is a fair representation of the chemistry that occurs.

Hydrolysis of the 2 and 4 Iminium Ions. Hydrolysis of iminium ions formed during isomerization of 1 and 3 kinetically followed established patterns.[43] Thus general-base catalysis of hydrolysis of an iminium ion by aminoethanol and nucleophilic attack by hydroxide ion on the iminium ion are routes to 2 and 4. We did not attempt to determine the pK_a of the iminium ions but assumed the pK_a to be greater than that of aminoethanol. Pollack and Kayser[41] determined the value of the pK_a of 2,2,2-trifluoro-*N*-(3-methyl-2-cyclohexenylidene)ethylammonium ion and found it to be a unit greater than the pK_a of trifluoroethylamine. In the present study we found that statistically, the best set of rate constants, k_{EA}^h and k_{OH}^h using eq 5, were generated by assuming the fraction of iminium ion was 1 throughout the pH range 8.9–10; effectively this assumption requires the pK_a to be ca. 11.

Acid-Catalyzed Isomerization. There are two kinetics reports of the acid-catalyzed isomerization of Δ^5- to Δ^4-3-keto steroids. In one of them, a study of the comparative reactivity of six $\Delta^{5,6}$-3-keto steroids, Nes et al.[13] found that the $\Delta^{5,6}$-3-keto steroids are about 10-50 times more reactive than the $\Delta^{5,10}$-3-keto steroids. In the other, a mechanisms study of the isomerization of 1 to 2, Malhotra and Ringold[4] concluded that enolization is rate determining on the basis of primary and deuterium solvent kinetic isotope effects and product isolation studies. In the present study, the values of the rate constants for isomerization of 1 and 3 (Tables I and II) are in very good agreement with those published.[4,13] The result that chloroacetic acid and methoxyacetic acid catalyze the isomerization of 1 supports rate-determining enolization as postulated;[4] this process is well-known to be general acid–base catalyzed. However, the curvilinear plots shown in Figure 3 for isomerization of 1 and 3 in D_2O/DCl suggest that 1 and 3 exchange C-4 protons with solvent during isomerization, and enolization is not cleanly rate determining. We are unaware of other enolization reactions that suggest that partitioning of an enol is kinetically important.[47] The approximate limiting rate constants obtained for short and long times give $k_2(H_2O)/k_2(D_2O)$ values of about 0.5 and 2, respectively. The former KIE is similar to those reported for the enolization of acetone,[44-46] and the latter is reasonable for rate-determining protonation of O-deuterated dienol. Further, the conclusion that partitioning of dienols is kinetically important during isomerization is supported by results of product-isolation studies carried out by Malhotra and Ringold, who found that isomerization of 17β-hydroxyandrost-5-en-3-one to 17β-hydroxyandrost-4-en-3-one, when taken to 50% completion, gave starting material containing 0.08 atom of deuterium at C-4.[4] Clearly, partitioning of dienol to product is kinetically favored over partitioning to starting material in this case.

The following conclusions of mechanism can be drawn from results of this study. (1) In solutions of tertiary amines, C-6 protonation of the 1 dienolate and C-10 protonation of the 3 dienolate are rate determining. (2) From a consideration of Brønsted β's, it may be concluded that the greater reactivity of 1 than 3 is due to the greater concentrations of the 1 dienolate than those of the 3 dienolate ions. (3) In solutions of aminoethanol, 1 and 3 rapidly form Schiff bases whose reactivity in isomerization markedly exceeds the reactivities of 1 and 3 with tertiary amines such as (dimethylamino)ethanol, but slow hydrolysis of the Schiff bases undercuts the efficiency of such catalysis. (4) In DCl/D_2O solutions partitioning of dienols is kinetically detectable. (5) Base-catalyzed isomerization is more efficient than acid-catalyzed isomerization.

Registry No. 1, 571-36-8; 2, 63-05-8; 3, 68-23-5; 4, 68-22-4.

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Double-Bond-Stabilizing Abilities of Dimethylamino, Alkylsulfonyl, and Acetyl Substituents[1]

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Equilibrium constants have been determined for the isomerization of *trans*-$XCH_2CH{=}CHY$ to *trans*-$XCH{=}CHCH_2Y$ for three combinations of X and Y. The values obtained were 40 ± 15 for X = dimethylamino and Y = phenyl, 40 ± 15 for X = methyl and Y = *n*-butylsulfonyl, and 4.8 ± 0.5 for X = acetyl and Y = methyl. These data give *D* values (double-bond-stabilizing parameters) of 8.2, −0.1, and 3.36 kcal/mol for dimethylamino, *n*-butylsulfonyl, and acetyl substituents, respectively. The dimethylamino substituent is thus by far the best double-bond-stabilizing substituent that has been studied. The equilibrium constant for isomerization of *n*-butyl *trans*-1-butenyl sulfone is about eight times as large as that reported by other workers and it yields a *D* value for the *n*-butylsulfonyl group that is much nearer the value for the methylsulfonyl group. The *D* value for acetyl is near that found earlier for carbomethoxy.

