

plain the reactivity patterns in reactions 15 and 16, indeed, the relative rates of reactions 15 and 16 have been calculated using the appropriate exchange rate constants and thermodynamic barriers.<sup>3</sup>

In comparing the (intrinsic) barriers in the  $\text{Cr}^{2+}$ - $\text{CrX}^{2+}$  and  $\text{Fe}^{2+}$ - $\text{FeX}^{2+}$  exchange reactions it is also necessary to consider the effect of X on the interaction energies in addition to its effect on the reorganization energies. When the interaction energies are very small (less than  $\sim 100$  cal/mol) the reactions will not be adiabatic and the value of the preexponential factor in the expression for the free energy of activation (eq 5) may change as X is varied. On the other hand, the reactions will be adiabatic when the interaction energy is larger than about 500 cal/mol. This is probably the case in the exchange reactions considered here. However, if the interaction energy becomes too large it may no longer be neglected in calculating the energy of activation for the reaction. The interaction energy will be relatively large when the redox orbitals have the appropriate symmetries to overlap with the orbitals of the

bridging group. Since an  $e_g$  electron is transferred in the  $\text{Cr}^{2+}$ - $\text{CrX}^{2+}$  exchange reactions while a  $t_{2g}$  electron is transferred in the  $\text{Fe}^{2+}$ - $\text{FeX}^{2+}$  exchange reactions,  $\sigma$  interactions with the bridging group will be important when chromium(II) is the reducing agent while  $\pi$  interactions may be more important in reductions by iron(II). The reactivity pattern in the exchange reactions may thus reflect, in part, the relative  $\sigma$ - and  $\pi$ -bonding abilities of the halide ions as bridging groups.

The interpretation of the reactivity patterns obtaining in other systems remains an interesting and challenging problem. However, as suggested by theory,<sup>6,7,36</sup> electron-exchange reactions appear to provide a useful reference or standard state for considering more complex electron-transfer processes.

*This work was supported, in part, by the U. S. Atomic Energy Commission. The author wishes to thank Professor Francis T. Bonner and his colleagues in the Chemistry Department of the State University of New York at Stony Brook for their hospitality as well as for many stimulating discussions.*

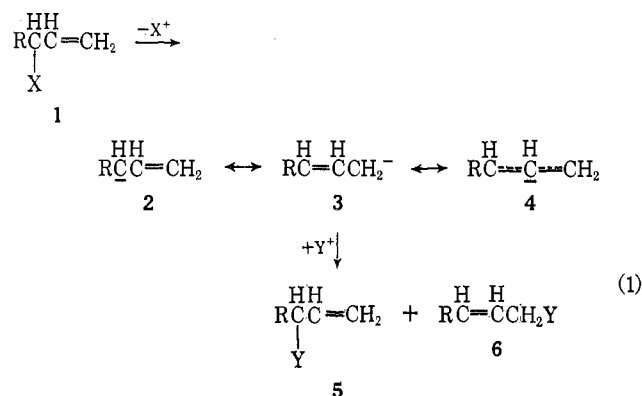
## Equilibria and Base-Catalyzed Exchange of Substituted Olefins

C. D. BROADDUS

The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239

Received February 15, 1968

Reactions at positions adjacent to double bonds, *i.e.*, allylic positions, are of interest for two basic reasons.<sup>1</sup> First, in unsymmetrically substituted systems two types of products may be formed. As shown in eq 1, generation of an allylic intermediate (in this case a negatively charged *carbanion*) can be followed by reaction at the original site of attachment of the departing group to give **5** or through an "allylic rearrangement" to give the isomeric product **6**. Examples of this type



of reaction are widespread and occur through positively charged (carbonium ions) and free-radical intermediates, as well as through allylic carbanions. It is then of interest to investigate what factors control

the product distributions from these various reactions.

Secondly, these processes proceeding through allylic intermediates are generally rapid as compared to the corresponding reactions in saturated systems. This has been attributed to electron delocalization in the transition states leading to allylic intermediates. Such delocalization (mesomerism) can be pictured as in structures **2-4**. While increased reactivity is generally observed, the extent of this increase is not well defined.

The present discussion is concerned primarily with anionic allyl intermediates.<sup>2</sup> The main points of interest are (1) the relative rates of formation of an anionic intermediate common to two unsaturated isomers (tautomers) and (2) the relative rates of protonation of the anionic intermediate to form the two isomers.

An early generalization of allyl anionic reactivity was stated by Ingold:<sup>3</sup> "when a proton is supplied by acids to the mesomeric anion of weakly ionizing tautomers of markedly unequal stability, then the tautomer which is most quickly formed is the thermodynamically least stable; it is also the tautomer from which the proton is lost most quickly to bases." This

(1) P. de la Mare in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 27.

(2) For reviews see (a) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 238; (b) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, Chapter V; (c) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 418; (d) M. J. S. Dewar, *Advan. Chem. Phys.*, **8**, 102 (1965).

(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 565.

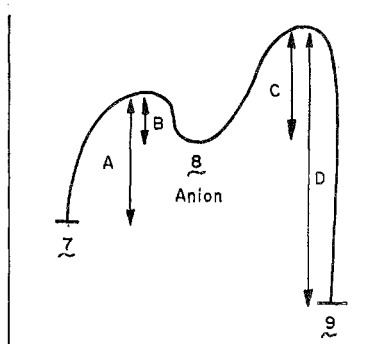
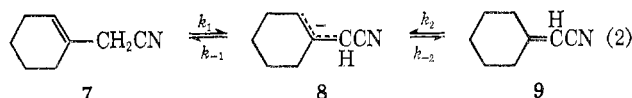


Figure 1.

statement implies control of the reaction systems by ground-state energy factors and resulted from such observations as the deuterium exchange data shown in eq 2. That is, equilibration of isomers **7** and **9** gave a



distribution of  $\sim 0\%$  **7** and  $\sim 100\%$  **9**, and deuterium exchange studies<sup>4</sup> showed that  $k_1 > k_2$  and  $k_{-1} > k_{-2}$ . A qualitative energy diagram for this system is shown in Figure 1.

