(30) scale that the existence of a better correlation with $\Delta G^\circ_{\mathrm{OMe}}$ may be suspected, and such a correlation may be useful, from the practical point of view, for predicting the effect of changing solvents on a reaction involving a charged transition state.

Experimental Section

The synthesis and equilibration by means of Amberlyst-15 (beaded polystyrenesulfonic acid) of the 2-isopropyl-5-alkoxy-1,3-dioxanes have been described previously.[3] Plots of $-\Delta G^\circ$ *vs.* E_T (30) were drawn by computer through a least-squares fitting program and correlation coefficients were computed by the standard formula.[33] The 6-methyl-2-methoxyoxanes were prepared and equilibrated as previously described;[18,23] $-\Delta G^\circ$ in carbon tetrachloride was found to be 0.74 kcal/mol (previous values, 0.74[18] and 0.73 kcal/mol[23]). The newly determined values were 0.55 kcal/mol in benzene and 0.46 kcal/mol in chloroform.

Acknowledgments. Financial support of this investigation through award of a postdoctoral fellowship to O. H. by the University of Notre Dame under an National Science Foundation Science Development Grant is gratefully acknowledged. We are greatly indebted to Professor Christian Reichardt for supplying us with an extensive amount of unpublished data and a number of references; both Dr. Reichardt and Professor Edward M. Arnett provided us with much helpful advice. We are thankful to them and also to Professors R. J. Abraham and Kenneth Wiberg for a critical reading of the first draft of the manuscript.

Supplementary Material Available. Figures 7 and 8 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-8041.

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(33) Documenta Geigy, Scientific Tables, 1956, p 42.

Stereochemistry of Base-Catalyzed Hydrogen Exchange in Cyclic Sulfonium Salts

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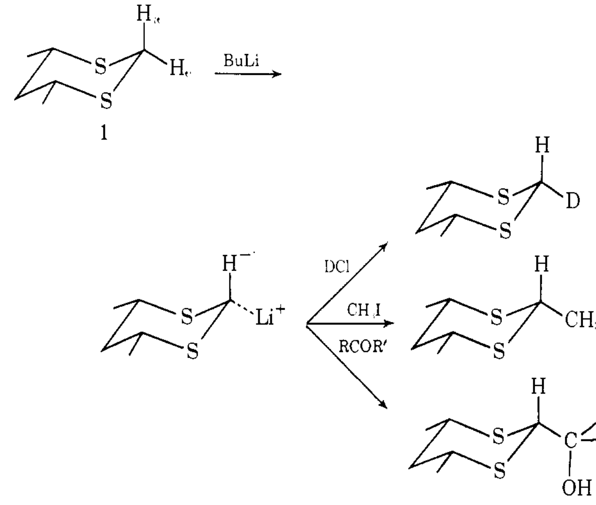
Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. *Received March 13, 1973*

Abstract: The relative rate constants of successive H/D exchange at carbons next to sulfur for the four α-methylene hydrogens in thiacyclohexylmethylsulfonium iodide (**3**) and thiacyclopentylmethylsulfonium iodide (**2**) with sodium deuterioxide in D_2O have been measured. The reactivity ratio for the two pairs of diastereotopic hydrogens in the six-membered ring (**3**) is near 1 : 1 but in the five-membered ring (**2**) it is *ca.* 12 : 1. The corresponding ratio for the two diastereomeric 2-methylthiacyclohexylmethylsulfonium salts **4** and **5** at the methylene carbon is about the same as for the parent compound **3**. The results for the thiacyclohexyl compound **3** agree with those found by others but those for the thiacyclopentyl compound **2** are only in qualitative agreement, the selectivity being less by a factor of over 30 than reported earlier. The findings are discussed in relation to the present status of the gauche effect.

In earlier work[2] we had found a ratio of well over 200 for formation of the equatorial lithium derivative of *cis*-4,6-dimethyl-1,3-dithiane (**1**) over the axial isomer, as gauged by nearly exclusive formation of further transformation products (H/D exchange products,[2] methylation products,[2] carbinol formation[3]) at the equatorial site (Scheme I). However, subsequent work[4] indicated that the high equatorial preference of the lithium derivative is the result of a thermodynamic preference and the difference in rate of abstraction between the equatorial and axial proton at C-2 (kinetic preference) in **1** ($k_{\mathrm{H_e}}/k_{\mathrm{H_a}}$) is only by a factor of *ca.* 9.[5]

Scheme I



Our interest in highly stereoselective hydrogen exchanges stemmed from our thinking that such exchanges might possibly be involved in certain highly stereoselective enzyme-catalyzed syntheses of compounds

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(2) A. A. Hartmann and E. L. Eliel, *J. Amer. Chem. Soc.*, **93**, 2572 (1971).

(3) E. L. Eliel and A. A. Hartmann, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Texas, Apr 1973, No. ORGN-64.

(4) E. L. Eliel, A. Abatjoglou, and A. A. Hartmann, *J. Amer. Chem. Soc.*, **94**, 4786 (1972).

