

(CONTRIBUTION FROM THE PROCTER & GAMBLE CO., MIAMI VALLEY LABORATORIES, CINCINNATI 39, OHIO)

The Relation of Proton Exchange to Tautomerism in Unsaturated Sulfoxides

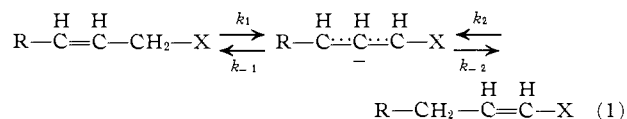
BY D. E. O'CONNOR AND C. D. BROADDUS

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Deuterium exchange experiments with 1-methylsulfinyl-2-dodecene (I) and 1-methylsulfinyl-1-dodecene (II) have shown that I exchanges faster than II. Both I and II exchange to form the same deuterated product 1,1-dideuterio-1-methylsulfinyl-2-dodecene. The proton exchange data are similar to those obtained previously in studies with α,β - and β,γ -unsaturated isomers; however, the relative ground state stabilities of these β,γ - and α,β -unsaturated isomers, I and II, are reversed to those of the previously studied systems. An explanation is offered based on protonation of a common allylic intermediate more rapidly at the point of higher electron density.

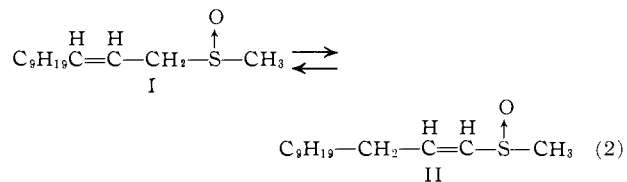
Introduction

The role of carbanionic intermediates in base-catalyzed isomerization reactions is of high current interest.^{1,2} Within this general area, a particular problem which has received very little attention recently concerns the nature of the factors governing base-catalyzed tautomerism in α,β - β,γ -unsaturated systems.³ In the mid-1930's Ives⁴ and Ingold⁵ showed, by deuterium exchange studies, that in certain systems β,γ -unsaturated isomers underwent exchange rapidly compared to the α,β -isomers. Furthermore, the β,γ -unsaturated compounds exchanged protons rapidly compared to their rate of isomerization. These results were discussed in terms of eq. 1 and required that $k_1 > k_2$ and $k_{-1} > k_{-2}$.



Since the thermodynamic equilibria in these systems were similar, a generalization was developed based primarily on ground state energy differences.^{6,7}

Recent work⁸ in these laboratories has established that base-catalyzed equilibration of the unsaturated system shown in eq. 2 greatly favors the β,γ -isomer I. Thus, treatment of the α,β -isomer II with potassium



t-butoxide in *t*-butyl alcohol for 5 hr. produced a mixture consisting of 96% I and 4% II. Treating this mixture with potassium *t*-butoxide in deuterated *t*-butyl alcohol

(1) D. J. Cram and R. T. Uyeda, *J. Am. Chem. Soc.*, **84**, 4358 (1962); S. Bank, C. A. Rowe, Jr., and A. Schriesheim, *ibid.*, **85**, 2115 (1963), and references therein; R. B. Bates, R. H. Carnighan, and C. E. Staples, *ibid.*, **85**, 3032 (1963).

(2) W. O. Haag and H. Pines, *ibid.*, **82**, 387 (1960); L. Reggel, S. Friedman, and I. Wender, *J. Org. Chem.*, **23**, 1136 (1958); F. Asinger, B. Fell, and G. Collin, *Chem. Ber.*, **96**, 716 (1963); E. A. Rabinovich, I. V. Astaf'ev, and A. I. Shatenshtein, *Zh. Obshch. Khim.*, **32**, 748 (1962), and references therein.

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

(4) D. J. G. Ives and H. N. Rydon, *J. Chem. Soc.*, 1735 (1935).

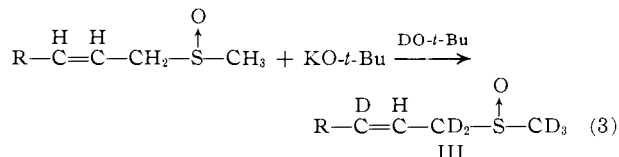
(5) C. K. Ingold, E. de Salas, and C. L. Wilson, *ibid.*, 1328 (1936).

