(m), C=C 6.26 μ (m); pmr δ 0.84 (s, 3, Me), 1.0–1.9 (m, 8, methylenes), 3.4–3.7 (m, 1, oxymethine), 3.86 (q, 2, J = 9.5 Hz, oxymethylene), AB pair 7.32, 7.77 (d, 2 each, J = 8.0 Hz, aromatic H's).

Anal. Calcd for $C_{16}H_{22}O_4S$: C, 60.39; H, 7.43. Found: C, 60.56; H, 7.27.

2,2-Dimethyl-3-ketocyclohexyl *p*-Toluenesulfonate. A mixture of 2.0 g of 2,2-dimethyl-1,3-cyclohexanedione[36] and 0.54 g of lithium aluminum hydride in 45 ml of ether was stirred at room temperature for 4 hr. Moist sodium sulfate was added, the mixture was filtered, and the filtrate was evaporated.[37] A solution of 2.7 g of *p*-toluenesulfonyl chloride in 25 ml of methylene chloride was added over a 2-hr period to a solution of the residue (2.1 g of viscous oily 2,2-dimethyl-1,3-cyclohexanediol epimer mixture) in 25 ml of pyridine at 0° and the mixture was then stirred at room temperature for 20 hr. It was poured onto 25 ml of concentrated hydrochloric acid and crushed ice and extracted with methylene chloride. The extract was washed with saturated brine solution, dried, and evaporated, leaving 2.7 g of viscous oily 2,2-dimethyl-3-hydroxycyclohexyl tosylate.[37] A solution of 0.86 g of chromium trioxide in 6 ml of 1:1 water–acetic acid was added dropwise to a solution of 3.5 g of the hydroxy tosylate in 25 ml of acetic acid at room temperature. The mixture was stirred at 65° for 2 hr, poured into ice water, and extracted with methylene chloride. The extract was washed with 2 *N* ammonium hydroxide and with saturated sodium chloride solutions, dried, and evaporated. Crystallization of the colorless residual oil, 2.9 g, from pentane–ether yielded **38**: mp 78–80°; ir (Nujol) C=O 5.81 (s), C=C 6.22 μ (w); pmr δ 1.01 (s, 3, Me), 1.07 (s, 3, Me), 1.5–2.2 (m, 4, methylenes), 2.3–2.5 (m, 2, α-ketomethylene), 2.42 (s, 3, aromatic Me), 4.57 (q, 1, J = 4.0, 6.0 Hz, oxymethine), AB pair 7.30, 7.73 (q, 4, J = 8.0 Hz, aromatic H's).

Anal. Calcd for $C_{15}H_{20}O_4S$: C, 60.80; H, 6.80. Found: C, 60.81; H, 6.72.

6-Methyl-5-heptenoic Acid (39a). A solution of 200 mg of **38** and 54 mg of sodium hydroxide in 5 ml of water and 10 ml of dioxane was stirred at room temperature for 24 hr. Work-up as in the above solvolyses yielded 3 mg of unidentified neutral material and 90 mg of colorless, viscous, oily **39a**.[38] Esterification of the latter with diazomethane (*vide supra*) gave colorless, liquid ester **39b**: one gpc peak (FFAP column at 90°); ir (neat) C=O 5.74 μ (s); pmr δ 1.60 (broad s, 3, Me), 1.70 (broad s, 3, Me), 1.5–2.5 (m, 6, methylenes), 3.67 (s, 3, OMe), 5.10 (t of m, 1, J = 7.0 Hz, olefinic H). Hydrogenation of this ester as above yielded methyl isoenanthate identical in infrared and pmr spectra and gpc retention time with the sample from the hydrogenation of **24a** (*vide supra*).

Acknowledgment. The authors are indebted to Eli Lilly and Co. and the National Science Foundation for support of this investigation.

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(36) S. Eskola, A. Auvinen, A. Hirvimies, T. Rinne, and R. Waris, *Suom. Kemistilehti B*, 27, 88 (1954); S. Swaminathan, S. Ramachandran, and S. K. Sankarappa, *Tetrahedron*, 20, 1119 (1964).

(37) *Cf.* E. Wenkert and Y. Gaoni, *J. Org. Chem.*, 31, 3809 (1966).

(38) M. F. Ansell and S. S. Brown, *J. Chem. Soc.*, 1788 (1957).

Configurational Stabilities of Strained α-Sulfonyl Carbanions. Kinetics of Base-Catalyzed Racemization and Deuterium Exchange of Representative Thiete and Thietane Dioxides[1]

Leo A. Paquette,* John P. Freeman,[2] and Matthew J. Wyvratt[3]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received October 16, 1970*

Abstract: Rate constants and activation parameters for racemization and hydrogen–deuterium exchange have been measured for optically active (*R*)-(+)-2-methyl-3,8-diphenyl-2*H*-naphtho[2,3-*b*]thiete 1,1-dioxide (**10**), a representative thiete dioxide, and (*R*)-(−)-2-methylthietane 1,1-dioxide (**11**), a typical saturated four-membered cyclic sulfone. Because these two molecules represent the smallest sulfone systems yet examined, knowledge of the stereochemical fate of the derived α-sulfonyl carbanions was of considerable interest. In the case of **10**, k_e/k_α values were essentially unity in *tert*-butyl alcohol-d_1–benzene (70:30), denoting complete racemization. In methanol-d_1–benzene (70:30), the rate constants for racemization were consistently somewhat larger than those for exchange ($k_e/k_\alpha \approx 0.90$). The isotopic exchange and racemization rates for **11** in methanol-d_1 were too slow to measure. In *tert*-butyl alcohol-d_1 (neat or admixed with benzene), **11** was seen to react approximately 10^5 times more slowly than **10** in both processes. Also, the k_e/k_α ratios were notably smaller (0.60–0.67). These results are discussed in terms of configurational and conformational considerations and proton transfer phenomena, and a comparison with open-chain α-sulfonyl carbanions is made.