(5) Much more substantial kinetic preferences for diastereotopic hydrogens have been found in a bridged biphenyl-derived sulfoxide [R. R. Fraser and F. J. Schuber, *Chem. Commun.*, 397 (1969); *Can. J. Chem.*, **48**, 633 (1970)] and in benzyl *tert*-butyl sulfoxide: R. Viau and T. Durst, *J. Amer. Chem. Soc.*, **95**, 1346 (1973) (see also ref 19).

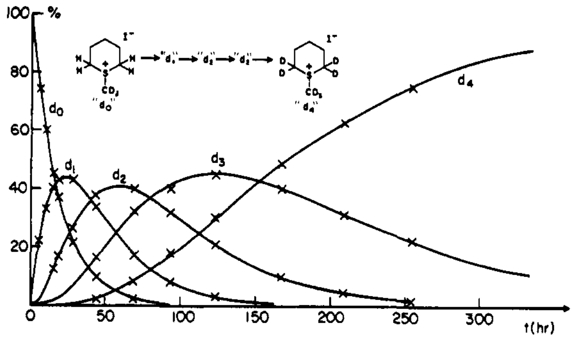
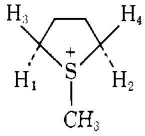


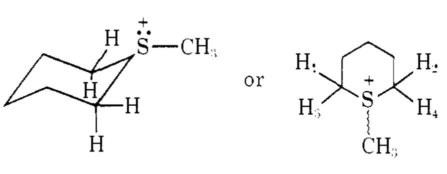
Figure 1. Rate plots for successive exchange of **3**-d_3 in NaOD–D_2O at 39°.

of type RCHDX[6] or, at the very least, that the processes could be used for laboratory syntheses with comparable stereoselectivity. We were therefore intrigued by the report[7a] that exchange of the α ring hydrogens of thiacyclopentylmethylsulfonium iodide (**2**) is highly stereospecific; *i.e.*, one of the two diastereotopic pairs undergoes exchange much faster than the other pair.[7,8] [Subsequent work of Fava and coworkers utilizing the nuclear Overhauser effect[9] has shown that the hydrogens syn to the methyl group (*i.e.*, anti-clinal with the unshared pair on sulfur, H_1, H_2) are the ones exchanged.] This result seemed especially interesting, since a methylsulfonium salt, *S*-adenosylmethionine ("SAME"), functions as the methyl transfer agent in many biochemical methylations; it seemed conceivable that this reagent might also undergo stereoselective H/D exchanges in one or other of its α-methylene groups leading ultimately to chiral RCHDX compounds in high enantiomeric purity.



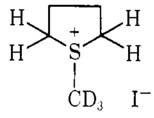
2

Because stereochemical preference might be related to conformation[10] and since conformation is more rigid and thus better defined in six-membered than in five-membered rings, we decided to study methylthiacyclohexylsulfonium iodide **3**. Unfortunately, because of the complexity of the nmr spectrum of **3**, we were not able clearly to discern exchange of axial *vs.* equatorial hydrogen atoms; only the overall extent of α deuteration could be readily determined by nmr. Since overall extent of deuteration does not allow one to distinguish between, say, a d_2 species and an equimolar mixture of d_1 and d_3 species, we abandoned the nmr method[7] in favor of mass spectrometry. Application of this technique, described in detail in the Experimental Section, gave very accurate composition data in terms of d_0, d_1, d_2, d_3, and d_4 species[11] and thus allowed determination of the rate constants for the essentially irreversible consecutive exchange. The composition



3

Table I. Percentage Exchange for Compound **2**-d_3[a]



2-d_3

Time, hr	Percentage of species with no. of deuterium atoms in ring indicated				
	d_0	d_1	d_2	d_3	d_4
8.3	51.0	40.6	8.4	0.0	0.0
11	41.6	45.8	12.8	0.0	0.0
16	27.7	48.2	22.9	1.2	0.0
21	19.3	48.7	30.7	1.3	0.0
24	13.5	46.6	37.6	2.3	0.0
28.5	10.3	41.3	44.0	4.4	0.0
29	10.5	40.6	44.0	4.6	0.3
44	2.4	23.3	62.8	11.0	0.5
50	2.5	24.0	63.0	9.8	0.7
67	0.5	12.7	68.0	18.3	0.5
75	0.3	8.3	68.9	21.3	1.2
98	0.0	4.3	62.0	30.2	3.5
150	0.0	1.6	46.0	43.0	9.4
214	0.0	1.3	30.8	49.6	18.3
320	0.0	0.7	14.5	48.6	36.2

[a] Conditions: 39°; 0.334 g of sulfonium salt (1.45 mmol) and 2.0 ml of 2.15 *N* NaOD in D_2O.

$$\mathbf{3} \xrightarrow{k_1} \mathbf{3}\text{-}d_1 \xrightarrow{k_2} \mathbf{3}\text{-}d_2 \xrightarrow{k_3} \mathbf{3}\text{-}d_3 \xrightarrow{k_4} \mathbf{3}\text{-}d_4$$

data were readily fitted by the rate equations for four successive processes[12] with $k_1:k_2:k_3:k_4 = 4.4:3.0:1.83:0.84$. As shown in Figure 1, the fit of the ex-

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(6) *Cf.* D. Arigoni and E. L. Eliel, *Top. Stereochem.*, **4**, 127 (1969).

