *J. Chem. Phys.*, **17**, 425 (1949).

(22) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).

(23) It is recognized that this approach is somewhat deficient in the absence of a complete assignment of the vibrational frequencies of those compounds (see ref 9). However, these assignments are supported by the observed shifts in our deuterium-substituted allylic compounds and are in accord with previous work (ref 14; also, L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 13, 34.)

(24) M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, **8**, 325 (1964).

(25) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

Propargyl-3,O-d_2 Alcohol. Propargyl alcohol (11.2 g, 0.20 mole) was equilibrated with 20 g of D_2O containing 6 mg of barium oxide overnight. The mixture was continuously extracted with 15 ml of ether for 6 hr, and the ether layer was stirred overnight with 20 g of fresh D_2O containing 35 mg of BaO. The latter equilibration was repeated twice more, and the final ether extract was dried and distilled in a micro spinning-band column affording 8.16 g of propargyl-3,O-d_2 alcohol, bp 108–110° (690 mm), homogeneous to capillary gas chromatography. Spectral analysis showed: nmr <1% τ 7.29 (C≡CH), *ca.* 10% τ 5.37 (OH), τ 5.75 (CH_2, singlet); λ_{max}^{film} 3.00 (OH, m), 3.86 (CD, s), 4.03 (OD, m), 5.04 (m), 7.36 (m), and 9.78 (m) μ.

Allyl-3,3-d_2 Alcohol. Propargyl-3,O-d_2 alcohol (8.0 g, 0.14 mole) dissolved in 100 ml of dry ether was added dropwise under a nitrogen atmosphere to a slurry of lithium aluminum hydride (5.7 g, 0.15 mole) in 70 ml of ether maintained at 4–6° in an ice bath. After the addition was complete (85 min), the reaction mixture was stirred at 0° for 12 hr when gas chromatographic examination of a quenched aliquot showed that the reduction was 95% complete and that less than 0.3% of propyl alcohol had been produced. Deuterium oxide (12 ml) was cautiously added, and the mixture was stirred for 14 hr when 9.6 ml of 10% aqueous NaOH solution was added. The precipitated inorganic solids were removed by filtration and washed well with ether. The combined filtrates and washings were distilled in a micro spinning-band column affording 2.88 g of allyl-3,3-d_2 alcohol, bp 92–94° (695 mm), containing less than 0.2% propyl alcohol and less than 0.6% propargyl alcohol by capillary gas chromatography. Spectral analysis showed: λ_{max}^{film} 3.00 (broad, OH), 3.49 (CH_2, m), 4.05 (broad, OD), 9.10 (m), 9.91 (s), 13.70 (m) μ; nmr absorptions (in τ) at 4.12 (1 H, broad), 3.98 (2 H, doublet, J = 5 Hz), and 6.78 (OH, 0.6 H, singlet), negligible absorption at 4.87 (δ-CH_2).

Allyl Thionbenzoate and Its Deuterated Analogs. These compounds were prepared from the appropriate allyl alcohol and thiobenzoyl chloride by the method of Smith. The spectra of all three allylic thionbenzoates had the following common features: $\lambda_{max}^{cyclohexane}$ 420 mμ (ϵ 122); λ_{max}^{film} 3.26 (w), 6.27 (w), 6.90 (w), 7.60 (s), 7.92 (s), 8.20 (s), 9.30 (m), 9.52 (m), 9.76 (m), 10.72 (m), 12.98 (m), 14.60 (s), and 15.76 (m) μ; nmr absorptions at τ 1.75–1.98 (2 H, *ortho*, multiplet) and τ 2.62–3.02 (3 H, *meta* and *para*, multiplet). In addition, allyl thionbenzoate had λ_{max}^{film} 10.10 (w), 10.90 (w) μ; and nmr absorptions at τ 3.65–4.34 (1 H, β-proton, multiplet), τ 4.53–4.95 (2 H, =CH_2, multiplet), and τ 4.97 (2 H, CH_2, weakly perturbed doublet, J = 6 Hz, overlapping =CH_2 peak).

Anal.[26] Calcd for $C_8H_{10}OS$: C, 67.38; H, 5.66; S, 17.99%. Found: C, 67.63; H, 5.80; S, 17.74.

Allyl-1,1-d_2 thionbenzoate had, in addition, λ_{max}^{film} 4.50 (w), 4.70 (w), 7.10 (m), and 10.90 (m) μ, and showed nmr absorptions at τ 4.02 (center of gravity, 4 lines, J_{AX} = 17 Hz, J_{BX} = 10 Hz, 1 H) and τ 4.54–4.95 (multiplet, 2 H, =CH_2). Allyl-3,3-d_2 thionbenzoate had, in addition, λ_{max}^{film} 4.31 (w), 11.20 (w), and 13.40 (m) μ, and showed nmr absorptions at τ 4.08 (broad, 1 H, half-height width 13 Hz) and τ 5.01 (doublet, J = 6 Hz, 2 H).

Kinetic Measurements. Rates were followed by the ampoule technique, 13 separate observations between 10 and 85% reaction being made in most runs. Three simultaneous kinetic determinations were made on allyl thionbenzoate (I) and its deuterated analogs II and III. Solutions were made up by accurately weighing the appropriate thionbenzoate into a 50-ml volumetric flask and diluting to the mark with spectro grade acetonitrile. Aliquots (3.3 ml) were transferred to Pyrex ampoules which were immediately sealed. Care was taken to randomize the order in which ampoules were sealed and later removed from the constant temperature bath.