(6) A. G. Catchpole, F. D. Hughes, and C. K. Ingold, *ibid.*, 11 (1948).

(7) Ingold's rule states "when a proton is supplied by acids to the meso-meric 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" (C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 565).

(8) D. E. O'Connor and W. I. Lyness, *J. Am. Chem. Soc.*, **85**, 3044 (1963).

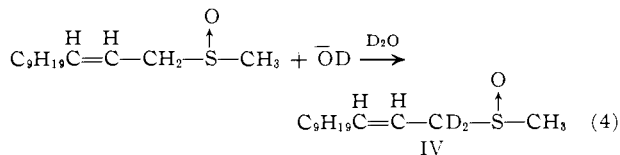
gave exchange of the active hydrogens with no change in the relative amounts of α,β - and β,γ -isomers (eq. 3).



These results clearly show that the β,γ -isomer is of lower ground state energy than the α,β -unsaturated compound, in contrast to the energetics of previously reported unsaturated systems of this type.⁹⁻¹² The sulfoxide system, therefore, offered an opportunity to study the relation of proton exchange to tautomerism with isomers in which the relative ground state stabilities were reversed to those previously reported.

Results

Treatment of 1-methylsulfinyl-2-dodecene¹³ (I) with OD in D₂O (0.9 M) 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 γ -position (eq. 4). Neither was there any evidence for



the appearance of 1-methylsulfinyl-1-dodecene (II), as shown by the nuclear magnetic resonance (n.m.r.) spectra before and after deuteration. Thus the starting material gave rise to a multiplet centered at 6.65 τ (relative area 1.8) attributed to the doubly-activated methylene protons, as well as bands due to allylic protons at 7.9 τ (relative area 2.0), methylsulfinyl protons at 7.58 τ (relative area 3.0), vinyl protons centered at 4.4 τ (relative area 1.8), and protons of the alkyl chain (multiplet at 8.7 τ , relative area 14.4, and a multiplet at 9.0-9.1 τ , relative area 3.0).⁸ The n.m.r. spectrum of the material recovered from the reaction was completely consistent with structure IV: the absorption at 6.65 τ had entirely disappeared and the vinyl proton multiplet at 4.4 τ had been somewhat simplified due to decoupling

(9) G. A. R. Kon, R. P. Linstead, and G. W. G. MacLennan, *J. Chem. Soc.*, 2454 (1932); R. P. Linstead and E. G. Noble, *ibid.*, 614 (1934); A. Kandiah and R. P. Linstead, *ibid.*, 2139 (1929).

(10) D. S. Tarbell and W. E. Lovett, *J. Am. Chem. Soc.*, **78**, 2259 (1956).

(11) C. C. Price and W. H. Snyder, *J. Org. Chem.*, **27**, 4639 (1962); *Tetrahedron Letters*, **No. 2**, 69 (1962).

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

(13) The mixture containing 96% of this compound and 4% of II was used in the exchange experiments.

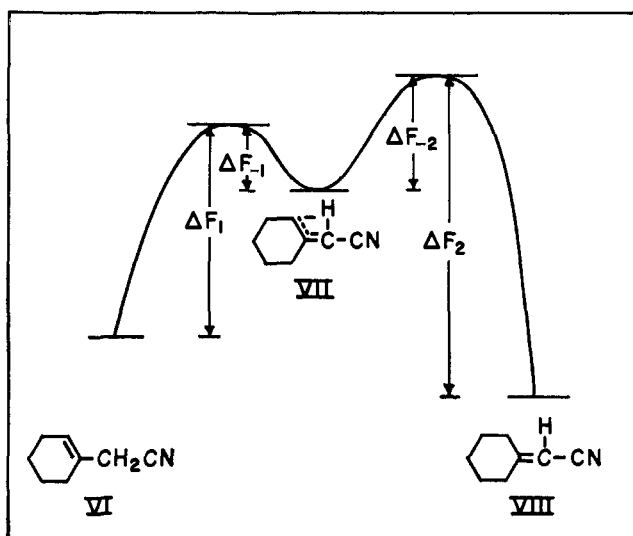
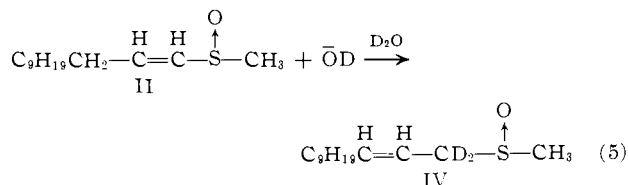


Fig. 1.—Energy diagram for the interconversion of cyclohexenyl nitriles.^{6,7}

of the doubly activated methylene. The relative area of the vinyl proton absorption, however, had not decreased at all indicating that very little or no exchange had occurred at the γ -position. The other absorptions remained intact.

