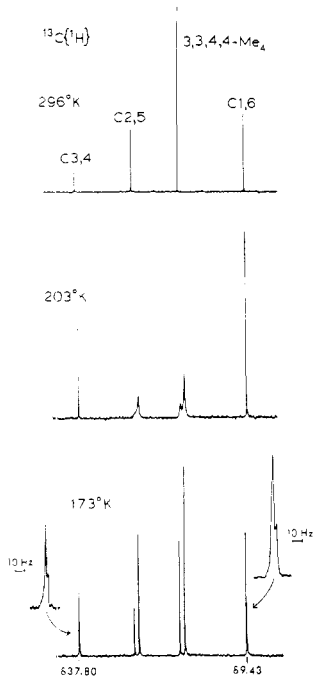

Figure 6. Experimental $^{13}C\{^1H\}$ DNMR spectra (50.2 MHz) of 3,3,4,4-tetramethylhexane (10% v/v in 50/50 CD_2Cl_2/CS_2).

barriers in similar chlorine-substituted systems led to a predicted barrier height of 9.6 kcal/mol.[25] However, we feel that an extrapolation from the experimental barrier heights for TMP and TMH, as supported by our EFF study of these compounds and of HME, provides a more reliable estimate of the barrier to central-bond rotation in HME. By examining the experimental barriers to rotation in TMP and TMH and trends in the calculated barriers for TMH, TMP, and HME (Table II), we conclude that the actual barrier to central-bond rotation in HME lies between 8.4 and 8.8 kcal/mol.

(25) Anderson, J. E.; Pearson, H. *J. Am. Chem. Soc.* **1975**, *97*, 764. An attempt to measure the barrier height thermodynamically can be found in: Scott, D. W.; Douslin, D. R.; Gross, M. E.; Oliver, G. D.; Huffman, H. M. *J. Am. Chem. Soc.* **1952**, *74*, 883.

Experimental Section

The 60-MHz ^1H DNMR spectra were recorded by using a Varian HR-60A continuous-wave NMR spectrometer equipped with a custom-built variable temperature probe.[26] Temperature measurements in this probe are accurate to ± 0.2 K. The 270-MHz ^1H DNMR spectra were recorded in the pulsed Fourier transform mode on a Bruker 270-MHz NMR system at the Southern New England High Field NMR Facility at Yale University. Temperature measurements are accurate to ±2.0 K. The 22.64- and 50.2-MHz $^{13}C\{^1H\}$ DNMR spectra were recorded, respectively, on a Bruker WH-90D NMR system and a Varian XL-200 NMR spectrometer. Temperature measurements for the latter two systems are accurate to ±5.0 K.

2,2,3,3-Tetramethylpentane and 3,3,4,4-tetramethylhexane were purchased from Chemical Samples Co. and were used without further purification. All NMR samples were degassed three times and the NMR tubes sealed.

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Registry No. 2,2,3,3-Tetramethylpentane, 7154-79-2; 3,3,4,4-tetramethylhexane, 5171-84-6; hexamethylethane, 594-82-1.

(26) Jensen, F. R.; Smith, L. A.; Bushweller, C. H.; Beck, B. H. *Rev. Sci. Instrum.* **1972**, *43*, 894.

(27) A more appropriate comparison might be made between the EFF barriers and ΔH^* obtained from the ^1H DNMR line-shape simulations. However, the overall magnitude of systematic errors in any determination of ΔH^* and ΔS^* values using the DNMR method is difficult to assess, and the most accurately determined activation parameter is consistently ΔG^*; cf.: Shoup, R. R.; Becker, E. D.; McNeel, M. L. *J. Phys. Chem.* **1972**, *76*, 71. With regard to the ΔH^* and ΔS^* values reported in the text, the rich complexity of the ^1H NMR spectra of both TMP and TMH should lead to accurate rate constants from simulation of the exchange-broadened spectra. This situation and our efforts to measure the sample temperature as accurately as possible give us reasonable confidence in these ΔH^* and ΔS^* values, but we choose to take a conservative approach in the values used for comparison in Table II.