It has been previously shown that a consistent scale of double-bond-stabilizing abilities may be obtained from data on equilibria such as eq 1, if allowance is made for the interaction of X and Y across the carbon–carbon

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$$trans\text{-}XCH_2CH{=}CHY \rightleftarrows trans\text{-}XCH{=}CHCH_2Y \quad (1)$$

double bond.[2,3] To allow for such interactions and for double-bond-stabilizing ability, the free energies for eq 1 are correlated by eq 2, in which the D's are double-bond-

$$\Delta G_{XY}^{chem} = D_Y - D_X + \tau_v(\sigma_X\sigma_{CH_2Y} - \sigma_Y\sigma_{CH_2X}) \quad (2)$$

stabilization parameters, the σ values used are Hammett σ constants for para substituents, and a least-squares value of 13.4 ± 2.4 kcal/mol was obtained for τ_V.[2,3] Of the substituents for which data were given, the best double-bond stabilizers were phenyl and methoxy, both of whose D values were within the estimated uncertainty of 5 kcal/mol. The order $D_{OMe} > D_F \sim D_{SMe} > D_{Cl} > D_{Br}$ suggested that substituents capable of strong electron donation by a resonance mechanism should be particularly effective at stabilizing carbon–carbon double bonds. Amino groups are the best electrically neutral substituents at resonance electron donation; hence their abilities to stabilize double bonds are of interest. Tertiary amines should be studied to avoid complications from imine formation. For this reason we have determined D for the dimethylamino substituent. In order not to have an equilibrium that is so one-sided that the equilibrium constant cannot be measured, the dimethylamino group should be pitted against a group that does not differ too much from it in double-bond-stabilizing ability. Because we expected the dimethylamino group to be very effective at double-bond stabilization, the methoxy and phenyl groups are the obvious possibilities as the other group in eq 1. The carbanion-stabilizing ability of the phenyl group promised to facilitate establishment of equilibrium by a carbanion mechanism. Hence we studied the base-catalyzed isomerization of *N,N*-dimethylcinnamylamine. After the completion of our work we learned that the base-catalyzed isomerization of *N*-methyl-*N*-phenylcinnamylamine goes largely to the isomeric enamines but that the equilibrium mixture may contain as much as 10% starting material.[4]

Although all the saturated straight-chain primary alkyl groups from methyl through *n*-butyl have very nearly the same double-bond-stabilizing ability,[2] the value of $D_{SO_2Bu\text{-}n}$ obtained from data on tautomerism of *n*-butyl 1-butenyl sulfone[5] was 1.68 kcal/mol larger than the value of D_{SO_2Me} obtained from data on tautomerism of methyl 1-propenyl sulfone.[6] This difference is much larger than the 0.20 kcal/mol standard deviation of the fit of eq 2 to the available data. Other observations show much smaller differences among the double-bond-stabilizing abilities of ethylsulfonyl, *n*-propylsulfonyl, and *n*-butylsulfonyl groups,[7] or between those of methylsulfonyl and ethylsulfonyl groups.[8] It seemed desirable to check this apparent discrepancy. Hence we redetermined the equilibrium constant for interconversion of *n*-butyl 1-butenyl and *n*-butyl 2-butenyl sulfones.

We are aware of only one directly relevant study of an aldehyde or ketone. This was based on the greater reactivity of iodine toward unconjugated than toward conjugated unsaturated carbonyl compounds. When 4-hepten-2-one was refluxed with 20% sulfuric acid, the iodine titer dropped about 75% of the way to the values reported for the 3-hepten-2-ones and then leveled off.[9] However, under the same conditions the iodine titer of neither *cis*- nor *trans*-3-hepten-2-one changed. Thus it seems that the process observed was not the desired equilibration. In order to learn the double-bond-stabilizing ability of a ketonic carbonyl group, we have studied equilibrium between 3-hexen-2-one and 4-hexen-2-one.