(7) (a) G. Barbarella, A. Garbesi, and A. Fava, *Helv. Chim. Acta*, **54**, 341 (1971); (b) *ibid.*, **54**, 2297 (1971).

(8) The diastereotopic reactivity ratio was initially set at >400:1.[7b] After learning of the results here reported, however, the authors[7] have rexamined system **2** and found that the reactivity of the slower pair had been greatly underestimated. Their present estimate indicates a ratio of *ca.* 28:1: A. Fava, personal communication; and footnote 4 in ref 9b.

(9) (a) A. Garbesi, G. Barbarella, and A. Fava, *J. Chem. Soc., Chem. Commun.*, 155 (1973); (b) G. Barbarella, A. Garbesi, A. Boicelli, and A. Fava, *J. Amer. Chem. Soc.*, **95**, 8051 (1973).

(10) *Cf.* S. Wolfe, A. Rauk, L. M. Tel, and I. G. Czismadia, *J. Chem. Soc. B*, 136 (1971); S. Wolfe, *Accounts Chem. Res.*, **5**, 102 (1972).

(11) The data for compound **3** are shown in Table II (see paragraph at end of paper regarding supplementary material). Corresponding data for compound **2** (see below) are shown in Table I.

(12) N. M. Rodiguin and E. N. Rodiguinor, "Consecutive Chemical Reactions," Van Nostrand, Princeton, N. J., 1964. If a_0 is the initial concentration of the d_0 species and *a*, *b*, *c*, *d*, and *f* are the concentrations of the d_0, d_1, d_2, d_3, and (where applicable) d_4 species after time *t*, the following equations apply.[11]

$$a = a_0 e^{-k_1 t} \tag{i}$$

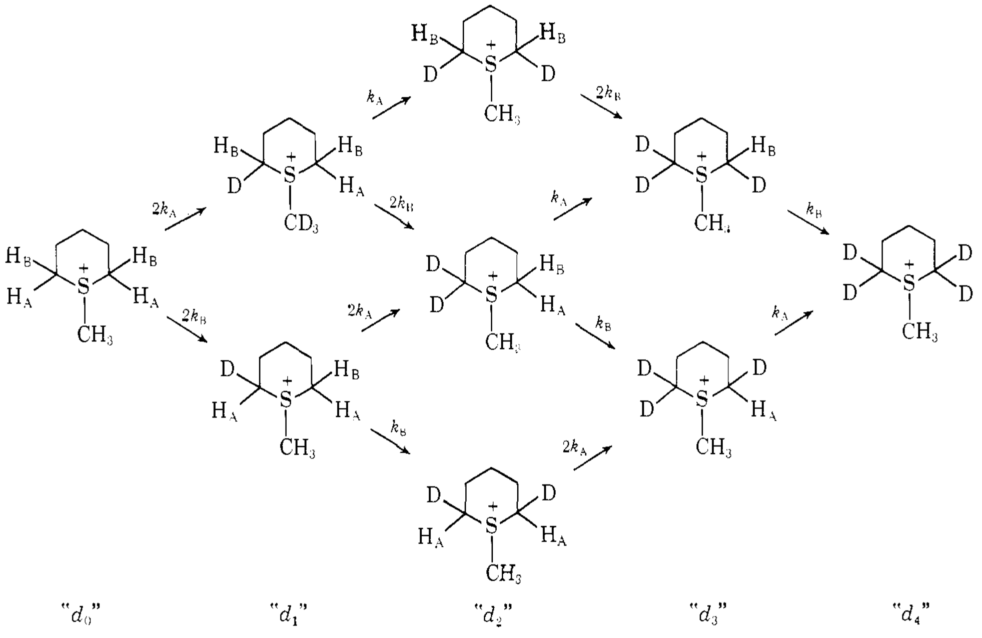
$$b = \frac{k_1 a_0}{k_2 + k_1}(e^{-k_1 t} - e^{-k_2 t}) \tag{ii}$$

$$c = k_1 k_2 a_0 \left[\frac{e^{-k_1 t}}{(k_2 - k_1)(k_3 - k_1)} - \frac{e^{-k_2 t}}{(k_2 - k_1)(k_3 - k_2)} + \frac{e^{-k_3 t}}{(k_3 - k_1)(k_3 - k_2)} \right] \tag{iii}$$