Acidities of Sulfoximines and Related Oxosulfonium Cations. Cyclopropyl Effects and Structures of α-Sulfonyl-Type Carbanions

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(Dimethylamino)methylphenyloxosulfonium cation, $PhS(O)(NMe_2)CH_3^+$, was found to be more acidic than the parent sulfoximine, $PhS(O)(NMe)CH_3$, by about 19 pK_a units. The latter is about equal in acidity to $PhS(O)CH_3$ and about 5 pK_a units less acidic than $PhSO_2CH_3$. The cyclopropyl compounds, c-PrG, with G equal to $Ph(NMe_2)SO^+$, $p\text{-}MeC_6H_4(NMe_2)SO^+$, F_3CSO_2, and $Ph(PhSO_2N)SO$, were found to be about 4–7 pK_a units less acidic than their acyclic methyl analogues, CH_3G. This is interpreted as evidence for a demand on the part of sulfone-type functions for p character in cyclopropyl carbanions. Evidence is presented to show that carbanions of the type GCH_2^-, where G is an electron-withdrawing function such as RSO_2, RS(O)(NR), RSO, Ph_2PO, $(RO)_2PO$, and the like, are planar or nearly planar. Acidity data indicate that the preferential generation of chiral, rather than achiral, planar α-sulfonyl carbanions is a consequence of a preferred kinetic pathway rather than an inherent greater thermodynamic stability. Factors controlling the stereoselective generation and reactions of carbanions are reviewed.

The sulfonyl function, SO_2G, where G is R, Ar, NRAr, or OR, has proved to be superior to other strongly electron-withdrawing functions [COPh, CN, $P(O)Ph_2$, $P(O)(OR)_2$, S(O)R, and the like] in promoting the generation

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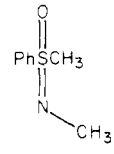
of chiral α-carbanions.[3] For this reason the structures and reactions of α-sulfonyl carbanions have received intensive theoretical and experimental attention. The establishment of an acidity scale for weak acids in dimethyl sulfoxide, Me_2SO, solution wherein carbanions can be examined free of counterion effects[4] has provided a new framework within which the relative stabilities of α-sulfonyl and related carbanions can be examined. In an earlier paper we presented acidity data showing that methyl trifluoromethyl sulfone, $CH_3SO_2CF_3$, has an acidity greater than methyl phenyl ketone and almost as great as that of nitromethane, indicating that the carbanions derived from these acids have stabilities in the order $O_2NCH_2^- > F_3CSO_2CH_2^- \gg PhCOCH_2^-$.[5] The corresponding acids in which these functions were attached to a cyclopropane ring were all less acidic by more than 4 pK_a units. The results were interpreted to mean that the F_3CSO_2 function, like the NO_2 and PhCO functions, demands p character from the cyclopropyl anion, thereby increasing the strain in the cyclopropane ring. In other words, α-sulfonyl carbanions, like nitronate ions and enolate ions, have planar structures. This result has now been corroborated by acidity measurements with several sulfoximine and oxosulfonium cation functions. These are sulfone-like functions wherein one of the oxygen atoms of O=S=O has been replaced by =NR or $=N^+R_2$.

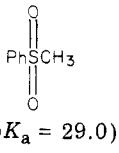
In the present paper we will (a) present data on the acidfying effects of sulfoximine, sulfone, and oxosulfonium cation functions, (b) review the evidence supporting a planar, or nearly planar, structure for α-sulfonyl and like carbanions, and (c) discuss the stereoselective generation and reactions of α-sulfonyl carbanions.

Results and Discussion

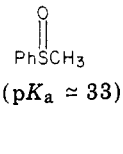
Acidities of Sulfoximines and Oxosulfonium Cations. Methyl phenyl *N*-methylsulfoximine (1) is too weakly acidic to measure the pK_a in Me_2SO solution. We estimate a pK_a of about 33, which makes it less acidic than methyl phenyl sulfone (2) by about 4 pK units. This



1 (p$K_a \simeq 33$)



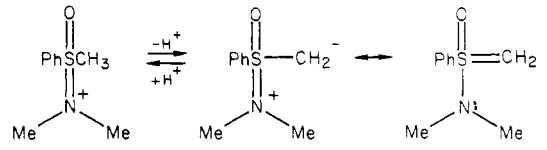
2 (pK_a = 29.0)



3 (p$K_a \simeq 33$)

substantial decrease in the acidifying effect of a sulfoximine vs. a sulfone function is not unexpected in view of the greater electronegativity of oxygen than nitrogen, the appreciable dipolar character of sulfur–oxygen bonds, and the (likely) acid-weakening effect of the *N*-methyl group. It is somewhat surprising to find, however, in comparing the acidity of 1 with the acidity of methyl phenyl sulfoxide (3), that combination of the $=NCH_3$ moiety with the sulfur atom of the sulfoxide function, i.e., O=S → O=S=NMe, produces little or no effect on the acidity of the α hydrogen atom.