Subjecting 1-methylsulfinyl-1-dodecene (II) to equivalent conditions (0.9 *M* $\bar{O}D$ in D_2O for 66 hr. at room temperature) caused a relatively slow exchange accompanied by tautomerism to 1-methylsulfinyl-1,1-dideuterio-2-dodecene (IV) (eq. 5). The areas of vinyl proton absorption of I and II in the n.m.r. are



sufficiently well separated that the percentage of each in a mixture of the two can be determined.⁸ The vinyl protons of II absorb at 3.5–3.9 τ , whereas the vinyl proton absorption of I is centered at 4.4 τ and is entirely within the range 4.0 to 4.8 τ . By determining the relative areas at 3.5–3.9 and 3.9–4.8 τ , it was found that 20% of the starting material had been isomerized to the β,γ -unsaturated isomer (accompanied by the appearance of deuterium in the α -position). The relative area of the allylic proton peak was practically unchanged, indicating that very little, if any, deuterium had been incorporated into the γ -position of the α,β -unsaturated isomer.

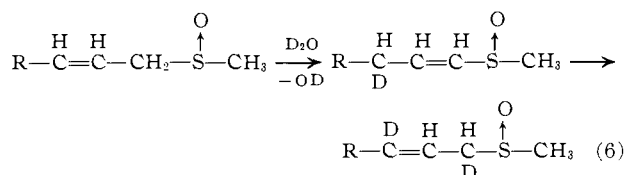
When the reaction of II with D_2O-OD^- (0.9 *M*) was allowed to proceed for 2 weeks at room temperature, 65% of II was converted to IV, the remaining 35% being unreacted II. Thus, both I and II react to form the same deuterated product, IV, and under equivalent conditions I reacts much faster than II.

Discussion of Results

It is apparent from a comparison of our data with that previously reported^{4,5} that these systems give quite similar results despite the reversal in relative ground state stabilities. In all these cases the β,γ -unsaturated isomers undergo exchange rapidly compared to the

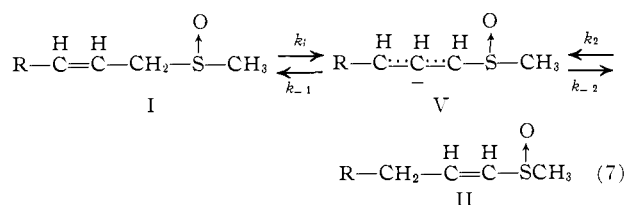
α,β -unsaturated compounds. Exchange of the allylic protons without accompanying isomerization is observed with the β,γ -unsaturated derivatives, while the α,β -unsaturated compounds isomerize during exchange.

While a mechanism based on a common allylic intermediate appears most attractive, concerted processes must also be considered. In the methylene-azomethine system, Ingold and co-workers^{14,15} presented convincing evidence that tautomerism occurs by a concerted bimolecular process. These studies involved base-catalyzed tautomerism of optically active compounds wherein it was shown that at short reaction times a completely racemic product was formed with no change in the optical activity of the recovered starting material.¹⁶ Our studies with 1-methylsulfinyl-2-dodecene (eq. 4) show that a concerted process of this nature is not important in the present system. Thus, exchange occurs exclusively at the doubly activated allylic position, whereas, if exchange were taking place through concerted formation of intermediate α,β -unsaturated isomer, incorporation of deuterium at the γ -vinyl position in exchanged 1-methylsulfinyl-2-dodecene would be required (eq. 6). Intramolecular hydrogen transfer processes have recently been reported¹ in



reactions of this nature. Thus isomerizations have been observed in deuterated solvents in which no deuterium was incorporated in the isomerized material. However, we are obviously concerned here with reactions in which hydrogen exchange does occur.