Another approach to the same data can be made by considering the reaction to be controlled by the relative rates of protonation of anion **8**. That is, in considering intermediate **8** it could be suggested that the carbon to which the cyano group is attached would bear a larger share of the electron pair contained in the  $\pi$  system than would the allylic carbon removed from the substituent. Then protonation at the adjacent site ( $k_{-1}$ ) would be expected to be faster than  $k_{-2}$ , and microscopic reversibility would demand that the less stable compound undergo proton loss more rapidly ( $k_1 > k_2$ ). While either of these approaches adequately accounted for the early observations in base-catalyzed tautomerism, it was a major portion of our work to show that neither is universally applicable.

Obviously, studies in this area must involve a determination of the relative stabilities of the tautomers as well as the relative rates of deuterium exchange.

During the course of these studies<sup>5</sup> rapid vinyl, as compared to allyl, base-catalyzed deuterium exchange was observed with  $\alpha,\beta$ -unsaturated sulfones. This observation and the fact that 1-alkenyl methyl sulfones undergo exchange most rapidly at the  $\text{SO}_2\text{-CH}_3$  position are considered in the latter part of the discussion.

### Stabilities of Olefinic Substrates

The olefinic substrates with which we have been concerned include alkenyl sulfoxides,<sup>5a</sup> allyl and propenyl ethers,<sup>5b</sup> cyclopentenyl sulfones,<sup>5c</sup> and alkenyl sulfones.<sup>5d</sup> O'Connor and Lyness<sup>6</sup> obtained the equilib-

(4) C. K. Ingold, E. de Salas, and C. L. Wilson, *J. Chem. Soc.*, 1328 (1936).

(5) (a) D. E. O'Connor and C. D. Broaddus, *J. Am. Chem. Soc.*, **86**, 2267 (1964); (b) C. D. Broaddus, *ibid.*, **87**, 3706 (1965); (c) C. D. Broaddus, *ibid.*, **88**, 3863 (1966); (d) C. D. Broaddus, unpublished work.

(6) D. E. O'Connor and W. I. Lyness, *J. Am. Chem. Soc.*, **86**, 3840 (1964).

Table I  
Percentage Composition of Equilibrium Mixtures of  $\alpha,\beta$ - and  $\beta,\gamma$ -Unsaturated Sulfides, Sulfoxides, and Sulfones

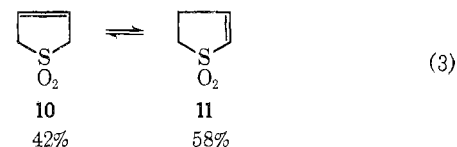
$$\text{RCH}_2\text{CH}=\text{CHX} \xrightleftharpoons{K} \text{RC}=\overset{\text{H}}{\text{C}}-\overset{\text{H}}{\text{C}}-\text{CH}_2\text{X}$$

Entry	R	X	% I	% II
1	C <sub>3</sub> H <sub>7</sub>	SCH <sub>3</sub>	66	34
2	C <sub>3</sub> H <sub>7</sub>	SCH <sub>3</sub>	67	33
3	C <sub>3</sub> H <sub>7</sub>	S(O)CH <sub>3</sub>	4	96
4	C <sub>3</sub> H <sub>7</sub>	S(O)CH <sub>3</sub>	4	96
5	C <sub>3</sub> H <sub>7</sub>	SO <sub>2</sub> CH <sub>3</sub>	<1	>99

rium data shown in Table I.

Since the effect of chain length on these equilibria is negligible, this study provides a direct comparison of the effect of  $\text{CH}_2\text{X}$  and X groups on the stabilities of double bonds. Entry 1 shows that  $\text{SCH}_3$  stabilizes a double bond slightly, relative to  $\text{CH}_2\text{SCH}_3$ ; entry 4 shows that the  $\text{CH}_2\text{S(O)CH}_3$ -substituted olefin is stabilized relative to the corresponding  $\text{S(O)-CH}_3$  isomer; and entry 5 indicates an even greater preference for the  $\text{CH}_2\text{SO}_2\text{CH}_3$ -substituted olefin. Thus, a direct relation between the electron-withdrawing ability of a substituent and the equilibrium amount of  $\beta,\gamma$  isomer is clearly indicated.

The cyclic sulfone system shown in eq 3 has been equilibrated at  $50^\circ$  to give the distribution shown.<sup>5c</sup> Since isomer **11** is favored statistically by a factor of

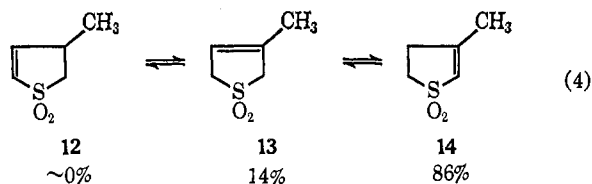


2:1, it can be seen that **10** is more stable by some 0.2 kcal/mol. This differs markedly from the acyclic system. However, this system involves a double bond substituted by  $-\text{CH}_2\text{SO}_2\text{CH}_2-$  (**10**) vs. one substituted by  $-\text{CH}_2\text{CH}_2\text{SO}_2-$ ; i.e., unlike the acyclic case, which provided a measure of  $\text{CH}_2\text{SO}_2\text{CH}_3$  vs.  $\text{SO}_2\text{CH}_3$  effects, both substituents on the double bond undergo change upon interconversion of these isomers. Then the inductive electronic effects are attenuated by factors which are difficult to estimate. Repulsion terms could also be of importance in this cyclic case. Crystallographic data for **10**<sup>7</sup> show that the  $\alpha$ -methylene hydrogens are opposed to the sulfur-oxygen bonds. It may be reasonably assumed that 1,2 interactions in **10** would involve repulsion between the C-H bonds of the methylene sites and the sulfur-oxygen bonds of the sulfone group. Then, if repulsive interactions between adjacent C-H bonds differ from the interactions between C-H and S $\rightarrow$ O bonds, an additional factor is added to the determination of the equilibrium distribution of **10** and **11**.