Unconstrained α-sulfonyl carbanions enjoy a unique position among reactive organic intermediates by virtue of their intrinsic ability to maintain configurational stability. The innate structure of such species and the causative factor(s) behind the relatively high activation energy for their racemization continue to be a subject of controversy. In the first alternative, these carbanions are denoted as having an effectively planar (sp²) geometry at carbon with electrostatic inhibition to rotation about the C_α–S bond. Because of their capability to support asymmetry, the model is required to be of structure 1 rather than 2 (plane of symmetry) with proton transfer to 1 (and its microscopic reverse) occurring almost totally from a single direction.[4] In an elegant experiment supporting this concept, Corey and Lowry[4b] have established that, in the case of the α-

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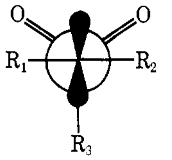
(1) Unsaturated Heterocyclic Systems. LXXXI. The previous paper in this series is L. A. Paquette, J. P. Freeman, and S. Maiorana, *Tetrahedron*, in press.

(2) American Chemical Society Petroleum Research Fund Graduate Fellow, 1968–1969; National Science Foundation Graduate Fellow, 1966–1968.

(3) National Science Foundation Undergraduate Research Participant, summers 1968 and 1969.

(4) (a) E. J. Corey, H. König, and T. H. Lowry, *Tetrahedron Lett.*, 515 (1962); (b) E. J. Corey and T. H. Lowry, *ibid.*, 793 (1965); (c) E. J. Corey and T. H. Lowry, *ibid.*, 803 (1965).

sulfonyl carbanion under study, proton transfer occurred almost totally from the direction syn to the oxygen atoms.



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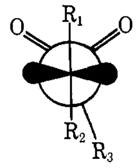

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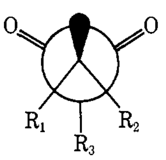

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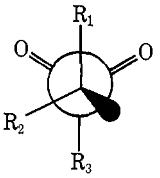

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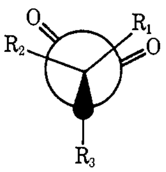
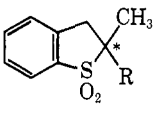


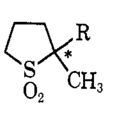
5

Alternatively, such carbanions are thought to be pyramidal (*i.e.*, **3–5**) with appreciable electrostatic inhibition to racemization by way of inversion.[5] In agreement with this view, recent LCAO–MO–SCF calculations have indicated that carbanion **3** with the lone pair directed along the bisector of the OSO angle is more stable than the two planar formulations and the remaining pyramidal structures **4** and **5**.[6]

By contrast, cyclic α-sulfonyl carbanions are subject to conformational factors which can be expected to alter significantly their preferred mode of generation, particularly if small-ring molecules are involved. To the present time, only four cyclic sulfone systems, all five-membered in size (**6–9**), have been examined;[4a,5b] however, distinct differences in behavior from open-chain analogs are already clearly apparent. The most obvious effect of incorporating both the anion and sulfone groups into a small ring system is to prevent extensive rotation about the C_α–S bond and to cause the carbanion to become optically inactive on attainment of planarity because of the enforced assumption of configuration **2**.

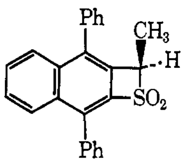


6, R = COOH
7, R = H

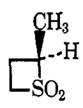


8, R = COOH
9, R = H

A more exhaustive study of the "anomalous" behavior of cyclic α-sulfonyl carbanions appeared to be in order, particularly since it could possibly shed light on the relative importance of the various type of interactions operative in nonconstrained systems. Accordingly, we have examined the isotopic exchange and racemization rates of the optically active naphtho-fused thiete dioxide **10** and its saturated counterpart **11**. Although both sulfones are four-membered heterocycles, it was recognized that the conformational demands on the two sulfones in their ground states are quite different. Whereas **10** is expected to be essentially planar, **11** likely enjoys a puckered conformation with the methyl group situated in a *quasi*-equatorial environment.[7] An additional characteristic which differentiates **10** from **11** is the benzylic nature of the asymmetric carbon in **10**.



10

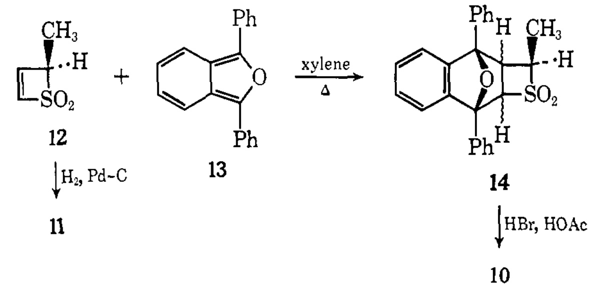


11

Results

Synthetic Considerations. Optically active 2-methyl-3,8-diphenyl-2*H*-naphtho[2,3-*b*]thiete 1,1-dioxide (**10**) was prepared by condensation of (*R*)-(−)-4-methylthiete 1,1-dioxide (**12**)[1,8,9] with diphenylisobenzofuran (**13**) according to the procedure of Paquette[10] (Scheme I). The resulting mixture of exo and endo (4 + 2)π adducts was dehydrated directly with 48% hydrobromic acid in refluxing acetic acid to give **10**, $[\alpha]^{22}\text{D}$ +104.7 ± 0.2° (c 3.338, $CHCl_3$). It follows that since **12** is in the *R* series, the absolute configuration of **10** is likewise *R*.