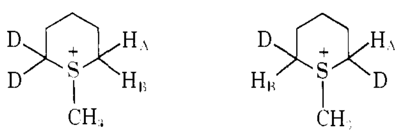
$$d = k_1 k_2 k_3 a_0 \left[\frac{e^{-k_1 t}}{(k_2 - k_1)(k_3 - k_1)(k_4 - k_1)} - \frac{e^{-k_2 t}}{(k_2 - k_1)(k_3 - k_2)(k_4 - k_2)} + \frac{e^{-k_3 t}}{(k_3 - k_1)(k_3 - k_2)(k_4 - k_3)} - \frac{e^{-k_4 t}}{(k_4 - k_3)(k_4 - k_2)(k_4 - k_1)} \right] \tag{iv}$$

$$f = a_0 - (a + b + c + d) \tag{v}$$

Scheme II[a]



[a] In the d_0 species, the two H_A's and the two H_B's constitute a diastereotopic pair of enantiotopic hydrogens; the enantiotopic hydrogens must necessarily exchange at the same rate. However, in the d_1 species, the introduction of a deuterium atom has destroyed the enantiotopic character of the remaining pairs (H_A's in the lower "d_1" species, H_B's in the upper) and to write a single "d_2" species in which H_A and H_B have exchanged (middle of diagram) is an over-simplication; there are actually two such species

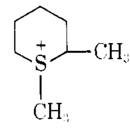


Disregard of the difference implies disregard of a possible secondary isotope effect, which may not be justified. Lack of knowledge of the magnitude of such a secondary isotope effect further complicates the interpretation of the simple consecutive rate constants k_1–k_4 in terms of k_A and k_B.

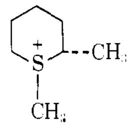
perimental composition data with the rate plots calculated[12] for the above rate constants is excellent.[13]

Unfortunately, we have not been able to interpret the consecutive rate constants k_1, k_2, k_3, and k_4 in terms of the basic rate constants k_A and k_B for the processes which actually occur and which are summarized in Scheme II. However, it is clear that for a completely nondiscriminatory process, *i.e.*, for one in which $k_A = k_B$, a statistically controlled exchange must occur, *i.e.*, $k_1:k_2:k_3:k_4 = 4:3:2:1$. Since our experimental figures are close to this ratio, it is clear that there is, at best, a very minor preference to abstraction of one diastereotopic pair of α hydrogens over the other. This conclusion is in complete accord with that of Fava and coworkers[7b] of which we learned after this phase of our investigation was completed.

The lack of stereoselectivity in the six-membered ring seemed, at least on the surface, not to be in agreement with the prediction made on the basis of the gauche effect[10] which would lead one to believe that the equatorial α hydrogens, being gauche to the unshared pair on sulfur, should be more acidic than the axial protons which are anti to the pair.[14] However, this prediction is based on the assumption that the *S*-methyl group is equatorial, an assumption which might *a priori* have been erroneous since methyl groups in phosphacyclohexanes have recently been shown to prefer the axial orientation.[15] We therefore synthesized the two *S*,2-dimethylthiacyclohexylsulfonium salts **4** and **5** and



4, cis



5, trans

studied their rates of hydrogen exchange at the α-methylene groups, by a procedure analogous to that used for the parent compound **3**. For one of the isomers $k_1:k_2:k_3 = 5.47:2.0:0.10$ and for the other 4.84:2.0:0.14. The mass spectral data are shown in Tables III and IV[11] and the kinetic plots in Figure 2. Once again the ratio for the exchanges of the first two protons is only slightly in excess of the statistical 2:1.[16] While we have not assigned configuration (*i.e.*, we do not

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(13) As implied in Figure 1, the species of 3 used in determining the kinetics of exchange was preexchanged in the methyl group in a prior step. It is known[7] that exchange in the methyl group is much faster than exchange in the ring; the prior methyl exchange technique (see Experimental Section) was used to avoid substantial dilution of the D_2O used by DHO before the beginning of the methylene exchange. The d_0, d_1, d_2, d_3, and d_4 species here referred to are thus really d_3, d_4, d_5, d_6, and d_7 species; however, for the sake of simplicity we shall henceforth disregard the deuteration of the methyl group in assigning the degree of exchange.

(14) The lack of stereoselectivity in the six-membered ring is in accord with the qualitative observations of H. Dorn, *Angew. Chem., Int. Ed. Engl.*, **6**, 371 (1967).

(15) L. D. Quin and J. H. Somers, *J. Org. Chem.*, **37**, 1217 (1972); S. I. Featherman and L. D. Quin, *J. Amer. Chem. Soc.*, **95**, 1699 (1973).

(16) The much lower rate of exchange of the tertiary hydrogen is as expected and reflects the lesser stability of the tertiary as compared to the secondary carbanion; *cf.* D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 21.