The ampoules were weighted with lead strips and placed in a wire mesh basket. The basket was placed in the constant temperature bath (controlled to 0.02° by a proportioning controller) and allowed to come to thermal equilibrium for 30–60 min. To start each run, other ampoules were similarly withdrawn and quenched at appropriate intervals to obtain each kinetic point. An ampoule was withdrawn and immediately quenched in ice–acetone. Control experiments showed that the temperature dropped more than 20° within 5 sec. The quenched ampoules were stored in the refrigerator at −5° until the run was completed. Infinity points were obtained after 10–12 half-lives at 100° and were about 2% of the initial absorption.[27] Before measuring the absorbance the ampoules were allowed to warm to room temperature. The absorbance at 410 mμ was read from the 520 to 350 mμ spectrum of the sample determined on a Cary Model 14 spectrophotometer. Duplicate determinations were reproducible to 0.003 absorbance unit.

Following the method of DeTar,[18] the rate constants were determined by fitting the data to the equation $A = a + be^{-kt}$, where A is the absorbance at time t, a is the absorbance at infinite time, and $b = A_0 - A_\infty$. The initial estimates of a and b required by this method were measured values and the initial estimate of k was obtained from a least-squares fit of the data to the equation $\ln (A - A_\infty) - \ln (A_0 - A_\infty) = -kt$. Table II contains data for a typical run, including a comparison of observed absorbances and those calculated from the parameters obtained from the exponential least-squares fit. The standard deviations of most rate constants were less than 0.8%, and calculated initial and infinity absorbances were within 0.01 absorbance unit of those observed. Temperatures were measured by a National Bureau of Standards calibrated thermometer.

Table II. Data for a Typical Kinetic Run[a]

Time, sec	Absorbance	
	Obsd	Calcd
0	1.131	1.134
3,555	0.970	0.971
7,210	0.829	0.828
10,800	0.708	0.708
14,430	0.606	0.605
18,005	0.519	0.519
21,605	0.443	0.445
25,155	0.383	0.383
28,800	0.330	0.329
32,400	0.283	0.283
36,000	0.243	0.244
39,605	0.212	0.211
43,200	0.181	0.183
46,755	0.161	0.159
∞	0.022	0.022

[a] Initial estimate: $A = 0.0220 + 1.1090 \exp(-0.000044644t)$; final parameters: $A = 0.0220 + 1.1125 \exp(-0.000044755t)$.

Reaction Products. Samples (*ca.* 150 mg) of allyl thionbenzoate and the two deuterium-substituted allyl thionbenzoates were sealed in small glass ampoules and immersed in the 100° oil bath for 200 hr (more than ten half-lives for the slowest reaction rate reported). The products were characterized as follows. Allyl thionbenzoate gave allyl thiolbenzoate: $\lambda_{max}^{cyclohexane}$ 420 mμ (ϵ 1.2); λ_{max}^{film} 3.27 (w), 3.41 (w), 6.02 (s), 6.32 (m), 6.91 (m), 8.30 (s), 8.51 (s), 10.14 (m), 11.00 (s), 12.97 (s), 14.56 (s), and 15.47 (s) μ; nmr absorptions at τ 2.02–2.25 (multiplet, 2 H, *ortho*), 2.51–2.75 (multiplet, 3 H, *meta* and *para*), 3.80–4.50 (multiplet, 1 H, β), 4.40–5.08 (multiplet, 2 H, δ), and 6.37 (doublet, J_{app} = 7 Hz, 2 H, α). Allyl-1,1-d_2 thionbenzoate gave allyl-3,3-d_2 thiolbenzoate: $\lambda_{max}^{cyclohexane}$ 420 mμ (ϵ 1.6); λ_{max}^{film} as in allyl thionbenzoate except that the 10.14-μ band was absent; bands at 4.31 (w), 4.51 (w), and 13.60 (m) μ; nmr absorptions as in allyl thiolbenzoate except that τ 4.40–5.08 δ-hydrogen absorption and weak perturbations of the τ 6.37 doublet were absent, and the τ 3.80–4.50 multiplet had collapsed to a broad absorption centered at τ 4.19, half-height width 14 Hz. Allyl-3,3-d_2 thionbenzoate gave allyl-1,1-d_2 thiolbenzoate; $\lambda_{max}^{cyclohexane}$ 420 mμ (ϵ 1.6); λ_{max}^{film} as in allyl thiolbenzoate except that the 3.42-μ band is absent and an absorption at 4.64 (w) μ is present; nmr as in allyl thionbenzoate except that the τ 3.80–4.50 multiplet has collapsed to a four-peak pattern centered at τ 4.17 (J_{AX} = 16 Hz, J_{BX} = 10 Hz), the τ 4.40–5.08 multiplet is simplified to an eight-line pattern centered at τ 4.92 (J_{AX} and J_{BX} as above, J_{AB} probably ~2 Hz), and the τ 4.37 doublet was absent.

---

(26) Galbraith Laboratories, Knoxville, Tenn.

(27) S. G. Smith[7] reported a similar observation.