The intermediacy of a common allylic intermediate, *i.e.*, V, appears most reasonable in explaining our observations (eq. 7). The exchange experiments with I



and II require that $k_1 > k_2$ and $k_{-1} > k_{-2}$. The similarity with the earlier data is striking. Since the relative ground state stabilities have been determined in these systems, their qualitative energy diagrams (Fig. 1 and 2) can be compared. As stated earlier, the data require that the relative activation energies in these systems remain the same while the ground state energies are reversed. From these observations it must be concluded that the differences in ground state energies cannot be the controlling factor in both cases. A more generally applicable explanation can be developed based on the relative rates of protonation of the π -system of these allylic anions at the two positions of high electron

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

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

(16) See ref. 3, pp. 239–240, for a complete discussion of this work.

density.¹⁷ Both sets of data show that protonation occurs more rapidly at the carbon adjacent to the

functional substituent ($-\text{CN}$ and $-\text{S}-\text{CH}_3$) than at the carbon adjacent to the alkyl group. In the allylic anions under consideration it appears that both the alkyl substituent and the inductively electron-withdrawing substituents should favor a relatively high electron density in the π -system at the α -carbon atom. Methyl-substituted allyl anions have been treated by Bowman and Hoijtink¹⁸ who suggest that donation of negative charge by the methyl group causes a lessening in the electrostatic interaction between a π -electron and the substituted carbon. This weaker interaction results in a relatively high electron density at the unsubstituted position. Extension of this line of reasoning to an electron-withdrawing group¹⁹ leads to the expectation that in the π -system of the present allyl anions the higher charge density would be located at the position adjacent to the functional group. It seems reasonable then to ascribe the greater rate of protonation at the α -position to its relatively high electron density.

Once it is established that $k_{-1} > k_{-2}$ in both systems, the principle of microscopic reversibility demands that VI undergo deprotonation more rapidly than VIII, because $\Delta F_{-1} < \Delta F_{-2}$ and the ground state energy of VI $>$ VIII (Fig. 1). However, the observation of the same order of reactivity in the sulfoxide case was not required. Thus, although $\Delta F_{-1} < \Delta F_{-2}$ (Fig. 2), the ground state energies are I $<$ II. Since the same order is actually observed, it follows that the activation energies required for protonation of the mesomeric anion V overshadow the energy differences of the ground state isomers (*ca.* 1.9 kcal.).

In summary, then, it appears that proton exchange in all these α,β,γ -unsaturated systems can be related to their tautomerism through a common allylic intermediate. Furthermore, the data reported to date can be rationalized on the basis of the allylic intermediate undergoing more rapid protonation at the center of higher electron density regardless of the ground state stabilities of the tautomers involved.

Experimental

Preparation of 1-Methylsulfinyl-2-dodecene (I).—Reaction of 147 g. (0.9 mole) of dodecene 1-oxide with 39 g. (0.8 mole) of methyl mercaptan in 500 ml. of ethanol containing 45 g. (0.8 mole) of potassium hydroxide at room temperature for 2 hr. gave 1-methylthio-2-hydroxydodecane, which was oxidized with 100 g. (*ca.* 0.88 mole) of hydrogen peroxide (30%) at room temperature for 6 hr. to yield 148 g. (75%) of 1-methylsulfinyl-2-hydroxydodecane, m.p. 69–71° (mixture of diastereoisomers).

To a solution of 0.07 mole of potassium *t*-butoxide in 100 ml. of *t*-butyl alcohol was added 12.4 g. (0.05 mole) of 1-methylsulfinyl-2-hydroxydodecane. The mixture was heated at 60° for 4 hr.

(17) Many authors have suggested that relative rates of protonation in resonating systems are directly dependent upon the amount of negative charge borne by the atoms in question. Among these are: R. G. Pearson and R. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953); G. S. Hammond, *ibid.*, **77**, 334 (1955); G. Russell, *ibid.*, **81**, 2017 (1959); A. J. Birch, *Quart. Rev. (London)*, **4**, 69 (1950); H. E. Zimmerman, "Molecular Rearrangements," edited by P. de Mayo, Interscience Publishers, Inc., New York, N. Y., 1963, p. 346; A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 418; ref. 3 and 18.

(18) N. Bowman and G. J. Hoijtink, *Rec. trav. chim.*, **76**, 841 (1957).

(19) See D. A. Brown and M. J. S. Dewar, *J. Chem. Soc.*, 2406 (1953), for a discussion of electron-withdrawing groups causing inductoelectromeric effects in heterocyclic systems.