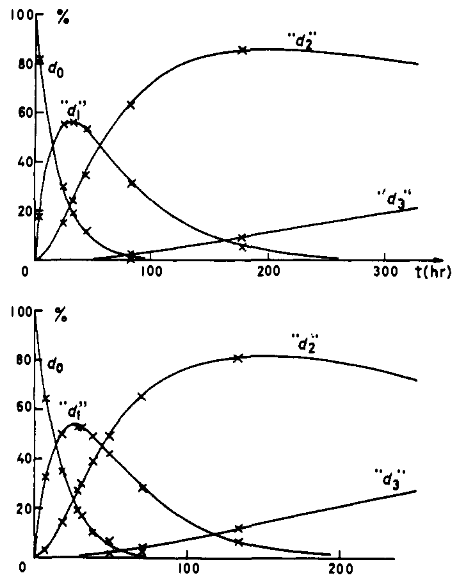
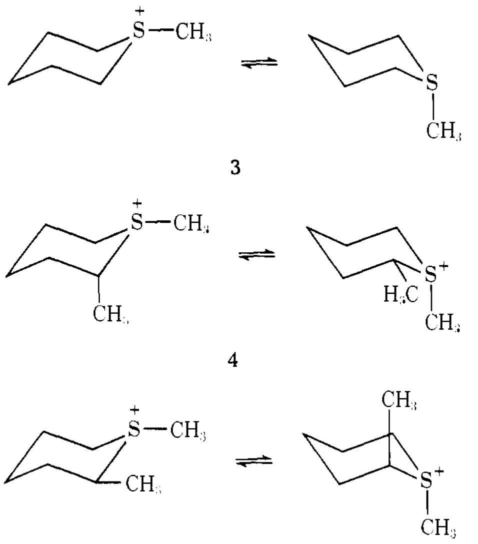


Figure 2. Rate plots for successive exchange of 4-d_3 (upper curve) and 5-d_3 (lower curve) in NaOD–D_2O at 39°.

know which isomer is **4** and which **5**), the similarity of the rate ratios for exchange of the diastereotopic methylene protons in **3**, **4**, and **5** is an argument against predominantly axial methyl in **3**. For, considering the conformational equilibria in **3**, **4**, and **5** (Scheme III), if **3** existed largely with the *S*-methyl group axial, the cis isomer **4** should be even more in that conformation (which allows the *C*-methyl group to be equatorial) but the trans isomer **5** would be much less so (since an axial *S*-methyl group in **5** forces the *C*-methyl group into the axial position also, with an unfavorable interaction of *ca.* 1.7 kcal/mol resulting). Thus, save for the unlikely possibility that the S-axial preference is so overwhelming that **5** as well as **3** and **4** exists largely with axial *S*-methyl, it seems very probable that the *S*-methyl group has a strong equatorial preference, such that **5** exists entirely in diequatorial conformation, **3** very largely in that conformation, and **4** in the conformation with enough predominance to make its $k_1:k_2$ similar to that of **5** and similar to $k_1:k_3$ or $k_2:k_4$ of **3**. Although this argument is not compelling, it is in agreement with the (equally tentative) conclusion based on the magnitude of the geminal coupling constant of the α hydrogens that the methyl group in **3** is very largely equatorial.[17,18]

Scheme III



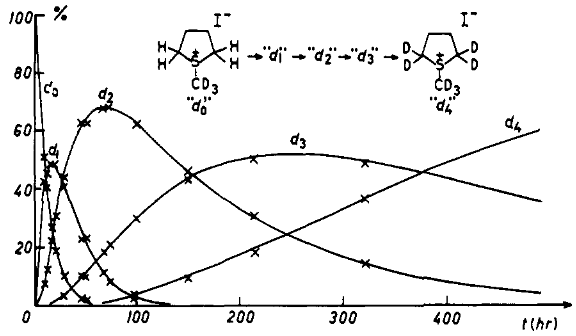


Figure 3. Rate plots for successive exchanges of 2-d_3 in NaOD–D_2O at 39°.

Since the mass spectrometric method was found so convenient in the analysis of the exchange of **3**, **4**, and **5** (see below), we decided to repeat the crucial exchange in **2** for which a diastereotopic selectivity of over 400 : 1 had originally been claimed on the basis of nmr measurements.[7] We did find, in agreement with Fava and coworkers,[7] that the selectivity in the five-membered ring was much larger than in the six-membered ring, though not as large as their measurements had indicated. In our hands, $k_1:k_2:k_3:k_4$ = 5.66 : 3.0 : 0.48 : 0.22; the mass spectral data are shown in Table I and the kinetic plots in Figure 3. If one makes the oversimplified assumption that the exchange of the first two protons is over before that of the third and fourth has progressed appreciably, the relative reactivity of the two pairs would be approximated by the ratio $k_1:k_3$ (= 12) or $k_2:k_4$ (= 14). While this is an oversimplification (see the earlier discussion),[19] we consider the result to be in satisfactory agreement with Fava's revised value[8] of 28 : 1; thus, unfortunately, the exchange is not by any means as stereoselective as was originally believed[7] (*cf.* also ref 9a).

Discussion

The finding that the α-methylene hydrogens syn to the methyl group in the five-membered ring[7,8] are more

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(17) J. B. Lambert, C. E. Mixan, and D. H. Johnson, *Tetrahedron Lett.*, 4335 (1972).