Results

The *N,N*-dimethylcinnamylamine prepared by the method of Kruglikova and Abramova was taken to be trans on the basis of its infrared spectrum, its method of synthesis, and comparison with the cis isomer, which had been prepared by hydrogenation of the appropriate acetylenic amine.[10] This conclusion is further supported by the vinyl hydrogen–hydrogen coupling constant of 15.7 Hz. This amine was isomerized by potassium *tert*-butoxide in *tert*-butyl alcohol solution, but temperatures above 100 °C were required to reach equilibrium in a reasonable time. The product (**2**), which was formed to an extent of more

$$\underset{\mathbf{1}}{trans\text{-}C_6H_5CH{=}CHCH_2NMe_2} \rightleftarrows \underset{\mathbf{2}}{trans\text{-}C_6H_5CH_2CH{=}CHNMe_2} \quad (3)$$

than 90% at equilibrium, was never isolated in a pure form. Attempts to prepare it in other ways were not successful. The structure assigned to **2** is supported by elemental analysis of mixtures of **1** and **2**, preparation of hydrocinnamaldehyde 2,4-dinitrophenylhydrazone from **2** under hydrolytic conditions, and the ^1H NMR spectrum, including a vinyl hydrogen–hydrogen coupling constant of 13.1 Hz. The vinyl hydrogen–hydrogen coupling constants for enamines have been reported to be in the ranges 13.4–13.9 Hz for trans and 7.8–9.1 Hz for cis hydrogen atoms.[4,11] The ^1H NMR spectra of the equilibrium mixtures showed only peaks arising from **1**, **2**, and the solvent.

1 reacted rapidly at room temperature with potassium *tert*-butoxide in pure dimethyl sulfoxide solution, but the solution turned black and many products were formed. In 1:1 (v/v) *tert*-butyl alcohol–dimethyl sulfoxide, 0.3 M potassium *tert*-butoxide established equilibrium at 35 or 55 °C in less than 2 weeks, with the formation of a yellow color but no side reactions detectable by ^1H NMR.

The small amount of reactant present at equilibrium and the sensitivity of the enamine product to oxygen and moisture made it hard to get a reliable equilibrium constant. An equilibrium content of **1** of 2.35 ± 0.10% was obtained by ^1H NMR measurements on the phenyl and methyl protons at 35 and 55 °C, with no clearly significant difference between the values at the two different temperatures. Addition of the reaction mixtures to pentane, which precipitated the catalyst, followed by filtration and GLC measurements gave 3.6 ± 0.1% **1**.

The preparation of butyl 1-butenyl sulfone and butyl 2-butenyl sulfone (by oxidation of the corresponding sulfides) has been reported, but the ratios of cis to trans isomers present were not known.[5,12,13] Our *n*-butyl 1-bu-

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Table I. Equilibria in Transformations of *trans*-$XCH_2CH=CHY$ to *trans*-$XCH=CHCH_2Y$

X	Y	% reactant trans	% product trans	solvent	temp, °C	K	−ΔG, kcal/mol
NMe_2	Ph	100	100	*t*-BuOH Me_2SO[c]	35[a]	40 ± 15[b]	2.3 ± 0.3
Me	SO_2Bu	100	82	*t*-BuOH	25	40 ± 15	2.2 ± 0.3
Ac	Me	70	100	*t*-BuOH	25	4.8 ± 0.5	0.93 ± 0.07

[a] Same results obtained at 55 °C. [b] Preferred value based largely on NMR analyses; uncertainty large enough to include results from GLC analyses. [c] 1:1 by volume.

tenyl sulfone was separated by fractional distillation into cis and trans isomers, which were identified by their vinyl hydrogen–hydrogen coupling constants of 11 and 15 Hz, respectively. The ^1H NMR spectrum of our butyl 2-butenyl sulfone showed that both isomers were present, even though the two GLC peaks could not be resolved on any of the 12 different columns tried. From the areas of the two methylene doublets present, the material was about 18% cis and 82% trans. With each of the three preparations as starting material, equilibrium was established at 25 °C with 0.05 M potassium *tert*-butoxide. The equilibrium mixture was found, by combined ^1H NMR and GLC measurements, to contain about 80% butyl *trans*-2-butenyl sulfone, 18% butyl *cis*-2-butenyl sulfone, 2% butyl *trans*-1-butenyl sulfone, and not enough butyl *cis*-1-butenyl sulfone to detect unambiguously. It seemed possible that a significant fraction of the sulfones was present as carbanions in the equilibration solutions. Part of the sulfones would then be formed from these carbanions when the reaction solutions were quenched for analysis. The equilibration was studied with 1:1 and 2.5:1 ratios of sulfone to potassium *tert*-butoxide to see whether our results were being complicated in this way. The contents of the equilibrium mixtures did not differ significantly.