Scheme I



(*R*)-(+)-2-Methylthietane 1,1-dioxide (**11**) has previously been synthesized in optically pure form, $[\alpha]^{21.5}\text{D}$ +21.0 ± 0.2° (c 9.740, C_2H_5OH), by catalytic hydrogenation of **12** over palladium on charcoal in methanol.[1,8,9] Unsaturated sulfone **12** was not suitable *per se* for this study because of its propensity for rapid Michael addition and allylic rearrangement in the presence of alkoxide ions.

Base-Catalyzed Exchange and Racemization of Sulfones 10 and 11. Treatment of dilute solutions of optically pure (+)-**10** in methanol-d_1–tetrahydrofuran with sodium methoxide was found to result in essentially complete hydrogen–deuterium exchange after several hours at room temperature. The recovered sulfone (**10**-*d*) was optically inactive and exhibited a singlet methyl absorption in the nmr at δ 1.15. When the sweep width of the spectrum was decreased to 50 Hz, this peak was seen to be cleanly separated from the methyl doublet absorption of admixed **10**. Accordingly, careful integration of these peak areas *vs.* time provided a convenient method for measurement of the kinetics for isotopic exchange. Racemization rates were determined polarimetrically.

Table I summarizes the kinetic data for the base-catalyzed exchange and racemization of **10**. Because of

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[5] (a) D. J. Cram and A. S. Wingrove, *J. Amer. Chem. Soc.*, **85**, 1100 (1963); (b) D. J. Cram and T. A. Whitney, *ibid.*, **89**, 4651 (1967); (c) D. J. Cram, R. D. Trepka, and P. St. Janiak, *ibid.*, **88**, 2749 (1966); (d) F. A. L. Anet, R. D. Trepka, and D. J. Cram, *ibid.*, **89**, 357 (1967); (e) A. Ratajczak, F. A. L. Anet, and D. J. Cram, *ibid.*, **89**, 2072 (1967).

[6] S. Wolfe, A. Rauk, and I. G. Csizmadia, *ibid.*, **91**, 1567 (1969).

[7] R. M. Dodson, E. H. Jancis, and G. Klose, *J. Org. Chem.*, **35**, 2520 (1970).

[8] L. A. Paquette and J. P. Freeman, *J. Amer. Chem. Soc.*, **91**, 7548 (1969).

[9] L. A. Paquette and J. P. Freeman, *J. Org. Chem.*, **35**, 2249 (1970).

[10] L. A. Paquette, *ibid.*, 30, 629 (1965).

Table I. Exchange and Racemization Rates for (*R*)-(+)-2-Methyl-3,8-diphenyl-2*H*-naphtho[2,3-*b*]thiete 1,1-Dioxide (**10**)

Run no.	Substrate concn, M	Solvent	Base: Type	Base: Concn, M	Temp °C	Exchange rates[a]: $k_{e_1} \times 10^4$, sec^{-1}	Exchange rates[a]: k_{e_2}, M^{-1} sec^{-1}	Racemization rates[a]: $k_{\alpha_1} \times 10^4$, sec^{-1}	Racemization rates[a]: k_{α_2}, M^{-1} sec^{-1}	k_e/k_α
1	0.01073	$\mathrm{CH_3OD}^b$–$\mathrm{C_6H_6}$ (7:3)	$\mathrm{CH_3ONa}$	0.00314	50.0	2.01 ± 0.02	0.0639	2.19 ± 0.02	0.0696	0.92
2	0.01073	$\mathrm{CH_3OD}^b$–$\mathrm{C_6H_6}$ (7:3)	$\mathrm{CH_3ONa}$	0.00314	50.0	2.06 ± 0.02	0.0656	2.40 ± 0.02	0.0764	0.86
3	0.01074	$\mathrm{CH_3OD}^b$–$\mathrm{C_6H_6}$ (7:3)	$\mathrm{CH_3ONa}$	0.00314	35.0	0.357 ± 0.005	0.0114	0.406 ± 0.007	0.0129	0.88
4	0.01074	$\mathrm{CH_3OD}^b$–$\mathrm{C_6H_6}$ (7:3)	$\mathrm{CH_3ONa}$	0.00314	35.0	0.374 ± 0.004	0.0019	0.397 ± 0.010	0.0126	0.94
5	0.01073	$\mathrm{CH_3OD}^b$–$\mathrm{C_6H_6}$ (7:3)	$\mathrm{CH_3ONa}$	0.00543	35.0	0.629 ± 0.018	0.0116	0.646 ± 0.009	0.0119	0.97
6	0.0135	$\mathrm{(CH_3)_3COD}^c$–$\mathrm{C_6H_6}$ (7:3)	$\mathrm{(CH_3)_3COK}$	4.34×10^{-5}	0.0	5.00 ± 0.06	11.51	4.92 ± 0.09	11.33	1.02
7	0.0135	$\mathrm{(CH_3)_3COD}^c$–$\mathrm{C_6H_6}$ (7:3)	$\mathrm{(CH_3)_3COK}$	4.34×10^{-5}	0.0	4.62 ± 0.08	10.64	4.88 ± 0.06	11.25	0.95
8	0.0135	$\mathrm{(CH_3)_3COD}^c$–$\mathrm{C_6H_6}$ (7:3)	$\mathrm{(CH_3)_3COK}$	4.11×10^{-5}	10.0	8.55 ± 0.10	20.80	8.46 ± 0.08	20.59	1.01

[a] The rate constants and root mean square deviations are computer-generated (IBM-7040) values using the method of least squares. [b] 99+% of one atom of deuterium per molecule. [c] Prepared by the method of A. T. Young and R. D. Guthrie, *J. Org. Chem.*, **35**, 853 (1970).