Whatever the reasons for the essentially equal distribution shown in eq 3, introduction of a methyl substituent in this system alters the isomer distribution

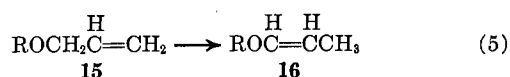
(7) G. A. Jeffrey, *Acta Cryst.*, **4**, 58 (1951).

markedly. As shown in eq 4, base-catalyzed equilibration of **13** and **14** at  $\sim 50^\circ$  gave a 14:86 distribution



of these compounds, while treatment of **12** with base resulted in complete disappearance of this isomer and formation of isomers **13** and **14**.<sup>5d,8</sup> Since alkyl substitution stabilizes olefinic species, isomer **12** would be expected to be the least stable of the three isomers, as is observed. The reasons for **14** being some 1.2 kcal/mol more stable than **13** are, however, not as straightforward. Thus, the two compounds are similarly substituted, and molecular models indicate that no steric interactions favor **14** relative to **13**. If the data outlined in eq 3 establish the relative stabilities of the unsubstituted ring systems, it follows that the methyl group in **14** stabilizes the system by some 1.4 kcal more than the methyl group of **13**.<sup>9</sup> This seems most readily attributable to an increase in effectiveness of inductive donation by methyl due to double-bond polarization by the highly electronegative sulfone substituent. Other examples of preferential stabilization of  $\alpha,\beta$  isomers in similar systems are found in methoxy-,<sup>10</sup> thioalkoxy-,<sup>11</sup> and amine-substituted<sup>5d</sup> thiophene 1,1-dioxides.

Also of interest for the later discussion of base-catalyzed deuterium exchange reactions is the relative stability of allyl and propenyl ethers. Two separate investigations<sup>12,13</sup> have shown that alkyl allyl ethers can be converted essentially quantitatively to alkyl *cis*-propenyl ethers, as shown in eq 5. This does not represent equilibrium, since *cis*-propenyl ethers can undergo conversion to the *trans* isomers.<sup>12,13</sup> However, it does provide a tautomeric system in which one tautomer, the propenyl isomer, is much more stable than



the other. Thus, Doering<sup>14</sup> has shown that equilibration of 1-methoxy-3-phenylpropene (**17**)  $\rightleftharpoons$  1-phenyl-3-methoxypropene (**18**) results in a distribution of 78.5% **17** and 21.5% **18** at  $25^\circ$  in DMSO, while Da-

(8) L. K. Brice, W. M. Chang, J. E. Smith, and S. M. Sullivan, *J. Phys. Chem.*, **71**, 2814 (1967), have recently reported the distribution of **4**  $\rightleftharpoons$  **5** to be 31:69 and that for **7**  $\rightleftharpoons$  **8** to be 11:89 in aqueous solution at  $35^\circ$ .

(9) Thus, the  $\beta,\gamma$  isomer is favored by 0.2 kcal/mol in the unsubstituted case while the  $\alpha,\beta$  isomer is favored by  $\sim 1.2$  kcal/mol in the methylated system.

(10) M. Prochazka and M. Palecek, *Collection Czech. Chem. Commun.*, **31**, 3744 (1966).

(11) K.-D. Gundermann and P. Holtmann, *Angew. Chem. Intern. Ed. Engl.*, **5**, 668 (1966).

(12) T. J. Prosser, *J. Am. Chem. Soc.*, **83**, 1701 (1961).

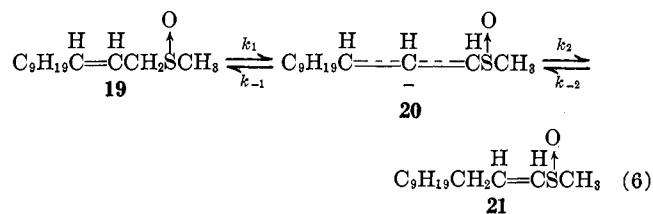
(13) C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961).

(14) W. von E. Doering and R. Vollrath, unpublished work quoted in ref 5b.

mico<sup>15</sup> has equilibrated pentenyl methyl ethers, using iron pentacarbonyl catalyst, to provide a distribution of 85% 1-, 5% 2-, 9% 3-, and 1% 4-pentenyl methyl ethers. These results indicate that an alkoxy group stabilizes double bonds to the extent of 4–5 kcal/mol<sup>16</sup> relative to hydrogen. The substituent changes which occur upon conversion of **15** to **16** are ROCH<sub>2</sub> and H to RO and CH<sub>3</sub>; both changes would stabilize **16** relative to **15**. It should also be mentioned that  $\beta,\gamma$ -unsaturated tertiary amines undergo base-catalyzed isomerization to the corresponding enamines<sup>17</sup> and that Hine<sup>18</sup> has concluded that a methoxy group stabilizes double bonds to a greater extent than does a methylthio substituent. All these observations point to large stabilizing influences by substituents containing first row elements which bear an unshared pair of electrons.

### Base-Catalyzed Deuterium Exchange of Substituted Olefins

Since studies of base-catalyzed reactions of olefinic substrates have been concerned primarily with allylic reactivity, this subject will be discussed first with emphasis on alkenyl sulfoxides and the allyl ether-propenyl ether systems. In the case of dodecenylyl methyl sulfoxide, treatment of **19** with OD<sup>-</sup> in D<sub>2</sub>O for 64 hr at



room temperature resulted in complete exchange of the doubly activated methylene protons between the sulfoxide group and the double bond with no appearance of deuterium at the  $\gamma$  position. Neither was there evidence for the appearance of isomer **21**, as shown by proton magnetic resonance spectra before and after deuteration.

It follows, therefore, that  $k_{-1} > k_{-2}$ . If  $k_{-2}$  were greater than or competed with  $k_{-1}$ , followed by reversion of the less stable  $\alpha,\beta$  isomer **21** to **19**, deuterium would have been incorporated in the  $\gamma$  position of **19**, and none was observed.

When isomer **21** was subjected to equivalent conditions, base-catalyzed reaction of this  $\alpha,\beta$ -unsaturated compound occurred more slowly than did exchange of the  $\beta,\gamma$ -unsaturated isomer. Moreover, with longer reaction times, the same deuterated product was formed as from **19**. These observations establish that  $k_1 > k_2$  and confirm that  $k_{-1} > k_{-2}$ . These results can be depicted on a reaction coordinate as in Figure 2.