(18) The possibility that **4** and **5** might be interconverted through inversion at sulfur and might have nearly equal $k_1:k_2$ ratios for that reason was considered and rejected on the following grounds. (a) The absolute rate of exchange for **5** is faster than for **4**, *cf.* Tables III and IV[11] and Figure 4 (note the difference in time scale for the two species). (b) Nmr analysis of the *C*-methyl group in **4** and **5** (partially deuterated) recovered after being subjected to base-catalyzed H–D exchange showed that equilibration was extremely slow on the time scale of the methylene exchange and was presumably caused only by inversion at the *C*-methyl group associated with exchange at the α-methine. (c) A. Garbesi, N. Corsi, and A. Fava [*Helv. Chim. Acta*, **53**, 1499 (1970)] have shown that the resolved 3,3-dimethyl homolog of **3** racemizes at the rate of 0.81×10^{-4} sec^{-1} at 100°, corresponding to a half-life of 2.4 hr. If sulfur inversion in **4** and **5** proceeds at a comparable rate, their half-life at 39° may be estimated at 150 hr; *i.e.*, interconversion must be entirely unimportant during the early stages of the H–D exchange, unless inversion in the very small stationary state concentration of ylide is extraordinarily fast: D. Darwish and R. L. Tomilson, *J. Amer. Chem. Soc.*, **90**, 5938 (1968).

(19) If the ratio $k_B:k_A$ had been in the vicinity of 400, as appeared at the inception of this work, the assumption would have been entirely justified and a complete interpretation of the mass spectral data in terms of k_A and k_B would have been possible.

acidic than either pair of α-methylene hydrogens in the six-membered ring[7] and that the rate ratio for diastereotopic α-methylene hydrogens is considerably greater in the five- than in the six-membered ring seems, at least at first sight, to be contrary to the predictions of the gauche effect.[10] According to quantum-mechanical *ab initio* calculations,[10] a carbanion should be most stable when the orientation of its orbital is gauche to that of the orbital (or orbitals) or unshared electrons on adjacent atoms. In a five-membered ring, even assuming substantial puckering, the torsional angle between the pair and the α-methylene hydrogen anticlinal to it should be between 80 and 160° whereas the corresponding angle for the syn-clinal hydrogen is 0 ± 40°.[20] In the six-membered ring, if the *S*-methyl group is equatorial, the pair on sulfur is axial (assuming sp^3 geometry, which, while not strictly accurate for sulfur, seems to be accepted in the interpretation of the gauche effect); thus one of the diastereotopic pairs of hydrogens (the equatorial pair) is gauche to the pair on sulfur and the other pair of hydrogens (the axial pair) is anti to it (*cf.* **3**); hence there should be a large difference in exchange rates between the two sets of protons and the equatorial set should presumably be more reactive than the anti-clinal set in the five-membered ring. Such is not the case.

Conclusions as to the incompatibility of the present results with prediction[10] may, however, be premature. First of all, the gauche effects refers to the equilibrium basicity of carbanions, not to the kinetic acidity of their corresponding acids;[21] it is not a foregone conclusion that kinetic and thermodynamic acidities correspond. Secondly, the above argument is based on the assumption that the *S*-methyl group in the six-membered sulfonium salts is very largely equatorial, and while this is supported by the experiments involving exchange of **4** and **5** discussed earlier and by Lambert's observation,[17] it is not a proven fact. The experiments discussed exclude a mild axial preference of *S*-methyl and favor a substantial equatorial preference, but they would be equally compatible with a substantial axial preference, unlikely though such a preference would appear. Thirdly, it cannot be excluded that effects of ring size unrelated to the gauche effect account for the greater reactivity of one pair of α-methylene hydrogens in the five-membered ring compared to either pair in the six-membered ring; the observed difference in reactivity between the two diastereotopic pairs within the five-membered ring in itself is in accord with what the gauche effect would predict. Fourthly the unproven assumption of retention of configuration in the exchange may falsify the interpretation. The lack of selectivity in abstraction of the diastereotopic α-methylene hydrogens in **3** is compatible with the interpretation that there is in fact a large rate difference between axial and equatorial sets, but that the exchange in the more reactive set proceeds with inversion rather than retention of configuration. This would automatically bring the unreactive proton into the reactive position where it could then exchange at the higher of the two rates. However,[23] an exchange with inversion should have led to a rate of $k_1:k_2:k_3:k_4$ of 4:4:3:2 at the outset with k_3 dropping from 3 to 2 during the reaction. This is in less good agreement with the experimental ratio (4.4:3.0:1.83:0.84) than a nonselective exchange proceeding with retention.

Finally it has recently been shown[22,24] that the relative reactivity of protons α to a sulfoxide function is strongly solvent dependent and that a proton nearly gauche to the pair may be substantially less easily abstracted than one which is nearly anti. In explanation, the statement has been made that "carbanion stabilities do not coincide with those predicted by MO calculations, presumably because of strong solvation effects."[22] This explanation may apply in the present case as well.