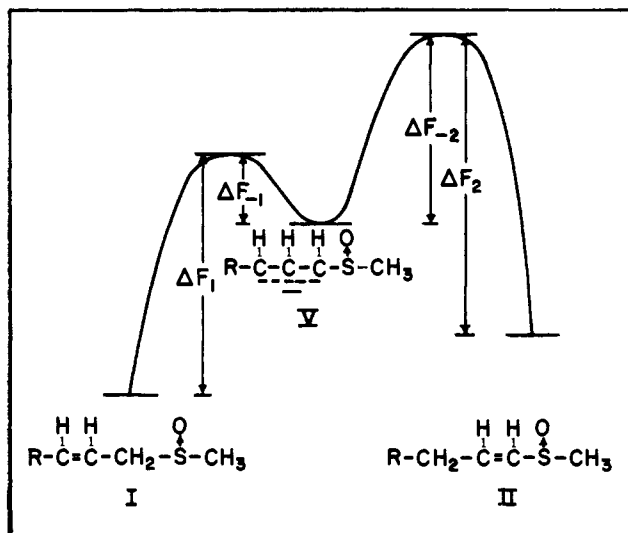


Fig. 2.—Energy diagrams for the interconversion of I and II.

and was then cooled and poured into 300 ml. of water. The product was extracted three times with ethyl acetate, the extracts were dried over magnesium sulfate, and the solvent was evaporated. The residue was taken up in hexane and cooled. A precipitate of 1.0 g. of starting material was obtained. The 10 g. of liquid residue remaining in the supernatant liquid was distilled to yield 8.1 g. of crude product. Redistillation of 5.0 g. of the crude product gave 2.1 g. (29%) of 1-methylsulfinyl-2-dodecene, b.p. 131° (0.2 mm.). *Anal.* Calcd. for $\text{C}_{13}\text{H}_{26}\text{OS}$: C, 67.8; H, 11.37; S, 13.9. Found: C, 67.6; H, 11.2; S, 13.6. An infrared spectrum had bands at 9.5 μ (s) (sulfoxide group) and 10.3 (m) (*trans* double bond). An n.m.r. spectrum (Varian A-60 spectrometer) determined on a 10% solution in carbon tetrachloride had absorptions due to olefinic protons (multiplet centered at 4.4 τ , rel. area 1.8), methylene protons between the double bond and the sulfinyl group (6.65 τ , rel. area 1.8), methylsulfinyl protons (7.58 τ , rel. area 3.0), allylic protons (7.9 τ , rel. area 2.0), alkyl methylene protons (8.7 τ , rel. area 14.4), and terminal methyl protons (9.1 τ , rel. area 3.0). The n.m.r. data were given previously and it was shown that 4% II was present in the sample of I.⁸

Preparation of 1-Methylsulfinyl-1-dodecene (II).—A 300-ml. autoclave was charged with 66.4 g. (0.40 mole) of 1-dodecyne, 14.4 g. (0.30 mole) of methyl mercaptan, and 1 g. of azobisisobutyronitrile (ABN). The autoclave was pressured to 500 p.s.i. with nitrogen and was heated at 65° for 4 hr. It was then cooled and vented overnight after which the products were removed and distilled through a Claisen head. Fractionation through a 24 in., 8 mm. diameter, spinning band column yielded 41.2 g. (64%) of 1-methylthio-1-dodecene, b.p. 84° (0.15 mm.), chromatographically pure by v.p.c. *Anal.* Calcd. for $\text{C}_{13}\text{H}_{26}\text{S}$: C, 72.8; H, 12.21; S, 14.9. Found: C, 72.6; H, 12.4; S, 14.7.

