

closed and 5 opened, pumped at about 1 mm. for a few minutes. Stopcock 1 is then turned to admit 2 p.s.i.g. of oxygen and the flask is warmed until the solution melts, is recooled, and re-evacuated. This process is carried out twice, then stopcock 5 is closed and the reactor is warmed to room temperature while maintaining 2 p.s.i.g. of oxygen pressure. Stopcocks 2, 3, and 4 are opened, the manifold is evacuated and then filled with oxygen, and stopcock 5 is opened. The buret L is filled and the recorder adjusted to near 100% and started. The apparatus is then lowered so that the reactor sits in the bath over a rotating magnet. By adjusting the valve F the mercury is brought as close as possible to J without actual contact. With stopcocks 2, 3, 4, and 5 open, the vacuum line is disconnected and stopcock 1 is opened briefly to the atmosphere or to some desired pressure for the reaction, and then closed. Stopcock 3 is then closed and the Thermocap turned to "high." The mercury in D will now show the reactor gases expanding slightly, or the recorder will show any uncatalyzed autoxidation. Usually no volume change occurred. After sufficient warm-up time the ball joint cap is adjusted so that the catalyst tube falls into the solution. The rapid stirring by the  $\frac{3}{4}$ -in. magnetic bar<sup>19</sup> quickly

(19) See ref. 6b for stirrer description.

brings about catalyst dissolution, and the recorder shows an immediate beginning of an accurate zero-order plot. The buret is read and the volume and time are marked on the recorder chart at the proper point. This is repeated when the buret is nearly empty. Valve V<sub>3</sub> is opened to allow the buret to fill quickly and recording is continued until sufficient data are obtained. We usually excite the transducer with 12 v. d.c. (an automobile battery can be used), which produces about 25 mv. from a 50-ml. buret filled with mercury. The transducer tends to produce a current even when the buret reads empty, and a negative zero adjust on the recorder is required. If the recorder is not so equipped, a small bucking voltage can be put in reverse series with the transducer by using a 1.5-v. battery and two resistors of about 1000 ohms and 1-2 ohms.

Using the technique described, as many as six cumene autoxidation runs can be carried out in 8 hr. The results are in very good agreement with published rates of cumene autoxidation.<sup>5</sup>

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## The Relation of Proton Exchange to Tautomerism in Unsaturated Ethers

C. D. Broaddus

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*Deuterium exchange experiments with alkyl allyl ethers, using potassium *t*-butoxide in refluxing *t*-butyl alcohol for 10 days, have shown that isomerization to alkyl *cis*-propenyl ethers occurs with incorporation of a deuterium atom in the methyl position of the propenyl group as the major process. Approximately 30% of the product does not contain deuterium. Alkyl *cis*-propenyl ethers, under the same conditions, undergo very little if any exchange. At higher temperatures, 175° for 24 hr., the *cis*-propenyl isomer undergoes exchange at the methyl position of the propenyl group. These results are interpreted in terms of a common allyl anionic intermediate which protonates more rapidly to produce the more stable isomer, i.e., alkyl *cis*-propenyl ethers.*

### Introduction

The role of carbanionic intermediates in base-catalyzed reactions of allylic systems is an area of high current interest. Reaction systems which have been investigated employing deuterium exchange techniques include vinylacetic acid,<sup>1</sup> cyclohexenyl nitriles,<sup>2</sup> cyclohexenones,<sup>3</sup> unsaturated sulfoxides,<sup>4</sup> in-

dene,<sup>5</sup> and aliphatic olefins.<sup>6,7</sup> Also studies have been conducted utilizing optically active compounds in conjunction with deuterium exchange.<sup>8-10</sup> Ingold<sup>9</sup> originally proposed that those systems involving relatively stable ionic intermediates isomerized through the formation of a common allylic anion while with less acidic compounds a concerted transition state was realized. Cram's<sup>8c</sup> very recent work with methylenazomethine equilibria demonstrates that the operation of concerted processes in these reactions has not been established. In several cases<sup>5-8</sup> intramolecular hydrogen transfer has been demonstrated.

(3) J. Warkentin and L. K. M. Lam, *Can. J. Chem.*, **42**, 1676 (1964).

(4) D. E. O'Connor and C. D. Broaddus, *J. Am. Chem. Soc.*, **86**, 2267 (1964).

(5) G. Bergson, *Acta Chem. Scand.*, **17**, 2691 (1963).