4-Hexen-2-one[14] was separated by preparative GLC into its cis and trans isomers (vinyl hydrogen–hydrogen coupling constants 10.9 and 15.3 Hz, respectively). Isomerization of the unseparated mixture of isomers by triethylamine in *tert*-butyl alcohol gave a product mixture from which *trans*-3-hexen-2-one (vinyl hydrogen–hydrogen coupling constant 15 Hz) was obtained by fractional distillation. Equilibrium was established in *tert*-butyl alcohol solution with 1,8-diazabicyclo[5.4.0]-7-undecene as a catalyst, starting from both the 4-hexen-2-one mixture (about 7% cis and 93% trans) and *trans*-3-hexen-2-one. At 25 °C, the equilibrium mixture contained about 77% *trans*-3-hexen-2-one, 16% *trans*-4-hexen-2-one, 7% *cis*-4-hexen-2-one, and not enough *cis*-3-hexen-2-one to detect.

Our results, including the estimated uncertainties in our equilibrium constants, are summarized in Table I.

Discussion

Application of eq 1 to the ΔG values in Table I, using the reported[2,3] D values for phenyl and methyl groups, gives D values of 8.2, −0.1, and 3.36 kcal/mol for the dimethylamino, *n*-butylsulfonyl, and acetyl groups, respectively. The σ_p values for (*n*-butylsulfonyl)methyl (0.17), dimethylamino (−0.82), and acetyl (0.44) were from the collection by Exner[15] used previously. For *n*-butylsulfonyl σ_p was assumed to be the same as for methylsulfonyl (0.73). The values for acetonyl (0.04) and (dimethylamino)methyl (−0.08) were obtained from σ_I values as described earlier.[2]

The D value for the dimethylamino group is more than 3 kcal/mol larger than any other D value that has been determined. This is presumably because of conjugation of the unshared pair of electrons on nitrogen with the double bond. The argument given previously[2] shows that D for the O^- group must be larger than that for hydroxy (whose D is probably near that of methoxy) and may well be larger than that for dimethylamino. Such substituents as NH^- and CH_2^- could have even larger D values. From the observation that *N*-methyl-*N*-phenylcinnamylamine isomerizes to at least 90% trans enamine at equilibrium[4] and from σ_p values of −0.40[16] and −0.12[16] for the *N*-methylanilino and (*N*-methylanilino)methyl groups, respectively, the D value for the *N*-methylanilino group is found to be greater than 6.8 kcal/mol.

The large D value for the dimethylamino substituent may be compared with results that might have been expected from ab initio calculations. For this purpose let us take the energy of reaction for eq 4 as a measure of the

$$CH_2{=}CHX + CH_3CH_3 \rightarrow CH_2{=}CH_2 + CH_3CH_2X \quad (4)$$

double-bond-stabilizing ability of X. Total energies calculated by using a minimal STO-3G basis set[18] give energies of reaction of 7.26, 8.53, and 4.26 kcal/mol for X = F, OH, and NH_2, respectively. That is, the amino group is calculated to be a poorer double-bond stabilizer than fluoro or hydroxy. The calculated $D_{OH} - D_{NH_2}$ is more than 7 kcal/mol larger than our value of $D_{OMe} - D_{NH_2}$. The difference could arise from the difference between hydroxy and methoxy groups and between amino and dimethylamino groups or from the fact that the calculations refer to the gas phase and our values to solutions. We think it likely, however, that the uncertainties in the ab initio calculations are large enough to explain the difference.

The D value for the acetyl group is near that for carbomethoxy, the only other carbonyl substituent for which a D value (3.15 kcal/mol) has been obtained.[2] The D value for the *n*-butylsulfonyl group is much smaller than that reported earlier,[2] because we have found only about 2% butyl 1-butenyl sulfone present in the same equilibrium mixture previously reported to contain 16 ± 3%.[5] We are not sure how to explain this difference in results. It may be relevant that the reaction mixtures were analyzed in the earlier study[5] by titration with bromine, which has different reactivities toward the different isomers present. It may also be relevant that the 16 ± 3% reported for the 1-butenyl sulfone is very near the 20% we find for the sum of the amounts of 1-butenyl sulfone and *cis*-2-butenyl sulfone present. The new D value for *n*-butylsulfonyl may be compared with values calculated from measurements on equilibria between $RSO_2CH{=}CHCH_3$ and

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$RSO_2CH_2CH{=}CH_2$ for various R groups. For R = Me a value of −0.4 kcal/mol was calculated[2] from measurements in refluxing triethylamine solution[6] (~90 °C), but from more recent measurements in *tert*-butyl alcohol at 20–50 °C[8] *D* may be calculated to be −0.8 kcal/mol, a difference that may arise from the differences in solvent and temperature as well as experimental errors. From further data in *tert*-butyl alcohol at 20–50 °C,[8] *D* may be calculated to increase from −0.5 for ethylsulfonyl to 0.0 for isopropylsulfonyl to 0.9 kcal/mol for *tert*-butylsulfonyl. This difference of 1.4 kcal/mol between the *D* values for ethylsulfonyl and *tert*-butylsulfonyl groups is somewhat larger than the difference of 0.8 ± 0.2 kcal/mol that may be calculated from equilibrations of $PhCH_2SO_2CH_2CH{=}CHSO_2R$, where R is ethyl and *tert*-butyl, in boiling ethyl acetate.[7] However, the mixtures obtained in ethyl acetate were analyzed by melting-point determinations and ozonolysis, which are probably less accurate methods than GLC, which was used in the reactions carried out in *tert*-butyl alcohol.