(15) R. A. Damico, *J. Org. Chem.*, **33**, 1550 (1968).

(16) Assuming that the 3-pentenyl isomer represents a typical dialkylated double bond in Damico's work, one arrives at alkoxy increasing the double bond stability by  $\sim 1.5$  kcal relative to alkyl. It is known that alkyl substituents stabilize double bonds by  $\sim 2.5$  kcal relative to hydrogen.

(17) C. C. Price and W. H. Snyder, *Tetrahedron Letters*, 69 (1962).

(18) J. Hine, L. G. Mahone, and C. L. Liotta, *J. Org. Chem.*, **32**, 2600 (1967).

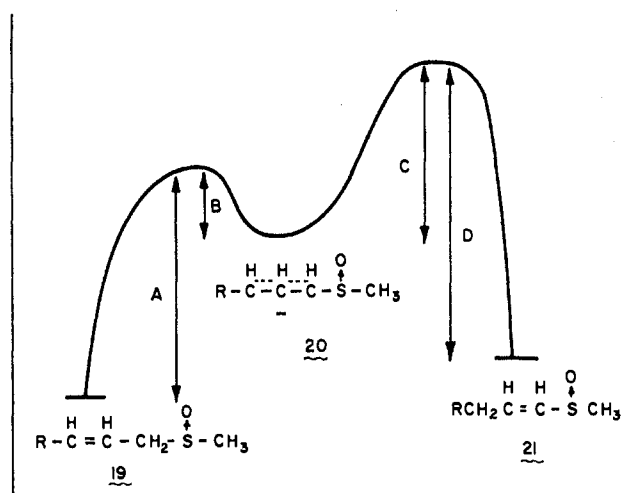


Figure 2.

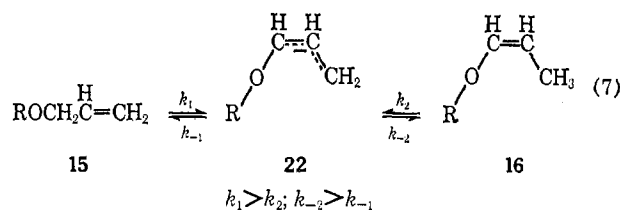
One significant feature of these data is, of course, that this system represents a tautomeric equilibrium in which the more stable isomer reacts faster to produce a common allyl anionic intermediate and is formed faster from that intermediate, clearly violating the Ingold postulate in all respects. Of greater interest, however, are the requirements which microscopic reversibility imposes on such a system. It can be seen by inspection of Figure 2 that the difference in activation energies for protonation must be greater than the difference in ground-state energies of the two isomers. The data clearly show that the activation energy for protonation of anion **20** at the site adjacent to the sulfoxide group (B in Figure 2) is less than the activation energy for protonation at the site removed from the sulfoxide group (C in Figure 2). The relative stabilities of **19** and **21** are established by the equilibrium data (Table I), with **21** being of higher energy. Since it has been shown that **21** undergoes reaction more slowly than **19**, it follows that the difference between B and C must be larger than the difference in ground-state energies of the two isomers. In other words, the fact that **21** is of higher ground-state energy than **19** would be expected to contribute to faster proton loss by **21**, yet this compound actually undergoes proton loss more slowly than does **19**. The reason must be that the transition state for proton transfer to the  $\gamma$  position is of sufficiently higher energy than the transition state for proton transfer to the  $\alpha$  position to offset the ground-state energy differences. The reaction can then be viewed as being controlled by the relative facility of protonation at the two sites of electron density, *i.e.*, by the carbanionic intermediate.

That protonation may occur faster at a center possessing relatively high electron density has a long history and has been treated theoretically by Streitwieser<sup>20</sup> and Dewar.<sup>2d</sup> In the allylic anion under consideration (**20**), it appears that both the alkyl substituent and the inductively electron-withdrawing sulfoxide substituent should favor a relatively high electron density in the  $\pi$  system at the  $\alpha$ -carbon atom, which is indeed the site of faster protonation.

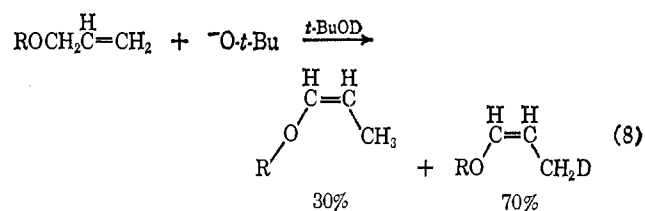
With respect to eq 2, electron density arguments also lead to the correct prediction of  $k_{-1} > k_{-2}$ . However, the ground-state energy differences of **7** vs. **9** as well as the difference in activation energies for protonation contribute to faster proton removal from the less stable isomer. In the sulfoxide system, as well as in sulfones which will be presented later, these two factors oppose each other with the difference in activation energies for protonation being larger than the difference in ground-state energies, as discussed above. Consequently a tautomeric system with very large ground-state energy differences was needed to test the possibility that the ground-state energy difference could be larger than the difference in protonation energies.

It was known from the work of Prosser<sup>12</sup> and Price<sup>13</sup> that alkyl allyl ethers underwent base-catalyzed conversion to alkyl *cis*-propenyl ethers in high yield, as shown in eq 5. Furthermore, there was reason to believe that there is a substantial difference in the ground-state energies of these two isomers, as discussed earlier in the section on olefin stabilities.

The base-catalyzed deuterium exchange of this system can be represented by eq 7. The experimental



results can be outlined as follows. Dodecyl allyl ether upon refluxing in potassium *t*-butoxide in *t*-butyl alcohol-*d* for 10 days gave a product whose infrared, pmr, and mass spectra were consistent with the products shown in eq 8. Some 30% of the isomerized product



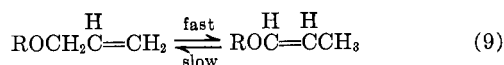
did *not* contain deuterium. This observation is similar to those recorded by other workers, and indicates intramolecular proton transfer. This phenomenon has been clearly described by Cram,<sup>19</sup> who has proposed that "hydrogen-bonded" species are involved which may collapse to product before deuterated solvent has replaced the conjugate acid formed by the initial proton-abstraction process. There seems no reason to believe that the collapse ratio (*i.e.*,  $k_{-1}/k_{-2}$ ) of the intermediate anionic species would differ depending upon whether it be associated with deuterated or nondeuterated conjugate acids. Since the present discussion focuses on these collapse ratios and the relative reactivities of the tautomers, inasmuch as

(19) D. H. Hunter and D. J. Cram, *J. Am. Chem. Soc.*, **86**, 5478 (1964).