(6) S. Bank, C. A. Rowe, and A. Schriesheim, *J. Am. Chem. Soc.*, **85**, 2115 (1963).

(7) (a) For studies with dienes see R. B. Bates, R. H. Carnighan, and C. E. Staples, *ibid.*, **85**, 3032 (1963). (b) Exchange with cycloheptatriene has also been reported: W. von E. Doering and P. P. Gaspar, *ibid.*, **85**, 3043 (1963).

(8) (a) D. J. Cram and R. T. Uyeda, *ibid.*, **84**, 4358 (1962); (b) D. J. Cram and R. T. Uyeda, *ibid.*, **86**, 5466 (1964); (c) D. J. Cram and R. D. Guthrie, *ibid.*, **87**, 397 (1965).

(9) C. K. Ingold and C. L. Wilson, *J. Chem. Soc.*, 1493 (1933); 93 (1934).

(10) S. K. Hsü, C. K. Ingold, and C. L. Wilson, *ibid.*, 1778 (1935).



an atmosphere of nitrogen and the temperature was maintained between 45 and 55°. Upon disappearance of the sodium metal, dodecyl bromide (350 g., 1.4 mole) was added to the reaction mixture which was stirred at 50° for 48 hr. After this period, the mixture was poured into 1.5 l. of water and extracted with ether, the extract was dried with anhydrous MgSO<sub>4</sub>, and the solvent was removed on a rotary evaporator to yield 322.0 g. of crude material. Distillation (86–87° at 0.1 mm.) gave 307 g. (98.5%) of pure material by gas chromatographic analysis. The n.m.r. data is recorded in the Results section.

Octyl allyl ether was prepared in a similar manner and hexyl allyl ether was purchased from Peninsular Chemical Co., Gainesville, Fla.

**Preparation of *cis*-Propenyl Ethers.** These compounds were prepared by a slight modification of the method developed by Prosser.<sup>11</sup> The corresponding allyl ethers were heated to 150° for 24 hr. in the presence of 10% by weight of potassium *t*-butoxide. Water was then added to the reaction mixture, the product was extracted with ether, and the ether extract was dried with anhydrous magnesium sulfate and distilled to give material having the spectral characteristics recorded in the Results section.

**Exchange Experiments in Refluxing Alcohol.** As an example of this type exchange experiment, the reaction of dodecyl allyl ether is given. To 10 ml. of *t*-butyl alcohol-*d* (purchased from Merck Sharp and Dohme), was added potassium metal (0.5 g., 0.013 g.-atom) and the resulting mixture was refluxed until the metal had reacted. The allyl ether (1.0 g., 0.0044 mole) was added to the reaction mixture and the resulting solution was refluxed for 10 days. All operations were conducted under an atmosphere of dry nitrogen. At the end of this period the solution was poured into *ca.* 50 ml. of water, extracted with diethyl ether, and dried with anhydrous magnesium sulfate, and the solvent was removed to give 0.85 g. of ether showing the n.m.r. and mass spectra discussed in the Results section.

**N.m.r. Data.** The n.m.r. spectra were recorded on a Varian A-60 spectrometer using tetramethylsilane as an internal standard and adopting the  $\tau$  scale.<sup>15</sup>

**Mass Spectral Data.** The mass spectra were recorded on an Atlas CH-4 mass spectrometer and percentage compositions were calculated from the relative heights in the parent peak region.

## Discussion

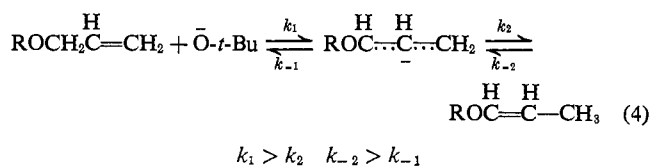
It is apparent from these results that alkyl allyl ethers undergo deuterium exchange during isomerization to alkyl *cis*-propenyl ethers with incorporation of a deuterium atom at the methyl position of the propenyl substituent.<sup>16</sup> Furthermore, under similar conditions alkyl *cis*-propenyl ethers undergo comparatively slow exchange. These results are consistent with either a concerted mechanism<sup>9</sup> in which conversion of alkyl *cis*-propenyl ether to the corresponding allyl isomer is slow (reaction 3), or with the formation of a common

(15) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(16) It is also evident that about 30% of the isomerization occurs in deuterated solvent without incorporation of deuterium. This data is quite similar to that obtained in an elegant study of the 3-phenyl-1-butene<sup>8</sup> system and suggests that an intramolecular process is also operative in ethers. The implications of this observation are the same as earlier reports<sup>5-8</sup> and will not be considered further.