The $\Delta G°$ value we have obtained for eq 1 where X is methyl and Y is butylsulfonyl is near what might be expected from thermochemical measurements on a related system. From gas-phase enthalpies of formation,[19] ΔH for eq 1 will be 2.6 kcal/mol when X is methyl and Y is *p*-toluenesulfonyl. The uncertainty on this figure is about 1.1 kcal/mol, which is much larger than that arising from our equilibrium measurements, even though our equilibrium constants are certainly not highly precise, as such measurements go.

Experimental Section

***trans*-*N*,*N*-Dimethylcinnamylamine (1).** The method of Kruglikova and Abramova, with only minor modifications, gave 1: bp 79–81 °C (1.25 mm) [lit.[10] bp 103–105 °C (10 mm)]; ^1H NMR[20] at 300 MHz (CD_3SOCD_3) δ 7.28 (d, 2, $J \simeq 7$ Hz, *o*-H), 7.18 (t, 2, $J \simeq 7$ Hz, *m*-H), 7.10 (t, 1, $J \simeq 7$ Hz, *p*-H), 6.44 (d, 1, $J = 15.7$ Hz, PhCH), 6.20 (d of t's, 1, $J = 15.7$, $J' = 6.2$ Hz, PhC=CH), 2.97 (d, 2, $J = 6.2$ Hz, CH_2), 2.19 (s, 6, CH_3).

***trans*-1-(Dimethylamino)-3-phenylpropene (2).** In the presence of 0.05 M potassium *tert*-butoxide in *tert*-butyl alcohol at 100 °C for 12 h, 1 was about 50% transformed to a product that could not be separated from it by fractional distillation but gave a slightly later peak on a six-foot 10% Carbowax column. The product mixture gave good carbon, hydrogen, and nitrogen analyses for $C_{10}H_{15}N$, showing that the process was an isomerization. Use of higher base concentrations (up to 0.6 M), higher temperatures (up to 160 °C), and longer times gave more extensive product formation. A mixture containing more than 90% product showed, in addition to the spectrum of the reactant, the following 300-MHz ^1H NMR spectrum[20] (CD_3SOCD_3): δ 7.17 (m, 5, Ar H), 5.94 (d, 1, $J = 13.1$ Hz, C=CHN), 4.29 (d of t's, 1, $J = 13.1$, $J' = 6.7$ Hz, NC=CH), 3.29 (d, 2, $J = 6.7$ Hz, CH_2), and 2.36 (s, 6, CH_3). The mixture also showed new IR peaks (in order of decreasing intensity) at 1640, 698, 1093, 727, 1320, and 941 cm^{-1}. Treatment of the mixture with 2,4-dinitrophenylhydrazine in aqueous solution gave yellow needles, mp 160.5–161.5 °C, with no melting point depression on mixing with authentic hydrocinnamaldehyde 2,4-dinitrophenylhydrazone.

Attempts were made to prepare *N*-hydrocinnamylidene-*N*,*N*-dimethylammonium perchlorate by treating hydrocinnamaldehyde with dimethylammonium perchlorate in refluxing benzene with a Dean–Stark trap.[21] After short times, starting material was obtained, and after longer times orange brown polymeric material was formed. Treatment of hydrocinnamaldehyde with dimethylamine in the presence of titanium tetrachloride[22] also gave yellow or brown products of high molecular weight. Preparative GLC purification of **2** removed most of the 1 but gave material containing several percent hydrocinnamaldehyde.

Equilibrium Constant for Isomerization of *trans*-*N*,*N*-Dimethylcinnamylamine. In a typical run, 3 mL of 0.64 M potassium *tert*-butoxide and 3 mL of 2.2 M *trans*-*N*,*N*-dimethylcinnamylamine, each in 1:1 (v/v) *tert*-butyl alcohol–dimethyl sulfoxide, were mixed. About 0.75 mL of the resulting solution was placed in an NMR tube and each of seven ampules. All the containers were sealed and put in a bath at 55 °C. At a recorded time the areas of the phenyl absorption, which ranges from about δ 7.0 to 7.35 and arises from both reactant and product, and the reactant methyl peak at δ 2.19 were measured. When this was finished the contents of the NMR tube was added to 75 mL of dry pentane. The resulting light brown precipitate was allowed to settle, and the solution was filtered and evaporated to slightly less than 1.0 mL, after 0.3 mL of 1:1 *tert*-butyl alcohol–dimethyl sulfoxide had been added. The residue was analyzed on a 6-ft 10% five-ring poly(phenyl ether) column at 120 °C, where the enamine had a slightly longer retention time.