To a solution of 15 g. (0.065 mole) of 1-methylthio-1-dodecene in 100 ml. of ethanol was added 8.0 ml. (0.071 mole) of hydrogen peroxide (30%) and the mixture was stirred for 4 hr. A few milligrams of platinum black was then added to decompose any unreacted peroxide and the mixture was allowed to stand overnight. The platinum black was filtered off and the ethanol was evaporated. The residue was distilled to yield 1-methylsulfinyl-1-dodecene, b.p. 132° (0.15 mm.). *Anal.* Calcd. for $\text{C}_{13}\text{H}_{26}\text{OS}$: C, 67.7; H, 11.37; S, 13.9. Found: C, 67.6; H, 11.6; S, 13.6. An infrared spectrum had bands at 9.5 (s) (sulfoxide), 10.4 (m) (*trans* double bond), 6.2 (w) μ (double bond). An n.m.r. spectrum had absorptions due to olefinic protons (3.7 τ , rel. area 1.9), methylsulfinyl protons and allylic protons (7.5 and 7.8 τ , combined rel. area 5.4), and protons of the alkyl chain (8.7 and 9.1 τ , rel. area 19.0). The n.m.r. spectral data have been discussed previously.⁸

Conversion of 1-Methylsulfinyl-1-dodecene (II) to 1-Methylsulfinyl-2-dodecene (I).—To 200 ml. of *t*-butyl alcohol was added 0.5 g. (0.013 g.-atom) of potassium. After the potassium was consumed, 10.0 g. (0.0435 mole) of 1-methylsulfinyl-1-dodecene (II) was added to the solution and the reaction mixture was stirred for 4 hr. The reaction mixture was then poured into 300 ml. of water and extracted three times with ethyl acetate. The extracts

were dried over magnesium sulfate and the solvent was evaporated. The residue remaining was distilled to yield 8.5 g. (85%) of 1-methylsulfinyl-2-dodecene (I), b.p. 131–137° (0.10–0.14 mm.). It was identical with the I described above as determined by infrared and n.m.r. spectra. On the basis of the relative areas at 3.5–3.9 τ (due to II) and 3.9–4.8 τ (due to I) it was determined that the product consisted of 96% I and 4% II.

Reaction of 1-Methylsulfinyl-2-dodecene with Sodium Deuterioxide in Deuterium Oxide.—Two-tenths gram (0.009 g.-atom) of sodium was added to 10 ml. of deuterium oxide after which 1.0 g. (0.0043 mole) of 1-methylsulfinyl-2-dodecene was added and the reaction mixture was stirred for 64 hr. at room temperature. The sulfoxide was then extracted with hexane, dried, and the hexane was evaporated to yield 0.85 g. of recovered material. An infrared spectrum was identical with that of starting material except that a new weak band had appeared at 11.6 μ . The n.m.r. spectrum of this material still had a multiplet at 4.4 τ (rel. area 1.9) which was only somewhat less complex than that of the starting material. The band at 6.65 τ in the starting material had disappeared completely. The other bands were the same as in the starting material: 7.6 and 7.9 τ (combined relative area 4.9), 8.7 and 9.1 τ (combined rel. area 17.0). The structure 1-methylsulfinyl-1,1-dideuterio-2-dodecene was therefore assigned to the product.

Reaction of 1-Methylsulfinyl-1-dodecene with Sodium Deuterioxide in Deuterium Oxide.—One-tenth gram (0.0045 g.-atom) of sodium was added to 5 ml. of deuterium oxide and 0.5 g. (0.0021 mole) of 1-methylsulfinyl-1-dodecene was then added. The

reaction mixture was stirred at room temperature for 66 hr. and was then worked up as described above. An n.m.r. spectrum of the isolated product indicated that 20% of the mixture had been isomerized to β,γ -unsaturated isomer (appearance of vinyl proton absorption around 4.4 τ), while 80% of the α,β -unsaturated material remained. The relative area of the absorption in the vinyl proton region remained at a value of 2.0, while the peaks at 7.5 and 7.8 τ still had a combined relative area of 5. The relative areas were based on the area of the terminal methyl group (9.1 τ , relative area 3.0), since the long-chain methylene protons (8.7 τ) would vary depending upon the amount of isomerization that had occurred. Both isomers have allyl protons; hence isomerization does not affect the relative area of the band at 7.8 τ .

Reaction of 1-Methylsulfinyl-1-dodecene with Sodium Deuterioxide in Deuterium Oxide.—Two-tenths gram (0.009 mole) of sodium was added to 10 ml. of deuterium oxide after which 0.5 g. (0.0021 mole) of 1-methylsulfinyl-1-dodecene was added. The reaction mixture was stirred at room temperature for 2 weeks and was then worked up as described above. The recovered material weighed 0.4 g. An n.m.r. spectrum of the recovered material was very similar to the one described above, except that the absorption at 3.5–3.9 τ was only 35% of the total vinyl proton absorption while the new absorption at 4.0–4.8 τ accounted for 65%. Again, the allylic proton absorption at 7.8–8.0 τ was undiminished.