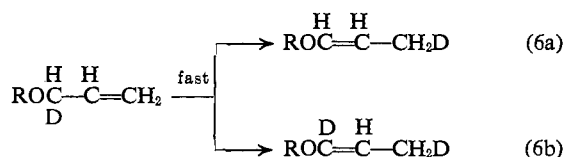
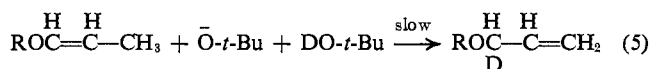


allyl anionic intermediate (more rapidly formed from the allyl isomer) which protonates more rapidly to produce the more stable isomer<sup>17</sup> (reaction 4).



To distinguish between these pathways it was necessary to effect exchange using the *cis*-propenyl isomer. As discussed in the Results section, this was accomplished by heating to 175° for 24 hr. and resulted in exchanged material which was predominantly monodeuterated (47% non-, 40% mono-, 11% di-, and 1.3% trideuterated).

This result does not appear compatible with a concerted exchange reaction. If one considers the relative amounts of mono- and dideuterated product it is apparent that an inversed<sup>18</sup> isotope effect would be needed to accommodate this data by concerted processes. Thus, the first step in the exchange would involve formation of deuterated alkyl allyl ether (reaction 5) followed by rapid reversion to the *cis* ether (reactions 6a and 6b).



The mass spectral data clearly show that monodeuterated compound is formed preferentially, requiring more rapid abstraction of deuterium (6a) than hydrogen (6b) in the reversion to *cis* ether. An occurrence of this nature seems highly unlikely.<sup>19</sup> Furthermore, the n.m.r. data do not indicate the presence of vinyl deuterons, as shown in reaction 6b, although at a low percentage of the composition (11%) it might not be detectable.

It then appears that our data is best accommodated by the formation of a common allyl anionic intermediate which protonates more rapidly to produce the more stable isomer and which forms more rapidly from the less stable isomer, *i.e.*, reaction 4.

Since only the *cis* isomer is obtained in the isomerization reaction<sup>11,12</sup> and exchange of *cis*-propenyl ether occurs at 175° without evidence for the formation of *trans* isomer,<sup>20</sup> it follows that a *cis*-allyl anionic inter-

(17) Operation of this mechanism would be another<sup>4,8b</sup> violation of Ingold's rule (C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 565) since the more reactive allyl isomer would be predicted to be formed more rapidly, *i.e.*,  $k_{-1} > k_{-2}$ .

(18) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961).

(19) Inversed or negative isotope effects have been observed in exchange reactions in which a pre-equilibrium step is involved: D. J. Cram, D. A. Scott, and W. D. Nielsen, *J. Am. Chem. Soc.*, **83**, 3688 (1961). However, pre-equilibrium is not obtained here nor in the 3-phenyl-1-butene case<sup>8</sup> where  $k_{\text{H}}/k_{\text{D}}$  ranged from 3.5 to 1.

(20) At equilibrium a mixture consisting of ~65% *cis* and ~35% *trans* is reported.<sup>11,12</sup>

mediate intervenes and retains its configuration.<sup>21</sup> It has been previously postulated that electrostatic interactions involving the cation of the basic catalyst favor the *cis* configuration.<sup>11,12</sup> The exchange studies reported here, while strongly indicating the intermediacy of a common allyl anionic species, offer no new insight concerning *cis* selectivity.

It is interesting to note that examples of tautomerization reactions have now been reported in which (1) the less stable isomer reacts faster to form a common anionic intermediate and is formed faster from that intermediate,<sup>1-3</sup> (2) the less stable isomer reacts faster to form the intermediate and is formed slower from the intermediate,<sup>8,22</sup> and (3) the less stable isomer reacts slower to give the intermediate and is formed slower from the intermediate.<sup>4</sup> Of the possible combinations of exchange rates and relative stabilities, only that system remains in which a less stable isomer would react more slowly to form a common intermediate and be formed faster from the intermediate. This hypothetical case is internally inconsistent since it would require increasing concentrations of the less stable isomer during equilibration.