Table II. Exchange and Racemization Rates for (*R*)-(+)-2-Methylthietane 1,1-Dioxide (**11**)

Run no.	Substrate concn, M	Solvent	Base: Type	Base: Concn, M	Temp, °C	Exchange rates[a]: $k_{e_1} \times 10^4$, sec^{-1}	Exchange rates[a]: $k_{e_2} \times 10^4$, M^{-1} sec^{-1}	Racemization rates[a]: $k_{\alpha_1} \times 10^4$, sec^{-1}	Racemization rates[a]: $k_{\alpha_2} \times 10^4$, M^{-1} sec^{-1}	k_e/k_α
9	0.0754	$\mathrm{(CH_3)_3COD}^b$	$\mathrm{(CH_3)_3COK}$	0.00797	45.0	0.50 ± 0.02	63.3	0.84 ± 0.05	104.8	0.60
10	0.1518	$\mathrm{(CH_3)_3COD}^b$	$\mathrm{(CH_3)_3COK}$	0.00797	45.0	0.49 ± 0.03	61.7	0.77 ± 0.01	97.0	0.64
11	0.1484	$\mathrm{(CH_3)_3COD}^b$	$\mathrm{(CH_3)_3COK}$	0.00797	30.0	0.10 ± 0.01	12.9	0.16 ± 0.01	20.1	0.64
12	0.1470	$\mathrm{(CH_3)_3COD}^b$	$\mathrm{(CH_3)_3COK}$	0.00797	30.0 0.0[c]	0.10 ± 0.01	13.2 0.335	0.16 ± 0.01	19.8 0.461	0.67
13	0.1463	$\mathrm{(CH_3)_3COD}$–$\mathrm{C_6H_6}$ (7:3)	$\mathrm{(CH_3)_3COK}$	0.00774	30.0	0.056	7.26	0.086	11.1	0.66

[a] The rate constants and root mean square deviations are computer-generated (IBM 7040) values. [b] Prepared by the method of A. T. Young and R. D. Guthrie, *J. Org. Chem.*, **35**, 853 (1970). [c] Extrapolated value.

the marginal solubility of this sulfone in hydroxylic solvents, it became necessary to employ a cosolvent. As a result, mixtures of 70% alcohol–30% benzene were utilized throughout. The rate profiles for both exchange and racemization are first order in both base and sulfone, and good linear plots were obtained through at least two half-lives. The rate constants were calculated by the method of least squares.

Inspection of Table I reveals that the rate constants for racemization (k_α) of **10** in methanol-d_1–benzene (7:3) are consistently larger than the rate constants for deuterium exchange, but only by a small margin ($k_e/k_\alpha \approx 0.90$). This is not the case in *tert*-butyl alcohol-d_1–benzene where the k_e/k_α values are essentially unity, an observation signifying that racemization occurs concurrently with exchange in this solvent system. Clearly, therefore, this derivative of thiete 1,1-dioxide is considerably more prone to racemization than **7** for which k_e/k_α values in methanol and *tert*-butyl alcohol have been determined to be 0.64 and 0.66, respectively.[5b]

The capability of the fused aromatic ring in **10** to promote rather extensive delocalization of the negative charge in the α-sulfonyl carbanion[11] is reflected in the slower rates exhibited by thietane dioxide **11**. In methanol-d_1 containing sodium methoxide (0.25 M), for example, the exchange and racemization rates of **11** at temperatures up to 100° (sealed tubes) were too slow to measure conveniently. On the other hand, potassium *tert*-butoxide in *tert*-butyl alcohol-d_1 was well accommodated by this sulfone. The exchange and racemization rates for **11** at 45.0 and 30.0° are given in Table II.[13] Also included are the extrapolated rate constants for 0° which reveal that **11** undergoes exchange 3.3×10^5 times more slowly than **10** at this temperature and racemizes less readily by a factor of 2.4×10^5. These values are certainly lower limits, since addition of 30% benzene to the *tert*-butyl alcohol-d_1 results in further reduction (approximately 50% at 30°) in both k_e and k_α for **11** (run 13, Table II). It is to be noted, however, that the k_e/k_α ratio for **11** is not affected by addition of this quantity of nonprotic diluent. Such a direct comparison reveals that the fused benzene ring causes an appreciable electron-stabilizing effect in the carbanion derived from **10**.

The activation parameters for exchange and racemization of **10** and **11** are grouped in Table III. Similar data for the three additional sulfones (**15–17**) are also included for comparison. It is particularly significant that these additional sulfones are acyclic and exhibit k_e/k_α values in aqueous ethanol at 72° of 58, 107, and 44, respectively.[14]

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(11) Although it is recognized that rates of proton abstraction are not necessarily accurate indicators of carbanion stabilization,[5c] the recent availability of pK_a values for a number of sulfones[12] provides unquestionable evidence that an attached phenyl ring accords enhanced stabilization to an α-sulfonyl carbanion.

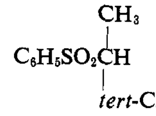
(12) F. G. Bordwell, R. H. Imes, and E. C. Steiner, *J. Amer. Chem. Soc.*, **89**, 3905 (1967).