Experimental Section

2-Methylthiane. Commercial 2-methyloxane (25 g, 0.25 mol) is added slowly to a mixture of 253 g (1.5 mol) of 48% hydrobromic acid and 74 g of concentrated sulfuric acid.[25] The mixture, which gets dark brown, is stirred and refluxed for 3 hr. After cooling, the heavy lower layer is separated and the upper layer twice extracted with 50 ml of methylene chloride. The extracts are combined with the lower layer and washed once with sodium bicarbonate solution and once with water. After drying over magnesium sulfate, filtration, and concentration, the residue is distilled to yield 35 g (58%) of product, bp 85–87° (8 mm). As shown below, the product is a mixture of 1,5-dibromohexane and 1,4-dibromohexane.

The dibromide (17.5 g, 0.072 mol) was dissolved in 30 ml of ethanol and 0.145 mol of sodium sulfide was added. The mixture was refluxed 4 hr and then exhaustively steam-distilled. The distillate was extracted three times with 30-ml portions of ether, dried over $MgSO_4$, filtered, concentrated, and distilled from metallic sodium, yield 4 g, bp 61–65° (20 mm) (lit.[26] bp 68–69° (45 mm)).

Gas chromatographic analysis showed the product to be a mixture of two components in about 1:1 proportion. Preparative separation was effected on a 6-ft Carbowax column at 150°; the compound of shorter retention time, obtained in 21% yield (1.8 g), proved to be the desired 2-methylthiane, as indicated by its nmr spectrum and mass spectrum which was identical with that published;[27] $n^{20}\mathrm{D}$ 1.4862 (lit.[26] 1.4906). The compound of longer retention time has the same parent mass but, instead of a large P − 15 mass peak, it had a large P − 29. The nmr spectrum showed a high-field triplet and the compound is very probably 2-ethyltetrahydrothiophene, suggesting that a partial rearrangement had occurred in the preparation of the dibromide.

The 2-methylthiane (1.8 g, 0.0155 mol) was dissolved in 20 ml of dry ether and 7.0 g (0.045 mol) of methyl iodide was added. After 60 hr standing at room temperature in the dark, the crystalline product (2.8 g, 70%) was collected. Its nmr spectrum indicated the presence of two isomers (**4** and **5**) in a 4:1 ratio. Chemical shifts and coupling constants for the *C*-methyl groups were 1.48 ppm (6.7 Hz) for one isomer and 1.38 ppm (7.0 Hz) for the other [shifts downfield from $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$]. The *S*-methyl shifts were 2.90 and 2.72 ppm, being 2.88 ppm for the parent methylpentamethylenesulfonium iodide (**3**). The isomers were separated by repeated crystallization from hot ethanol. Fortunately, the minor product is the less soluble. Both isomers were obtained in 95–97% purity, as indicated by nmr; both melted at 165–167° dec (sealed capillary) (lit.[24] mp 165–167°).

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(20) Fava, *et al.*, have adduced nmr evidence[9b] that **2** exists in a conformation of a half-chair with maximum puckering at C-3–C-4 and minimum puckering at C-2–S-1–C-5. Hence the torsion angles are near 120° for the anti-clinal hydrogen (the reactive one) and near 0° for the syn-clinal one.

(21) *Cf.* ref 4, footnote 10. It has been argued (ref 22) that kinetic and thermodynamic acidity should run parallel, but this argument presumes a Brønsted relationship to hold. We feel the Brønsted relationship may break down in case the conformation of the transition state for proton abstraction does not correspond to the conformation of the resulting carbanion.

(22) R. R. Fraser, F. J. Schuber, and Y. Y. Wigfield, *J. Amer. Chem. Soc.*, **94**, 8795 (1972).

(23) We thank Professor Fava for this observation.

(24) T. Durst, R. R. Fraser, M. R. McClory, R. B. Swingle, R. Viau, and Y. Y. Wigfield, *Can. J. Chem.*, 48, 2148 (1970).

(25) *Cf.* the preparation of pentamethylene dibromide from tetrahydropyran: D. Andrus, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 692.

(26) Yu. K. Yur'ev and O. M. Revenko, *J. Gen. Chem. USSR*, **31**, 1760 (1961).

(27) American Petroleum Institute Research Project 44, Mass Spectrum No. 566, April 30, 1951.

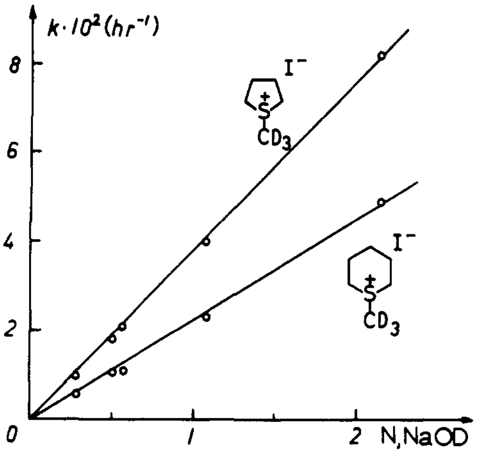

Figure 4. First-order rate constant (hr^{-1}) for exchange of **2**-d_3 and **3**-d_3 in NaOD–D_2O as a function of base concentration (at 39°).