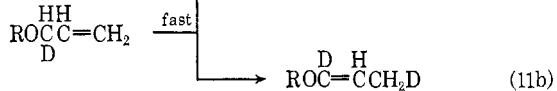
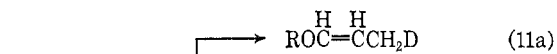
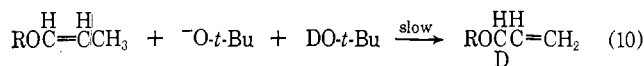
these kinetic factors are related to the relative ground-state stabilities of the isomers, attention will be directed to the deuterium incorporation process.

When an alkyl *cis*-propenyl ether (**16**) was subjected to the above exchange conditions, no significant amount of deuterium incorporation occurred within a 10-day period.

These base-catalyzed deuterium exchange data are consistent with either of two mechanisms. A common anionic intermediate, as pictured in eq 7, could be involved, in which case the data would require that  $k_1 > k_2$  and that  $k_{-2} > k_{-1}$ . Alternatively, a concerted deuterium incorporation process could be operative in which the forward step of eq 9 was rapid.



Strong evidence that eq 7 more accurately represents the true situation was obtained by subjecting an alkyl *cis*-propenyl ether to extreme exchange conditions. The octyl *cis*-propenyl ether recovered after 24 hr at 175° in potassium *t*-butoxide-*t*-butyl alcohol-*d* comprised, according to its mass spectrum, 47% non-deuterated, 40% monodeuterated, 11% dideuterated, and ~1% trideuterated octyl propenyl ether. For concerted processes to account for this distribution, the reactions outlined in eq 10, 11a, and 11b would be required. Furthermore, the data would require that



eq 11a be more rapid than eq 11b since the amount of monodeuterated product greatly exceeds the amount of dideuterated material. Such an inverse isotope effect is highly unlikely. The data are best accommodated<sup>20</sup> by eq 7 with the requirements that  $k_1 > k_2$  and  $k_{-2} > k_{-1}$ . This situation is depicted by the energy profile shown in Figure 3.

It is apparent that protonation of anionic intermediate **22** occurs more rapidly at the site removed from the alkoxy substituent. This is consistent with the electron density arguments presented earlier, providing that alkoxy groups are electron-repelling substituents as was indicated by the early work of Birch.<sup>21</sup> In resonance terminology, this selectivity in protonation is consistent with more rapid protonation at the site of higher electron density only if canonical form **23** makes a larger contribution to allylic inter-

(20) The isotopic distribution calculated [using a computer program based on the method described by D. F. DeTar, *J. Chem. Educ.*, **44**, 191 (1967)] assuming consecutive first-order steps with relative rates of 3:2:1 to correspond to the number of exchangeable hydrogens on methyl is 47.0 non-, 40.6 mono-, 11.4 di-, and 1.0 trideuterated species, in excellent agreement with the experimental data. I wish to thank Dr. R. D. Temple, of these laboratories, for performing this calculation.

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

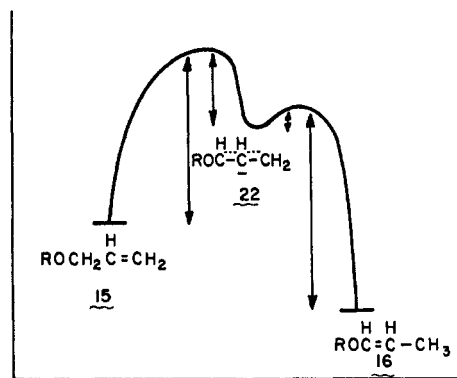
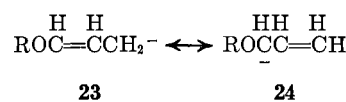


Figure 3.

mediate **22** than does canonical form **24**. Such an effect may be attributable to the unshared pairs of electrons on oxygen.



The more significant feature of these data is, however, that isomer **16** reacts slower to form the anionic intermediate than does **15**, despite the fact that the activation energy for protonation of **22** to produce **16** is lower than that required to produce **15**. Thus, the ground-state energy differences and relative rates of protonation operate as opposing factors. In other words, the higher ground-state energy of **15** contributes to faster reaction by this isomer despite the fact that the transition state for proton transfer from **15** is of higher energy than the transition state for proton transfer from **16**, as shown by the difference in relative rates of protonation of intermediate **22**. The difference in ground-state energies is larger than the difference in activation energies for protonation.

Inspection of Figures 1-3 shows that attempts to generalize allylic reactivity from either ground-state energy differences or relative rates of protonation at the two reactive sites, using either approach separately, must be fruitless. The only three possible combinations of these variables are (1) a system wherein the less stable isomer reacts faster to form the common intermediate and is formed faster from the intermediate (Figure 1), (2) a system wherein the less stable isomer reacts slower to form the intermediate and is formed slower from the intermediate (Figure 2), and (3) a system wherein the less stable isomer reacts faster to form the intermediate and is formed slower from the intermediate (Figure 3). Since these are all the possible combinations, and examples of each are known, it is obvious that generalizations using either approach alone are unfeasible.

In continuing these studies more quantitative data were collected for both cyclic and acyclic sulfones.<sup>22</sup>

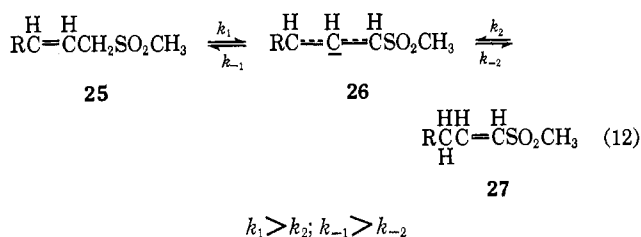
(22) Exchange experiments were conducted at 25° in deuterium oxide-dioxane (3:2 by volume) using sodium deuterioxide as base. Only three points were taken, and samples were analyzed by nmr. While these experiments do not provide highly precise kinetic data, the relative orders of reactivity shown in Tables II and III seem secure.