(13) The two protons attached to the secondary (nonasymmetric) α-sulfonyl carbon in **11** undergo approximately 90% exchange before measurable deuterium incorporation is observed at C-2.

Table III. Activation Parameters for Exchange and Racemization of **10**, **11**, and Other Selected Sulfones

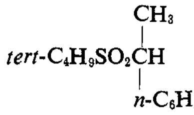
Compound	Solvent	Exchange		Racemization	
		$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/deg mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/deg mol
10	$CH_3OD:C_6H_6$ (7:3)	22.1	4.2	22.7	6.2
10	$(CH_3)_3COD:C_6H_6$ (7:3)	9.1	−20	8.7	−22
11	$(CH_3)_3COD$	19.5	−7.6	20.1	−4.7
15[a]	$C_2H_5OH:H_2O$ (2:1)	14	−26	25	−14
16[b]	$C_2H_5OH:H_2O$ (2:1)	15	−33	29	−1.7
17[b]	$C_2H_5OH:H_2O$ (2:1)	16	−5.4	23	+0.1

[a] E. J. Corey, H. König, and T. H. Lowry, *Tetrahedron Lett.*, 515 (1962). [b] T. H. Lowry, Ph.D. Thesis, Harvard University, 1965.



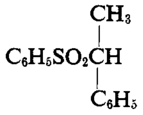
$C_6H_5SO_2CH(CH_3)(tert\text{-}C_4H_9)$

15



$tert\text{-}C_4H_9SO_2CH(CH_3)(n\text{-}C_6H_{13})$

16

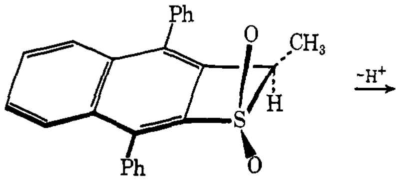


$C_6H_5SO_2CH(CH_3)(C_6H_5)$

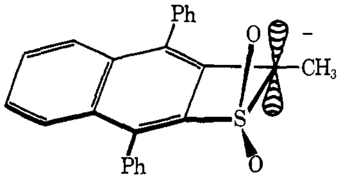
17

Discussion

The most important *intrinsic* properties of acyclic α-sulfonyl carbanions which may be the cause of their configurational stability are inductive electron withdrawal, conjugative interactions, electrostatic effects, and steric influences. *Extrinsically*, solvation factors could be important. Although a thorough understanding of the *relative* importance of these forces is still lacking, the recent calculations of Wolfe, Rauk, and Csizmadia[6] suggest that pyramidal conformer **3** is the most stable, with planar **1** being a close second. However, sulfone **10** is a molecule which must necessarily adopt planar conformation **18**. As a result, the proton to be abstracted occupies a position which eclipses one of the sulfonyl oxygen atoms. For electrostatic reasons, removal of this proton by a base very probably entails approach of the reagent from the rear side of the sulfone (as viewed in **18**). In *tert*-butyl alcohol-d_1-benzene (70:30), (*R*)-(+)-**10** gave k_e/k_α values of unity, thereby indicating racemization under the reaction conditions. In methanol-d_1-benzene (70:30), the rate constants for racemization exceeded slightly those for exchange ($k_e/k_\alpha \approx 0.9$). The anion derived from **10** (or **18**) would appear therefore to be planar, the observed racemization being the result of the structurally imposed symmetric conformation **19** for the carbanion.



18



19

Despite the fact that the enforced conformation of carbanion **19** (*i.e.*, **2**) is known to be energetically unfavorable on theoretical[6] and experimental grounds,[4,5] the rates of racemization and deuterium exchange of **10** are seen to be rapid relative to **11**. Similar rate differences (in the order of 10^4) have been noted previously for the acyclic sulfone pair $PhCH(CH_3)SO_2Ph$ and $HexCH(CH_3)SO_2Ph$.[4c] Of special relevance in these examples is the observation that replacement of hexyl by phenyl at the carbanion site does not facilitate racemization of the reactive intermediate (k_e/k_α = 44 and 41, respectively). To accommodate these facts, the carbanion has been represented as planar with a barrier to rotation,[4c,15] at least in the phenyl case.[16] In anion **19** where no rotation of the C_α–S bond is possible, the unfavorable electrostatics appear to be of much less consequence than the charge delocalization resulting from its benzylic nature. Since the α-methyl group in **18** shifts from an eclipsed to a staggered conformation in passing to **19**, it is quite possible that relief of steric strain contributes to some degree to the rate acceleration.

As previously mentioned, monocyclic sulfone **11** enjoys greater conformational mobility than **10**. Nevertheless, of the two most favorable ground state conformers (**20a** and **20b**), **20a** is likely to be preferred for steric reasons.[7] However, if the proton abstraction process is controlled chiefly by electrostatic factors, removal of C_α–H from **20b** could be kinetically preferred because it bisects more favorably the OSO angle.[4] The k_e/k_α values for **11** (0.60–0.67) are in agreement with two mechanistic possibilities reflecting either exchange with net inversion or an appropriate blend of isoinversion (inversion without exchange), inversion, and racemization processes. In the first case, the acidic tertiary proton must be detached from the α-carbon and transported without exchange to the opposite face of the carbanion where it is rebonded to carbon. The process need not be as elaborate as Cram's "conducted tour" scheme.[5] For example, if proton loss does occur from conformer **20b**, approach of the potassium *tert*-butoxide ion pair will be along the equatorial plane. If the rapid anion equilibrium **21b** $\leftrightarrows$ **23b** is operative, then