The composition of the mixture was clearly changing during the first 24 h. Analyses at 72, 140, and 190 h were well within the experimental uncertainty of each other. The GLC analyses were all in the range 3.50 ± 0.05% reactant; the NMR analyses were all in the range of 2.28 ± 0.02% reactant. No NMR peaks could be seen except those of the solvent components, the trans reactant and the trans product.

To test the possibility that the reaction had not reached equilibrium but had stopped because the catalyst had been deactivated, we added more reactant to "final" reactions mixtures in several cases. In each case most of the added reactant was transformed to product at about the expected rate.

Butyl 1-Butenyl Sulfones. Butyl 1-butenyl sulfide of unknown cis–trans content was prepared by reaction of dibutyl sulfoxide with acetic anhydride.[23] Hydrogen peroxide oxidation of this product gave a mixture of butyl 1-butenyl sulfones. An Apiezon L column (at 175 °C) gave the best separation of a number of columns tried. Fractional distillation through a 14-in. column packed with stainless-steel HeliPak gave the lower boiling (and more rapidly eluted) isomer in 95% purity, the higher boiling isomer in >99% purity, and larger amounts of intermediate fractions. 300-MHz ^1H NMR spectra[20] ($CDCl_3$): lower boiling isomer δ 6.40 (d of t's, 1, $J = 11$, $J' = 7$ Hz, $SO_2C{=}CH$), 6.21 (d of t's, 1, $J = 11$, $J' = 7$ Hz, $SO_2CH{=}C$), 2.98 (m, 2, SO_2CH_2), 2.61 (quintet of d's, $J = 7$, $J' = 1$ Hz, $C{=}CCH_2$), 1.72 (m, 2, $CH_2CH_2SO_2$), 1.46 (sextet, 2, $J = 7$ Hz, $CH_3CH_2CH_2$), 1.06 (t, 3, $J = 7$ Hz, $CH_3CH_2C{=}C$), and 0.93 (t, 3, $J = 7$ Hz, $CH_3CH_2CH_2$); higher boiling isomer δ 6.87 (d of t's, 1 $J = 15$, $J' = 6$ Hz, $SO_2C{=}CH$), 6.42 (d of t's, 1, $J = 15$, $J' = 1.5$ Hz, $SO_2CH{=}C$), 2.97 (m, 2, SO_2CH_2), 2.30 (m, 2, $C{=}CCH_2$), 1.68 (m, 2, $CH_2CH_2SO_2$), 1.44 (sextet, 2, $J = 7$ Hz, $CH_3CH_2CH_2$), 1.09 (t, 3, $J = 8$ Hz, $CH_3CH_2C{=}C$), and 0.93 (t, 3, $J = 7$ Hz, $CH_3CH_2CH_2$). Thus the lower boiling isomer is cis and the higher boiling one trans. The cis and trans products each gave satisfactory analyses for C, H, and S.

Butyl 2-Butenyl Sulfones. Hydrogen peroxide oxidation of a mixture containing about 80% butyl 2-butenyl sulfide (cis–trans content unknown) and 20% butyl 1-methylallyl sulfide gave a mixture of sulfones. Fractional distillation separated the resulting butyl 1-methylallyl sulfone in the lower boiling fractions. The ^1H NMR of this isomer could not be seen in the higher boiling fractions: bp 100 °C (0.3 mm); ^1H NMR (360 MHz, $CDCl_3$) δ 5.9 (m, 1, $C{=}CHCH_3$), 5.6 (m, 1, $SO_2CH_2CH{=}C$), 3.7 (2 d, 2, $SO_2CH_2C{=}C$), 3.0 (m, 2, $SO_2CH_2CH_2$), 1.8 (m, 5, $C{=}CCH_3$ and $SO_2CH_2CH_2$), 1.49 (sextet, 2, $SO_2CH_2CH_2CH_2$), and 0.99 (t, 3, CH_3CH_2). The two doublets near δ 3.7 included one at δ 3.81, which we assigned to the cis isomer and another, 4.5 times as large, at δ 3.65, which we assigned to the trans isomer. In no other case could the cis and trans contributions be separated so cleanly. Irradiation at δ 3.65 turned the δ 5.6 peak largely into a doublet ($J = 15$ Hz) as did irradiation at δ 1.8 for the δ 5.9 peak. From the areas of the doublets near δ 3.7, the sample is seen to be 18% cis and 82% trans.