**Table II**  
Relative Rates of Deuterioxide-Catalyzed Exchange of Acyclic Sulfoxes<sup>a</sup>

Entry	Compd	Rate relative to C <sub>3</sub> H <sub>7</sub> CH <sub>2</sub> SO <sub>2</sub> CH <sub>3</sub>
1	C <sub>3</sub> H <sub>7</sub> CH <sub>2</sub> SO <sub>2</sub> CH <sub>3</sub>	1.0
2	C <sub>3</sub> H <sub>7</sub> CH <sub>2</sub> SO <sub>2</sub> CH <sub>3</sub>	5 × 10 <sup>2</sup>
3	<i>C</i> <sub>3</sub> H <sub>7</sub> CH <sub>2</sub> C=CSO <sub>2</sub> CH <sub>3</sub> <sup>b</sup>	7 × 10 <sup>2</sup>
4	<i>C</i> <sub>3</sub> H <sub>7</sub> C=CCH <sub>2</sub> SO <sub>2</sub> CH <sub>3</sub>	7 × 10 <sup>2</sup>
5	<i>C</i> <sub>3</sub> H <sub>7</sub> C=CCH <sub>2</sub> SO <sub>2</sub> CH <sub>3</sub>	7 × 10 <sup>3</sup>
6	C <sub>3</sub> H <sub>7</sub> CH <sub>2</sub> C=CSO <sub>2</sub> CH <sub>3</sub>	~25
7	C <sub>3</sub> H <sub>7</sub> CH <sub>2</sub> C=CSO <sub>2</sub> CH <sub>3</sub>	~10

<sup>a</sup> The positions which undergo exchange at the relative rate shown are in italics. <sup>b</sup> No significant differences were observed using mixtures enriched in both *cis* and *trans* isomers.

Since the observations on allylic reactivity of the acyclic compounds are very similar to the foregoing sulfoxide case, it will suffice to outline this system by eq 12.



From Table II, which records the relative rates of deuterioxide-catalyzed exchange of various acyclic sulfoxes in deuterium oxide-dioxane solution at 25°, and the data in Table I, it can be seen that this tautomeric equilibrium can also be represented by the reaction coordinate shown in Figure 2.

Allylic exchange of unsaturated cyclic sulfoxes<sup>20</sup> was quite similar, as shown in eq 13. Data on the relative rates of exchange of these compounds are presented in

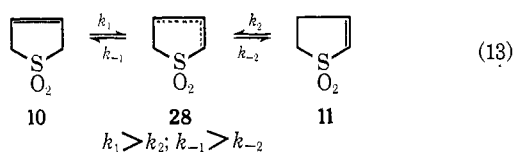







Table III. Again the allyl anionic intermediate undergoes protonation more rapidly at the position adjacent to the sulfone group. This preference would be expected from the earlier discussion pointing to charge distribution in the anionic species as the controlling factor.<sup>23</sup>

Allylic exchange of unsaturated sulfoxes clearly fits

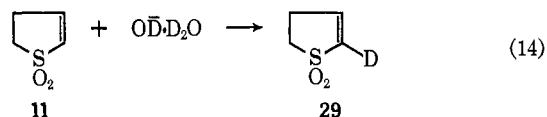
(23) Deuterioxide-catalyzed exchange of the methyl-substituted system, *i.e.*, 12 ⇌ 13 ⇌ 14, has also been examined. Isomer 13 underwent exchange exclusively at the 2 and 5 positions. This process occurred rapidly compared to the rate of reaction at the allylic positions of either 12 or 14. Since the equilibration studies show 13 to be more stable than 12 but less stable than 14, exchange may be viewed as being controlled by the difference in activation energies for protonation at the allylic sites.

**Table III**  
Relative Rates of Deuterioxide-Catalyzed Exchange of Cyclic Sulfoxes<sup>a</sup>

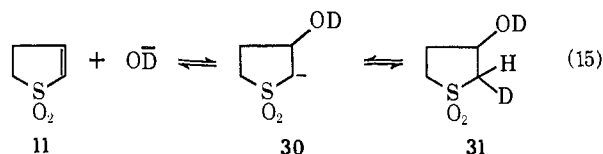
Entry	Compd	Rate relative to 
1		1.0
2		6 × 10 <sup>4</sup>
3		7 × 10 <sup>4</sup>
4		30

<sup>a</sup> The positions which undergo exchange at the reported relative rates are circled.

within the framework of the earlier discussion, thus lending support to the conclusions derived from those studies. However, these exchange experiments proved to be especially interesting due to the observation of vinyl isotopic exchange under basic conditions. For example, base-catalyzed exchange of 11 resulted in more rapid deuterium incorporation at the α-vinyl position (eq 14) than at allylic sites. Either an addition-elimination mechanism or vinyl proton ab-



straction could account for the appearance of deuterium at this position. It had been postulated previously that unsaturated ketones undergo vinyl proton exchange by a Michael type addition of deuterioxide, deuterium capture at the α position, and finally reelimination of water to produce the α-deuterio unsaturated ketone.<sup>24</sup> The analogous mechanism for unsaturated sulfoxes is shown in eq 15.



Two observations eliminate this course of reaction (15) as a possibility for α-vinyl isotopic exchange. First, to observe extensive exchange by this mechanism would require that 11 be thermodynamically favored with respect to 31. This is not the case since high yields of 31 can be realized from 11 under these basic conditions.<sup>25</sup> Secondly, operation of eq 15 requires rapid elimination of water from 31 to account for deuterium incorporation. Preparation of this material and exposure to the reaction conditions showed that 31

(24) (a) B. W. Rockett, T. M. Harris, and C. R. Hauser, *J. Am. Chem. Soc.*, **85**, 3491 (1963); (b) J. Warkentin and L. K. M. Lam, *Can. J. Chem.*, **42**, 1676 (1964).