Methylpentamethylenesulfonium iodide (**3**), mp (sealed capillary) 187–189° dec (lit.[26] mp 192° subl), and methyltetramethylene sulfonium iodide (**2**), mp (sealed capillary) 183–186° dec (lit.[28] mp 185–190° subl), were similarly prepared from commercially available thiane or tetrahydrothiophene and methyl iodide.

Deuterium Exchange. Sodium was cut and cleaned under nitrogen in a glove box and dissolved in 99.5% D_2O to give an approximately 2 *N* solution of NaOD. Titration showed the solution to be 2.15 *N*. To exchange the deuterium into the methyl group of the sulfonium salt, part of the above stock solution was diluted tenfold with D_2O. The appropriate sulfonium salt (1.45 mmol, *e.g.*, 0.354 g of **3**) was dissolved in 2 ml of 0.215 *N* NaOD in D_2O and heated in a sealed ampoule at 39° for 10 hr. At the end of this period, the nmr spectrum showed that the *S*-CH_3 signal had disappeared. The solution was quickly neutralized with 1 *N* HCl in H_2O (no back exchange was observed to occur in the time involved in this procedure) and the water solvent distilled at reduced pressure. The dry residue was submitted to mass spectral analysis (see below). For **3** the analysis showed 95% d_3 and 5% d_4 (henceforth called d_0 and d_1, referring only to deuterium in the ring). For **2**, the percentages were 92% d_3 and 8% of d_4. The amount of mono-ring-deuterated material formed in the preliminary exchange was allowed for by adding 1 hr to the recorded exchange time in the kinetic experiments, since exchange with 0.215 *N* NaOD–D_2O for 10 hr corresponds to exchange with 2.15 *N* NaOD–D_2O for 1 hr.

The preexchanged sulfonium salt, 0.145 mmol (35 mg of **3**, 33 mg of **2**, or 37 mg of **4** or **5**), was dissolved in 0.2 ml of 2.15 *N* NaOD in D_2O (0.43 mmol of NaOD, 10 mmol of D_2O) and the solution sealed in a 1-ml ampoule. The ampoules were suspended in a vaporstat at 39° (boiling methylene chloride) for periods ranging from 4 to 328 hr. At periodic intervals, they were withdrawn, cooled, and opened and the contents quickly neutralized with 1 *N* HCl, the residue being concentrated as indicated above.

At the end of the exchange for **4** and **5** (178 and 134 hr) the nmr spectra of the respective solutions were monitored in the *C*-methyl region. Samples undeuterated at C-2 (methine) showed no contamination with the doublet of the stereoisomer, *i.e.*, no epimerization at the sulfonium function occurs. (Deuteration at C-2, which collapses the methyls to broad singlets, of course entails equilibration of **4** and **5**.)

Deuterium Analysis. The dry residue obtained as described above was introduced directly into the ionization chamber of an MS-9 mass spectrometer through the vacuum lock, using the solid-sample probe available for that purpose. The chamber was at 189–200° and the sample was positioned so that a steady pressure was obtained.

Analysis of undeuterated samples showed that the P − 1 peak was suppressed at ionizing voltages of 9–10 V. Since the methylsulfonium salts apparently thermally decompose to give sulfide and methyl iodide, it was considered desirable to observe the (large) parent peak of the sulfide rather than the (small) parent peak of the sulfonium salt. Analysis was carried out by measuring the P, P + 1, P + 2, P + 3, etc. peaks and by making the usual correction for ^{13}C, ^{33}S, and ^{34}S isotopes by measuring the corresponding peaks in the undeuterated sample and assuming that the P:(P + 1):(P + 2):(P + 3) ratio due to the above isotopes is the same for the undeuterated and the deuterated species. It was also assumed that the sensitivity was the same for the undeuterated and all deuterated species, so that the ratio of corrected peak heights would, directly, yield the mole ratio of the corresponding species.

After each analysis, the probe was placed closer to the heater block so as to vaporize the sample completely and pump it out. After a few seconds, no appreciable background spectrum was left. The probe was removed and the next sample introduced after an interval of 10–20 min. Each sample was analyzed 5–10 times and the results were averaged. The deuterium analyses for **2** as a function of time are tabulated in Table I and plotted in Figure 3. The analyses for **3**, **4**, and **5** are tabulated in Tables II–IV[11] and summarized in Figures 2 and 3.

Check on Kinetic Order. For **2** and **3**, the bimolecular nature of the H–D exchange was checked by repeating the exchange in 1.075, 0.54, and 0.27 *N* NaOD at the same sulfonium salt concentration as above. The exchange data are tabulated in Table V[11] and plotted in Figure 4. The reaction is cleanly pseudounimolecular, first order in sulfonium salt and first order in base.

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Supplementary Material Available. Tables II–V will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-8045.

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[28] J. V. Braun and A. Trümpler, *Ber.*, **43**, 549 (1910).