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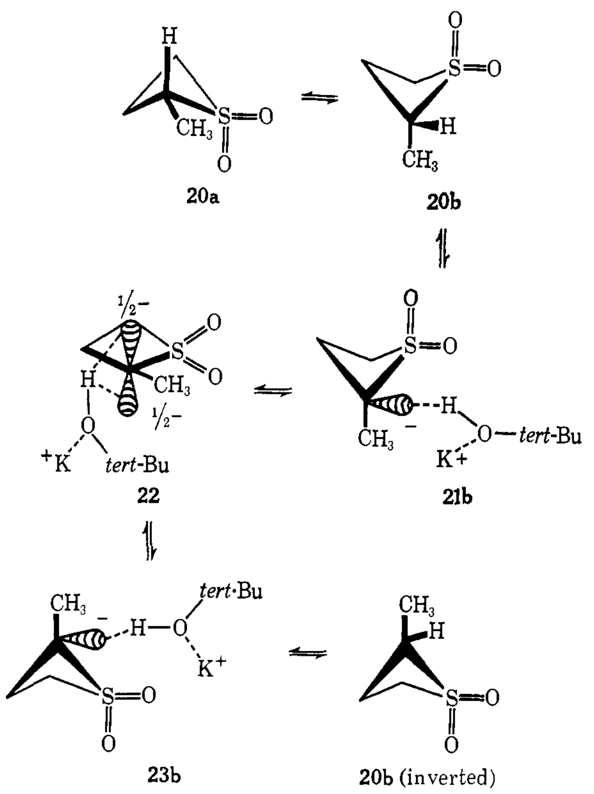
(14) T. H. Lowry, Ph.D. Thesis, Harvard University, 1965.

(15) F. G. Bordwell, D. D. Phillips, and J. M. Williams, Jr., *J. Amer. Chem. Soc.*, **90**, 426 (1968).

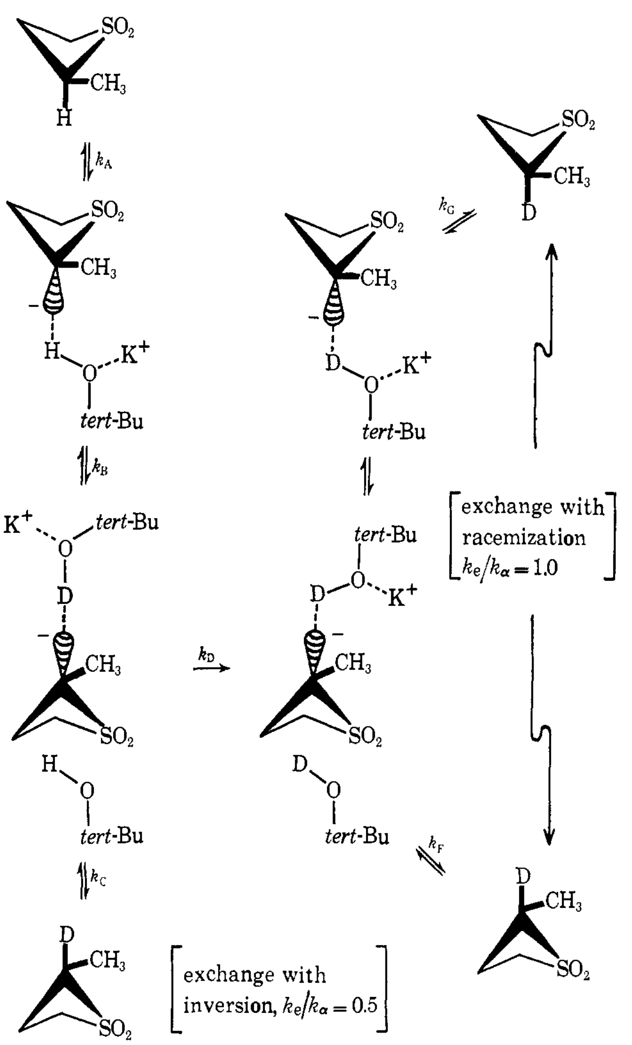
(16) Subsequently, Cram[5c] has expressed the opinion that since a moderate amount of delocalization can be achieved if the electron pair of the carbanion is in an sp^3 orbital, the results can be explained by either a planar or pyramidal carbanion, if a proper balance of inductive and conjugative effects is invoked.



the solvated proton can undergo rebonding to the opposite surface of the carbon atom with minimal movement through the solution. As shown, passage of **21b** to **23b** *via* the symmetric intermediate **22** involves a temporary oblique displacement to allow the methyl group to pass through the equatorial plane. In pure isoracemization, k_e equals zero by definition and the ratio k_e/k_α likewise equals zero. The observed k_e/k_α of 0.60–0.67 can be explained by formation of most of the racemized product by exchange with deuterium, with a lesser amount arising from pure isoracemization.

The second possibility, illustrated in the ensuing scheme, involves inversion of the carbanion, still hydrogen bonded to the *tert*-butyl alcohol molecule, *via* rapid equilibrium B to produce a new carbanion species now hydrogen bonded to *tert*-BuOD (note that the original *tert*-BuOH remains trapped in the solvent cage on the opposite side of the ring). In two rapid reactions, this species is partitioned to give either exchange with inversion (reaction C) or exchange with racemization *via* reaction D and equilibrium E. Although sp^3 carbanion orbitals have been used for the simple thietane dioxide, it should be noted that solvated sp^2 carbanions can also be employed with no change in the analysis.