(25) R. C. Krug, G. R. Tichelaar, and F. E. Didot, *J. Org. Chem.*, **23**, 212 (1958).

was stable.<sup>20</sup> For these reasons, it was concluded that the observed  $\alpha$ -vinyl exchange was due to a simple vinyl proton abstraction mechanism.<sup>26</sup>

In considering these sulfone systems, it must be recalled that the reported evidence on vinylic *vs.* allylic exchange, although not extensive, clearly points to more rapid reaction at the allylic position of unsubstituted olefins. Thus, Shatenshtein<sup>27</sup> has reported that ethylene exchanges slowly relative to propene and that five of the propene hydrogens are exchanged rapidly compared to the sixth. This is clearly consistent with exchange occurring more rapidly through allylic intermediates. It then appears that substitution by a sulfone group alters this order of relative reactivities. Although the cyclic case shown in eq 14 represents a more dramatic example of rapid vinylic proton abstraction, as can be seen by comparing Tables II and III, there is less evidence to allow an assessment of vinylic *vs.* allylic reactivity in isotopic exchange of the corresponding unsubstituted system, *i.e.*, cyclopentene.<sup>28</sup> The acyclic system (Table II) can, however, be compared to Shatenshtein's observations,<sup>29</sup> leading to the conclusion that vinylic reactivity is enhanced relative to allylic upon replacement of hydrogen by a sulfone group. Thus, as shown in Table II, the rates of vinyl and allyl proton abstraction from 1-hexenyl methyl sulfones are very similar, while previous work indicates more rapid allylic proton abstraction with unsubstituted olefins.

It is well to remember that diverse factors are operative in promoting carbanion formation at vinylic *vs.* allylic positions. Allylic reactivity is most probably due to inductive and resonance effects of the double bond, while vinylic reactivity is promoted by the increased *s* character of an  $sp^2$ -hybridized C-H bond relative to an  $sp^3$  C-H position. Therefore, introduction of a substituent which could diminish the importance of resonance stabilization or enhance vinylic reactivity would change the relative rates of vinylic *vs.* allylic reactivity. Since the sulfone group causes such a change, some consideration will be given to the probable methods by which it operates.

The extent to which *d* orbitals of sulfones stabilize adjacent carbanionic transition states has received considerable attention. For example, tetramethylammonium ion<sup>30</sup> requires much more drastic exchange conditions than does dimethyl sulfone.<sup>31</sup> Since inductive electron withdrawal by  $(CH_3)_3N^+$  is greater than that of  $CH_3SO_2^-$ , as measured by  $\sigma^*$  values,<sup>32</sup> it

may be suggested that *d*-orbital stabilization of the transition state for proton removal adjacent to sulfone groups is an important factor.<sup>33</sup>

One of the more interesting observations on these base-catalyzed exchange studies of acyclic unsaturated sulfones is the rapid reaction at the  $\alpha$ -methyl position (see Table II). This apparently requires an important contribution from *d*-orbital stabilization (see later discussion) and further sheds some light on the reasons for increased reactivity at the vinylic relative to the allylic position. It might be suggested that *d*-orbital stabilization of the transition state for vinylic proton removal is more effective than for allylic proton removal, resulting in enhanced vinylic reactivity relative to unsubstituted olefins. Some of the data of Table II tend to discount this proposal. The most rapid process observed during deuterioxide-catalyzed exchange of 1-hexenyl methyl sulfone was deuterium exchange at the  $\alpha$ -methyl position.

The relative rates of reaction at the  $\alpha$ -methyl, as compared to the  $\alpha$ -vinyl, position indicate that *d*-orbital effects increase with increasing amounts of *p* character in the forming carbanion. Thus, if the inductive effect of the  $SO_2$  group is taken as being equal at these two  $\alpha$  positions, it might be expected that the vinylic position would undergo more rapid exchange than the  $\alpha$  methyl due to its increased *s* character. However, it was observed that  $\alpha$ -methyl exchange was  $\sim 30$  times faster than vinylic. It may be reasonably proposed that *d*-orbital effects favor reaction at the  $sp^3$  methyl site to such an extent that reaction at this position is favored over vinylic proton abstraction.<sup>34</sup> This difference between  $\alpha$ -vinylic and  $\alpha$ -methyl exchange tends to rule out the possibility that the increase in rate of  $\alpha$ -vinylic exchange relative to allylic in  $\alpha,\beta$ -unsaturated sulfones could be due to selective *d*-orbital participation. It can be seen that, for such a factor to be important, *d*-orbital stabilization of an incipient  $sp^2$ -hybridized carbanion would have to be greater than that of an incipient allylic species in which negative charge would be contained in either a *p*- $\pi$  system or an  $sp^3$  orbital. This is, of course, opposite to the expected extent of *d*-orbital overlap of  $sp^2$  *vs.*  $sp^3$  or *p* species.<sup>35</sup>

Another reason for the observed change in vinylic *vs.* allylic reactivity of these unsaturated sulfones, relative to unsubstituted olefins, can be based on the proposal that resonance stabilization involving the double bond is *not* an overwhelming factor in this system. Some indication of the effectiveness of this electron delocalization can be gained from the data displayed in Table II. It will be noted that re-

(26) Rapid vinyl exchange was also observed with the methyl-substituted sulfolenes 12 and 14.

(27) A. I. Shatenshtein, *Advan. Phys. Org. Chem.*, **1**, 178 (1963).

(28) G. Schröder, *Chem. Ber.*, **96**, 3178 (1963), has exchanged cyclopentene using *t*-BuOK in *t*-BuOD. Competitive exchange at vinyl and allyl positions cannot be eliminated by the data. However, it is apparent that allyl exchange must be at least as fast as reaction at the vinyl position. The observation that the  $\alpha,\beta$ -unsaturated sulfolene gives rapid vinylic as compared to allylic exchange (Table II) is consistent with the present discussion.

(29) Discussed in ref 2b, p 23.

(30) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **77**, 521 (1955).

(31) J. Hochberg and K. F. Bonhoeffer, *Z. Phys. Chem.*, **A184**, 419 (1939).

(32) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 618.

(33) See also (a) ref 2b, p 71, and (b) G. Cilento, *Chem. Rev.*, **60**, 147 (1960), for *d*-orbital effects of sulfones.