Acknowledgment.—We are indebted to Dr. T. J. Flautt for help with the n.m.r. spectra and to Mr. A. L. Voegele for invaluable technical assistance.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE UNIVERSITY, CORVALLIS, OREGON]

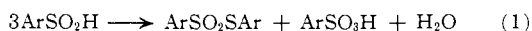
Mechanisms of Reactions of Sulfinic Acids. VI. The Mechanism of the Disulfide-Sulfinic Acid Reaction¹

BY JOHN L. KICE AND EVA H. MORKVED

RECEIVED NOVEMBER 20, 1963

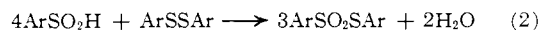
A recent paper² described a new reaction between *p*-tolyl disulfide and *p*-toluenesulfinic acid and outlined its probable mechanism. Confirmation of the important details of this mechanism and a significant extension of our understanding of the disulfide-sulfinic acid reaction have now been achieved through study of the reaction of a wide variety of disulfides with *p*-toluenesulfinic acid. For all alkyl disulfides the principal reaction product is the alkyl *p*-toluenethiolsulfonate, accompanied by small amounts of *p*-tolyl *p*-toluenethiolsulfonate and alkyl *p*-tolyl disulfide. Because of the relative availability of the starting materials and the predominant formation of the alkyl *p*-toluenethiolsulfonate, the reaction offers a potentially practical route for the synthesis of unsymmetrical thiolsulfonates. The kinetics of the reaction vary with disulfide structure, being second order in disulfide for nucleophilic primary alkyl disulfides, such as methyl or *n*-butyl, and first plus second order for both less nucleophilic primary ones, such as benzyl, and *sec*-alkyl disulfides, such as isopropyl. This behavior results because the second-order term arises from nucleophilic attack of disulfide on ion II, and such an attack is sterically hindered in the *sec*-alkyl case and inductively disfavored in the case of less nucleophilic disulfides. The disulfide-sulfinic acid reaction can be powerfully catalyzed by suitable alkyl and aryl sulfides. Study of the dependence of such sulfide catalysis on sulfide concentration and sulfide structure shows that it results from the fact that sulfides, being in general more nucleophilic, react more readily with II than the disulfide can. Possible application of such catalysis in other reactions is discussed.

The disproportionation² of aromatic sulfinic acids (eq. 1) is a reaction that has seen use^{2e} as a preparative



method for the corresponding thiolsulfonates ArSO_2SAr . However, it has one serious shortcoming—as a result of its oxidation to sulfonic acid, one-third of the sulfinic acid is in effect wasted. Recently Kice and Bowers³ discovered that, under reaction conditions similar to those best employed for its disproportionation, *p*-

toluenesulfinic acid ($\text{Ar} = p\text{-CH}_3\text{C}_6\text{H}_4$) also reacts readily with *p*-tolyl disulfide to give the same thiolsulfonate (eq. 2), but with a reaction stoichiometry that



does not lead to any waste of sulfinic acid. By suitable adjustment of conditions, this latter reaction can be made to predominate over the normal disproportionation.

In moist acetic acid as solvent this disulfide-sulfinic acid reaction was found to be strongly acid catalyzed, strongly retarded by added water, and first order in sulfinic acid. To explain the fact that at the same time it exhibited a first plus second-order dependence on disulfide concentration, the mechanism shown in Chart I was suggested.³ In it the second-order term in disulfide results from that compound functioning as a

(1) This research supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AFOSR-106-63.

(2) (a) C. Pauly and R. Otto, *Ber.*, **10**, 2182 (1877); (b) J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 605 (1962); (c) H. Bredereck, A. Wagner, E. H. Beck, H. Berlinger, and K. G. Kottenhahn, *Angew. Chem.*, **70**, 268 (1958); (d) P. Allen and L. Reich, *J. Phys. Chem.*, **64**, 1928 (1960); (e) C. M. Bere and S. Smiles, *J. Chem. Soc.*, **125**, 2359 (1924); (f) J. von Braun and K. Weissbach, *Ber.*, **63**, 2837 (1930).

(3) J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 2384 (1962).