In the case of **10** (or **18**), the derived carbanion enjoys a notably higher order of stability and less tight ion pairs are required in the solvation process. Also, the C_α proton must be transported completely to the opposite surface of the asymmetric carbon atom because of the absence of conformational flexibility in this thiete dioxide. Because these factors, as well as those considered earlier, exert additive destabilizing configurational effects, **19** is prone to ready racemization and exchange. Interestingly, however, in methanol-d_1–benzene (70:30) **19** appears to maintain some capability for isoinversion, albeit at a low level ($k_e/k_\alpha \approx 0.90$). This would suggest that in this solvent system sufficiently tight hydrogen bonds remain available to offset the exclusive operation of stereochemically indiscriminant processes.



Experimental Section[17]

Optically Active 2a,3,8,8a-Tetrahydro-2-methyl-3,8-diphenyl-3,8-epoxy-2*H*-naphtho[2,3-*b*]thiete 1,1-Dioxide (14). A solution of 6.5 g (0.024 mol) of 1,4-diphenyl-2,3-benzofuran (**13**)[18] and 2.83 g (0.024 mol) of (*R*)-(−)-4-methylthiete 1,1-dioxide (**12**)[8,9] in 8 ml of xylene was heated at reflux under nitrogen for 24 hr. When the solution had cooled, petroleum ether was added and the precipitated solid was filtered and dried to give 8.82 g (94.6%) of a light-brown solid with a wide, ill-defined decomposition range (160–247°), $\nu_{max}^{CHCl_3}$ 2985, 1320, 1125, and 1190 cm^{-1}. This mixture was not purified further.

In preliminary studies with racemic materials, the crude product was repeatedly recrystallized from benzene to separate the two stereoisomers. Isomer A exhibited a melting point range of 190–196°, while isomer B had a melting point of 240–241°.

Anal. Calcd for $C_{24}H_{20}O_3S$: C, 74.20; H, 5.19; S, 8.25. Found: C, 74.13; H, 5.38; S, 8.13.

(*R*)-(+)-2-Methyl-3,8-diphenyl-2*H*-naphtho[2,3-*b*]thiete 1,1-Dioxide (10). A mixture of 4.65 g (0.012 mol) of **14**, 30 ml of glacial acetic acid, and 3 ml of 48% hydrobromic acid was refluxed for 1 hr, and allowed to cool to room temperature. Water was slowly added to the reaction mixture from which a precipitate had already been deposited. The solid product was filtered, washed with

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[17] All melting points were determined with a Thomas-Hoover melting point apparatus and are corrected. Nuclear magnetic resonance spectra were recorded with Varian Associates A-60 and A-60A spectrometers. Rotations were taken with Perkin-Elmer Model 141 and Rudolph manual polarimeters. Mass spectra were measured with an AEI MS-9 mass spectrometer at an ionizing energy of 70 eV.

[18] M. S. Newman, *J. Org. Chem.*, 26, 2630 (1961).

water, and dried to give 4.38 g (98.7%) of grayish powder. The purification sequence involved one recrystallization from benzene–hexane, sublimation at 185° (0.01 mm), and two additional recrystallizations from benzene–hexane. The resulting white crystals melted at 192–193°: $[\alpha]^{22}\mathrm{D}$ +104.7 ± 0.2° (*c* 3.338, $CHCl_3$); $\nu_{\max}^{\mathrm{CHCl_3}}$ 2950, 1595, 1447, 1370, 1315, 1188, 1175, 1130, and 1120 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{C_6D_6}}$ 6.93–8.25 (m, 14, aryl), 5.08 (q, J = 7.1 Hz, 1, $>CHSO_2-$) and 1.16 (d, J = 7.1 Hz, 3, methyl); mass spectrum, *m/e* (relative intensity) 370 (68), 306 (71), 305 (71), 291 (100), and 289 (53).

Racemic **10**, prepared in analogous fashion, was obtained as colorless crystals, mp 213–215°, from benzene–hexane.

Anal. Calcd for $C_{24}H_{18}O_2S$: C, 77.81; H, 4.90; S, 8.66. Found: C, 78.04; H, 4.93; S, 8.71.

(±)-2-Methyl-3,8-diphenyl-2*D*-naphtho[2,3-*b*]thiete 1,1-Dioxide (10-*d*). The optically active protium isomer **10** was racemized and exchanged by stirring 75 mg of the sulfone for 6 hr at room temperature in 15.5 ml of 81:19 methanol-d_1–tetrahydrofuran containing 0.0217 mol of sodium methoxide. The base was neutralized with acetic acid-d_1 and the solvents were removed *in vacuo*. The resulting solid was washed with water and dissolved in methylene chloride. The organic solution was dried over calcium sulfate, methylene chloride was evaporated, the solid residue was sublimed at 160–180° (0.05 mm), and the sublimate was recrystallized from benzene–hexane to give 55 mg (73%) of white crystals: mp 208–213°; $\delta_{\mathrm{TMS}}^{\mathrm{C_6D_6}}$ 6.93–8.25 (m, 14, aryl) and 1.15 (s, 3, methyl); mass spectrum, *m/e* (relative intensity) 371 (61), 307 (74), 306 (81), 292 (100), 290 (52), and 230 (52).