(34) T. Jordan, H. W. Smith, L. L. Lohr, Jr., and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 846 (1963).

(35) See also (a) H. E. Zimmerman and B. S. Thyagarajan, *ibid.*, **82**, 2505 (1960); (b) A. Ratajczak, F. A. L. Anet, and D. J. Cram, *ibid.*, **89**, 2072 (1967).

placement of an *n*-propyl by a 1-pentenyl group results in an increase in the rate of exchange of  $\sim 10^4$ . However, replacement of hydrogen by 1-pentenyl (compare entries 3 and 5) causes an increase of only  $\sim 10$  in rates of base-catalyzed deuterium exchange. Since the inductive effects of hydrogen and 1-pentenyl are similar, as measured by  $\sigma^*$  values, it appears that resonance stabilization of the allylic intermediate is *not* a predominant factor.

Saunders<sup>36</sup> has discussed "electrostatic inhibition of resonance-stabilization" in trimethylammonium-substituted allyl anionic intermediates. Similar forces may well be operative in these sulfone systems. In essence, this proposal is that electrostatic factors favor one canonical form over another and thus decrease resonance stabilization due to a lessening of electron delocalization.<sup>37</sup> This factor may indeed operate to favor vinylic proton abstraction. However, it should be noted that enhanced vinylic reactivity, due to the inductive effect of the sulfone group, rather than depressed allylic reactivity could account for the present results.

A marked difference in vinylic *vs.* allylic reactivity was seen in comparing  $\alpha,\beta$ -unsaturated acyclic to five-membered cyclic sulfones. As shown in Table III, vinylic proton abstraction from 2,3-dihydrothiophene 1,1-dioxide occurred on the order of  $10^3$  faster than did allyl proton abstraction from this compound. Contrast this with the nearly equivalent rates of deuterium exchange at  $\alpha$ -vinylic and allylic positions of acyclic sulfones (entries 6 and 7 of Table II). This further enhancement of vinylic proton abstraction seems to be due to inordinately rapid vinyl proton abstraction rather than a depression in rate of allylic reaction. Comparison of the rates of proton abstraction at the allylic positions of the two isomeric sulfolenes **10** and **11** relative to the corresponding saturated compound (sulfolane) with the rates of proton abstraction at the allylic positions of the isomeric acyclic isomers **25** and **27** relative to the corresponding saturated acyclic compound (the methylene position of butyl methyl sulfone) shows similar rate enhancements at the allylic positions. Thus, the allylic positions flanked by sulfone and double-bond substituents undergo base-catalyzed exchange on the order of  $10^3$ – $10^4$  times more rapidly than do the corresponding saturated isomers in both cyclic and acyclic systems (compare entries 1 and 5 of Table II to entries 1 and 2 of Table III) and the allylic positions removed from the sulfone substituent react from 10 to 30 times faster than do the saturated compounds in both systems (compare entries 1 and 7 of Table II to entries 1 and 4 of Table III). While the correspondence is not exact, these values for the rate enhancements due to the introduction of a double bond in sulfone systems seem

(36) M. Saunders and E. H. Gold, *J. Am. Chem. Soc.*, **88**, 3376 (1966).

(37) See earlier discussion on disparities in electron density at the two allylic positions of these substrates.

surprisingly close in view of the structural differences of cyclic and acyclic systems. At least, it appears safe to conclude that the observed rapid exchange at vinyl relative to allyl positions in the cyclic case is due to enhanced reactivity at the vinylic position rather than depressed allylic proton abstraction. While such factors as conformational effects and preferential solvation may play a role, the present results seem most reasonably attributed to an increase in the character of the vinylic C–H bond upon inclusion in a five-membered ring, causing increased ease of proton removal.<sup>38</sup>

In closing this discussion of vinylic reactivity it should be emphasized that it would be premature to assume that these relative reactivities reflect the relative stabilities of the carbanionic intermediates involved. Such a conclusion assumes the Brønsted catalysis law, *i.e.*, that kinetic acidity is directly related to thermodynamic acidity. There is no reason to believe that such widely disparate positions as  $sp^2$  and resonance-stabilized  $sp^3$  sites conform to such a relationship. As a matter of fact, it is known that  $sp^2$ -hybridized amines promote proton-transfer processes more readily than would be expected from their basicities, when compared to resonance-stabilized amines.<sup>39</sup> If these studies can be used as a model for carbanionic reactions, it might be expected that inordinately rapid proton transfer would be observed at vinylic sites. The point of the present discussion is not that incorporation of a sulfone substituent results in  $\alpha$ -vinyl carbanionic species being more stable than the corresponding allylic intermediates, but that this substitution results in a reversal in relative rates of proton abstraction at the two types of positions.

More experimental work will be required to assess the importance of such factors as "internal return,"<sup>40</sup> specific solvation of the carbanionic intermediate,<sup>41</sup> and effect of variation in the strength of the base used to promote exchange.<sup>42</sup> However, it is clear from these observations that relatively rapid base-catalyzed reaction at allylic positions cannot be assumed in olefinic systems bearing inductively electron-withdrawing substituents.

*I wish to thank my colleagues at The Proctor and Gamble Company, some of whom are named in the references, for their many contributions to this work.*

(38) A dramatic example of apparent rapid vinyl proton abstraction from cyclopentene is found in its reaction with alkylsodium reagents. See (a) A. A. Morton and R. A. Finnegan, *J. Polymer Sci.*, **38**, 19 (1959); (b) C. D. Broaddus and D. L. Muck, *J. Am. Chem. Soc.*, **89**, 6533 (1967).

(39) (a) R. P. Bell and G. L. Wilson, *Trans. Faraday Soc.*, **46**, 407 (1950); (b) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959.

(40) Ref 2b, p 28.

(41) (a) B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Am. Chem. Soc.*, **88**, 1911 (1966); (b) A. I. Shatenshtein, I. O. Shapiro, and I. A. Romanskii, *Dokl. Akad. Nauk SSSR*, **174**, 1138 (1967).

(42) R. P. Bell and D. M. Goodall, *Proc. Roy. Soc. (London)*, **A294**, 273 (1966), and references therein.