(19) Mackle, H.; Steele, W. V. *Trans. Faraday Soc.* **1969**, *65*, 2069–72.
(20) The assignments shown are supported by decoupling experiments.
(21) Cf.: Leonard, N. J.; Paukstelis, J. V. *J. Org. Chem.* **1963**, *28*, 3021–4.
(22) Cf.: White, W. A.; Weingarten, H. *J. Org. Chem.* **1967**, *32*, 213–4.
(23) Horner, L.; Kaiser, P. *Justus Liebigs Ann. Chem.* **1959**, *626*, 19–25.

Equilibration of the Butyl Butenyl Sulfones. Sulfone mixtures were analyzed by a combined GLC–NMR method. The *cis*-1-butenyl isomer is eluted more rapidly on a 6-ft 10% diisodecyl phthalate column at 140 °C than the trans isomer, whose peak overlaps badly with the peak for the 2-butenyl isomers. The amount of *trans*-1-butenyl isomer present was determined from the area of the vinyl hydrogen peak at δ 6.87 related to the total area for vinyl hydrogen atoms. The ratio of *cis*- to *trans*-2-butenyl isomer was determined from the ratio of the areas of the SO_2C-H_2C=C peaks at δ 3.81 and 3.65, respectively.

In a typical equilibration 100 mL of 0.10 M butyl *trans*-1-butenyl sulfone (>99% pure) and 100 mL of 0.10 M potassium *tert*-butoxide, both in *tert*-butyl alcohol solution, were mixed and placed in a 25 °C bath. After 20 h an 80-mL sample was withdrawn and added to 100 mL of standard pH 7 phosphate buffer to which 0.5 mL of 12 M hydrochloric acid had been added. (Earlier experiments had shown that the reaction goes more than 90% to equilibrium in 2 h under these conditions.) Two 100-mL methylene chloride extracts of this solution were combined, washed with saturated sodium chloride, dried over magnesium sulfate, and concentrated to 1–2 mL. The 60-MHz ^{1}H NMR spectrum of the residue at normal amplitude was essentially identical with that of the butyl 2-butenyl sulfone mixture that had been synthesized. The GLC revealed no *cis*-1-butenyl sulfone. The high amplitude 100-MHz NMR showed that 2.3 ± 0.5% *trans*-1-butenyl sulfone was present.

Equilibrium was also approached by starting from 5% trans–95% cis butyl 1-butenyl sulfone and from 82% cis–18% trans butyl 2-butenyl sulfone. In all cases 18 ± 2% *cis*-2-butenyl, 80 ± 2% *trans*-2-butenyl, and 2.1 ± 0.3% *trans*-1-butenyl sulfone were found at equilibrium.

When the *cis*-1-butenyl sulfone was the starting material, about 1.2% of it still seemed to be present after 20 and 95 h. With the other two starting materials no *cis*-1-butenyl sulfone could be detected; 0.5% would have been detectable.

When initial concentrations of 0.13 M sulfone and 0.05 M potassium *tert*-butoxide were used, 1.7 ± 0.3% *trans*-1-butenyl, 18 ± 1% *cis*-2-butenyl, and 80 ± 1% *trans*-2-butenyl sulfone were found at equilibrium. Experiments carried out at 35 °C gave essentially the same results.

***cis*- and *trans*-4-Hexen-2-one.** A 6-ft Carbowax 20M column was used at 70 °C to separate 4-hexen-2-one.[14] For the more rapidly eluted trans isomer: ^{1}H NMR (360 MHz, benzene-d_6) δ 5.46 (m, 1, $CHCH_2CO$), 5.28 (m, 1, CH_2CH), 2.68 (br d, 2, CH_2CO), 1.65 (s, 3, CH_3CO), and 1.50 (br d, 3, CH_3CH). Decoupling experiments confirmed these assignments and gave the following coupling constants: $J_{3,4}$ = 6.9, $J_{3,5}$ = 1.0, $J_{4,5}$ = 15.3, $J_{4,6}$ = 1.6, and $J_{5,6}$ = 6.3 Hz. For the cis isomer: ^{1}H NMR (360/MHz, benzene-d_6) δ 5.59 (m, 1, $CHCH_2CO$), 5.47 (m, 1, CH_3CH), 2.72 (br d, 2, CH_2CO), 1.62 (s, 3, CH_3CO), and 1.37 (br d, 3, CH_3CH). These assignments were confirmed by decoupling which showed the following: $J_{3,4}$ = 6.8, $J_{3,5}$ = 1.5, $J_{4,5}$ = 10.9, $J_{4,6}$ = 1.6, and $J_{5,6}$ = 6.5 Hz.