Explanations for the relative rates of formation of the various isomers from the anionic intermediates have been offered on the basis of the charge distribution in the allylic system, *i.e.*, that protonation occurs more rapidly at the position of higher electron density. This approach has been discussed by many workers and is apparently consistent with the experimental data.<sup>3,4,23,24</sup> In the present case such an explanation would require that the alkoxy group exert an electron-repelling effect on the  $\pi$ -system of the allyl anionic intermediate, thereby increasing the relative charge density and the rate of protonation at the terminal position. An electron-repelling effect, by a methoxy group, has been used to explain the position of protonation during Birch reductions.<sup>25,26</sup> However, as noted previously,<sup>4</sup> a postulate of this nature allows prediction of the forward rate of reaction, *i.e.*, proton loss, only in those cases in which the less stable isomer is formed faster. Thus, microscopic reversibility demands in these systems that the less stable isomer also lose protons more rapidly. In the sulfoxide case,<sup>4</sup> in which the less stable isomer is formed more slowly and loses protons more slowly, energy differences between the

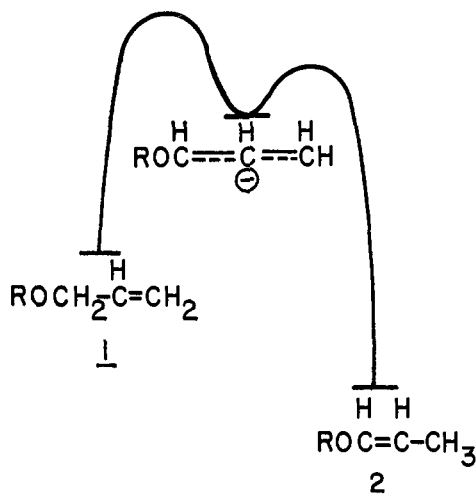


Figure 1. Energy diagram for the interconversion of 1 and 2.

allyl anionic intermediate and the transition states for protonation apparently control the course of the reaction, outweighing differences in ground-state energies.

In the present case, however, the isomer which is formed more rapidly during the protonation step, alkyl *cis*-propenyl ether, loses protons more slowly than does the alkyl allyl isomer. This leads to the conclusion, that while electron distribution may control the position of protonation, ground-state energies control the relative rates of proton loss.<sup>27</sup> This can be illustrated as in Figure 1.

In considering all these systems then it becomes apparent that generalizations based on either the position of protonation or the ground-state energy differences alone are incomplete and that both factors must be considered in any individual case. It appears fortuitous that those systems which were first examined had the proper combination of ground-state stabilities and relative rates of protonation of the allyl anionic intermediates to result in Ingold's rule.

**Acknowledgments.** I would like to thank Dr. D. E. O'Connor for stimulating discussions, Dr. J. H. Collins for mass spectral analyses, and Dr. T. J. Flautt for n.m.r. determinations.

(27) From the observation that at least 99% of the *cis* isomer is formed<sup>11,12</sup> one can calculate a minimum energy difference on the order of 3 kcal./mole for these two isomers. In an unpublished study W. von E. Doering and R. Vollrath have shown that the methoxy group conjugatively interacts with a double bond to the extent of about 5.75 kcal./mole. Thus, 1-methoxy-3-phenylpropenes were equilibrated in dimethyl sulfoxide with potassium *t*-butoxide at 26° to yield 21.5% 1-phenyl-3-methoxypropene-1 and 78.5% 1-methoxy-3-phenylpropene-1. Since phenyl has a conjugative interaction of about 5 kcal./mole with a double bond, the conjugative interaction of methoxy is concluded to be about 5.75 kcal./mole. Since the double bond of alkyl *cis*-propenyl ether would be stabilized by methyl as well as an alkoxy group, relative to the allyl isomer, the energy difference in this case would be expected to be even larger. I would like to thank Professor Doering for making these results available before publication.

(21) For other allyl anionic systems which retain their configuration see D. H. Hunter and D. J. Cram, *J. Am. Chem. Soc.*, **86**, 5478 (1964).

(22) This paper.

(23) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 418, and references therein.

(24) J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 238.

(25) A. J. Birch, *Quart. Rev. (London)*, **4**, 69 (1950).

(26) See A. P. Krapcho and A. A. Bothner-By, *J. Am. Chem. Soc.*, **81**, 3658 (1959), for recent work on the mechanism of the Birch reduction.