Reagents. The methanol-d_1 was obtained from Diaprep, Inc., and shown to be essentially isotopically pure by nmr analysis. Water was shown not to be present above 0.5% by vpc analysis on a 12 ft × 0.25 in. column packed with 5% Carbowax 500 on Teflon, a technique sensitive to at least this level. *tert*-Butyl alcohol-d_1 prepared by the method of Yound and Guthrie (*cf.* Tables I and II), was stored over Molecular Sieves (Linde 4A, $^1/_8$ in. diameter, heated to 470° for 24 hr under a dry nitrogen train). Analyses similar to the above did not reveal detectable isotopic or water impurities. Benzene was dried by passing it through a column of molecular sieves and storing over sodium. Nitrogen was deoxygenated by first bubbling it through a solution of 0.1 *M* sodium metavanadate in 4 *N* sulfuric acid in the presence of amalgamated mossy zinc, followed by a concentrated sulfuric acid scrubber and a potassium hydroxide tower. Stock solutions of metal alkoxides were prepared by dissolving clean sodium or potassium in the appropriate alcohol or alcohol–benzene solvent under a pure nitrogen atmosphere.

Racemization and Exchange of (*R*)-(+)-2-Methyl-3,8-diphenyl-2*H*-naphtho[2,3-*b*]thiete 1,1-Dioxide (10) in 70:30 Methanol-d_1–Benzene (Runs 1–5). The substrate, 400 mg, was dissolved in 30 ml of benzene in a 100-ml volumetric flask under a blanket of pure nitrogen. The flask was filled to the mark with methanol-d_1 using syringe technique, the contents were mixed, and the solution was equilibrated in a constant-temperature bath for 15 min at the desired temperature. Using a 1-ml vpc syringe, 600 μl of 0.5265 ± 0.0015 *M* sodium methoxide was injected into the solution, the contents were shaken, and the flask was quickly returned to the bath. Seven aliquots (*ca.* 14 ml) were withdrawn at appropriate intervals up to two half-lives and quenched in 150-μl portions of acetic acid. Solvents were removed *in vacuo*, water was added to the residue, and the mixture was extracted three times with methylene chloride. The combined extracts were dried, the solvent evaporated, and the residue sublimed at 170° (0.2 mm). Per cent deuterium was measured by careful planimetric integration of the δ 1.4 singlet nmr absorption of the d_1 product and the doublet of the protium species in methylene chloride at 50-Hz sweep width. Per cent optical activity was determined on the recovered nmr samples in chloroform with a Perkin-Elmer 141 polarimeter at 436 nm, at which wavelength the large absolute rotation of pure substrate, $[\alpha]^{36}{}_{436}$ 163° ($CHCl_3$), allowed satisfactory rotations on as little as 17 mg of sample. The absolute rotation of the substrate was found to be constant over the range of concentrations employed, 0.17–0.45 g/100 ml.

Racemization and Exchange of 10 in 70:30 *tert*-Butyl Alcohol-d_1–Benzene (Runs 6–8). The substrate, approximately 50 mg, was weighed separately into each of seven 10-ml volumetric flasks. The samples were dissolved in 3 ml of dry benzene under a blanket of pure nitrogen and the flasks filled to the mark with *tert*-butyl alcohol-d_1 using syringe technique. The solutions were mixed and the flasks equilibrated at the desired temperature, either in an ice–water bath (0°) or in a refrigerated constant-temperature bath (10.0°). Using a 10-μl vpc syringe, 2 μl of 0.217 *M* potassium *tert*-butoxide was injected into each solution (in run 8, 10 μl of 0.0411 *M* KO-*tert*-Bu was used), the contents were shaken, and flasks were returned quickly to the bath. After appropriate reaction times up to 2 half-lives each sample was quenched with 50 μl of acetic acid. Work-up and analyses for per cent deuterium and per cent optical activity were carried out as described above.

Racemization and Exchange of (*R*)-(+)-2-Methylthietane 1,1-Dioxide (11) in *tert*-Butyl Alcohol-d_1 (Runs 9–12) and in 70:30 *tert*-Butyl Alcohol-d_1–Benzene (Run 13). The substrate, 230–460 mg, was dissolved to the mark in a 25-ml volumetric flask under a blanket of pure nitrogen in either *tert*-butyl alcohol-d_1 or 70:30 *tert*-butyl alcohol-d_1–benzene. After equilibration to the desired temperature, 335 μl of 0.603 *M* potassium *tert*-butoxide was injected into the solution, the contents were mixed by shaking, and the flask was returned quickly to the bath. Five 5-ml aliquots were withdrawn at appropriate intervals up to 2 half-lives (runs 9 and 10) or 1.5 half-lives (runs 11–13) and quenched in *ca.* 0.5 ml of 5% hydrochloric acid. Solvents were removed under vacuum, 5–10 ml of water was added to each residue, and the mixture was extracted with four small portions of methylene chloride. The combined extracts were dried, the solvent was evaporated, and the liquid residue was pumped down to 0.03 mm for 2–3 min to remove the last traces of methylene chloride. Per cent deuterium was measured as before by nmr analysis in deuteriochloroform by careful integration of the δ 1.5 methyl absorption. In this compound deuterium at C-2 splits the methyl group into a closely spaced (J = 0.9 ppm), equal-intensity triplet, but integration of this triplet absorption was no more difficult to separate from the doublet (J = 7.0 ppm) of the protium species than in the case of the naphtho-fused analog. Per cent optical activity was determined on recovered nmr samples which were molecularly distilled at 45–50° (0.02 mm) prior to weighing. Polarimetry at 365 nm gave a maximum rotation which for pure substrate was $[\alpha]^{30}{}_{365}$ 75.3° ($CHCl_3$), constant over the range of concentrations employed, 0.16–1.16 g/100 ml.

Acknowledgment. The authors wish to express appreciation to the National Science Foundation for their support of this research.