***trans*-3-Hexen-2-one.** A solution of 11 g of cis–trans 4-hexen-2-one and 10.5 g of triethylamine in 100 mL of *tert*-butyl alcohol was refluxed and analyzed at various times by GLC. After 50 h its content was essentially the same as it had been after 10 h. The remaining solution was fractionally distilled, first at atmospheric pressure and then at reduced pressure. The best fraction contained 9% 4-hexen-2-ones and 91% *trans*-3-hexen-2-one: ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.58 (d of t's, 1, J = 15, J' = 6 Hz, COC=CH), 5.97 (d of t's, 1 J = 15, J' = 1.5 Hz, COCH=C), 2.18 (s, ~3, CH_3CO), 2.15 (~q, ~2, J ~ 7 Hz, CH_3CH_2), and 1.05 (t, 3, J = 7 Hz, CH_3CH_2).

Equilibration of Hexen-2-ones. A mixture of 2 mL of 2.2 M 4-hexen-2-one (6.6% cis and 93.4% trans) and 2 mL of 2.0 M 1,8-diazabicyclo[5.4.0]-7-undecene, both in *tert*-butyl alcohol, was kept at 25 °C. Samples were analyzed by GLC using a 6-ft Carbowax 20M column, where *trans*-3-hexen-2-one has a considerably longer retention time than that of either of the 4-hexen-2-ones.

Samples taken after 11, 11.5, 32, and 50 h showed that 16.6 ± 0.5% *trans*-4-ene, 7.0 ± 0.4% *cis*-4-ene, 76.4 ± 0.6% *trans*-3-ene, and no detectable *cis*-3-ene were present.[24] Starting from trans-3-ene gave 15.5 ± 0.6% *trans*-4-ene, 7.4 ± 0.4% *cis*-4-ene, and 77.0 ± 0.4% *trans*-3-ene after 24–29 h. The reaction went about 90% to equilibrium in 4 h under these conditions.

Registry No. 1, 42817-44-7; 2, 73687-55-5; hydrocinnamaldehyde 2,4-dinitrophenylhydrazone, 73687-56-6; hydrocinnamaldehyde, 104-53-0; butyl *cis*-1-butenyl sulfide, 73687-57-7; butyl *trans*-1-butenyl sulfide, 73687-58-8; butyl *cis*-1-butenyl sulfone, 73687-59-9; butyl *trans*-1-butenyl sulfone, 73687-60-2; butyl *cis*-2-butenyl sulfone, 73687-61-3; butyl *trans*-2-butenyl sulfone, 73687-62-4; butyl *cis*-2-butenyl sulfide, 73687-63-5; butyl *trans*-2-butenyl sulfide, 3001-22-7; butyl 1-methylallyl sulfide, 689-90-7; butyl 1-methylallyl sulfone, 73687-64-6; *cis*-4-hexen-2-one, 51024-76-1; *trans*-4-hexen-2-one, 763-92-8; *trans*-3-hexen-2-one, 4376-23-2.

(24) If *cis*-3-hexen-2-one has the same GLC retention time as its trans isomer, as much as 5% could have been present in the equilibrium mixture (limit established by NMR measurements).

Reactivity–Selectivity Correlations. 2.[1] Reactivity of Alkyl Aryl Sulfates toward Oxygen Nucleophiles and the Reactivity–Selectivity Principle

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The reaction of a series of alkyl aryl sulfates with oxygen nucleophiles (methanol, methoxide ion, phenoxide ion), in methanol at 25 °C, has been investigated spectrophotometrically. The results show that the mode of reaction along the series is uniformly by alkyl–oxygen scission, i.e., nucleophilic displacement on the methyl carbon with $ArOSO_3^-$ as the leaving group. The Hammett σ plots yield ρ values of 1.39, 0.90, and 0.74 for the reactions of MeOH, MeO^-, and PhO^-, respectively. Since reactivity in these processes increases in this order, taking ρ as a selectivity parameter, it follows that selectivity bears an inverse relationship to reactivity. This result is in accord with the reactivity–selectivity principle (RSP). It is suggested that a number of studies in which the RSP has apparently failed to hold are subject to certain inherent problems in experimental design, e.g., differential solvent, structural or steric effects along the reaction series, or mechanistic variation, which could lead to a variety of patterns of reactivity and selectivity. The design of the present system allows one to modulate the nature of the nucleophilic and the nucleofugic moieties, ensuring a constancy of mechanism within a series of transition states whose structures and properties should vary in uniform fashion.

The reactivity–selectivity principle (RSP) would seem intuitively to be one of the fundamental guiding principles of chemical behavior, as expressed in its basic form that selectivity in a series of related processes on varying the

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