The (dimethylamino)methylphenyloxosulfonium cation (4), produced by attachment of a second methyl group to the nitrogen atom in 1, is more acidic than 1 by about 19 pK_a units. The effect on acidity of introducing a positive charge onto the nitrogen atom in 1 is much greater than that for a similar structural change in G of GCH_2COPh, GCH_2SO_2Ph, or GCH_2CN substrates for which the effects of Me_3N^+ vs. Me (or Me_2N) substitution range from 10 to 12 pK units.[6] (The effect for Me_3N^+ vs. Me_2N will be smaller than for Me_3N^+ vs. Me if, as seems likely, the acid-strengthening inductive effect of Me_2N outweighs its acid-weakening lone-pair-repulsion effect.[7]) An appreciable amount of the positive charge in 4 is expected to be present on nitrogen, as shown. If so, a larger acidifying effect is produced in 4 by a positive charge separated from the acidic site by an additional atom than when the charge is on an adjacent atom (compare 4 with $Me_3N^+CH_2SO_2Ph$). Evidently the anion generated from 4 is stabilized not only by an inductive effect but also by resonance delocalization involving the sulfur function (e.g., **5b**).



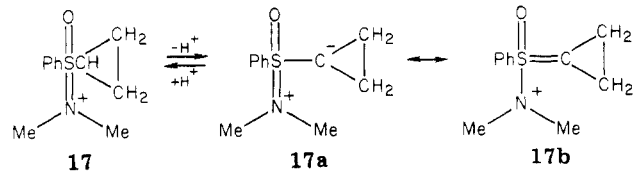
4 5a 5b

Substitution of *p*-$TolSO_2$ for the methyl on N in 1 to give compound 11 (Table I) causes an increase in acidity of 8.5 pK units. This is a large effect but is small compared to the almost 20-pK-unit increase in acidity resulting from substitution of $PhSO_2$ for Me in $MeCH_2SO_2Ph$.[6] The smaller effect is understandable since the latter substitution has been made directly at the acidic site, whereas that in 1 has been made at a site two atoms removed.

Replacement of Ph in 4 by Me causes an acidity decrease of 2 pK_a units (Table I). This is comparable to the effect observed for $PhSO_2CH_3$ vs. $MeSO_2CH_3$[4] and is believed to be due to the polar (inductive) effect of Ph vs. Me. (The replacement of Me_2N by Et_2N in these cations should have only a slight effect.)

Methyl substitution for hydrogen at the acidic site in oxosulfonium cations (compare 4 with 7), trifluoromethyl sulfones (compare 8 with 9 and 10), or *N*-$ArSO_2$ sulfoximines (compare 11 with 12 and 13) causes an acidity decrease of about 1.5 pK_a units per Me, taking into account statistical corrections (Table I). These effects are comparable to the effect of α-Me substitution observed in other sulfones or in nitriles.[8] It has been suggested that these effects are primarily of polar origin.[8]

Cyclopropyl Effects. The $Ph(Me_2N)SO^+$ function exerts a strong demand for increased p character on the cyclopropyl anion, judging from the 6 pK_a unit lower acidity of c-PrS(O)$(NMe_2)Ph^+$ (17) than $CH_3S(O)(NMe_2)Ph^+$ (4) (Table II). In valence bond terminology this can be explained by the strain introduced when the carbanion from 17 is rehybridized in order to conjugate



17 17a 17b

effectively with the oxosulfonium cation function. Because of this strain the contribution of **17b** to the resonance hybrid is much less than that of **5b**. A relatively high

(1) Northwestern University.
(2) Wayne State University.
(3) Cram, D. J. "Fundamentals of Carbanion Chemistry"; Academic Press: New York, 1965; pp 48–52.
(4) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006–7014.
(5) Bordwell, F. G.; Vanier, N. R.; Matthews, W. S.; Hendrickson, J. B.; Skipper, P. L. *J. Am. Chem. Soc.* **1975**, *97*, 7160–7162.
(6) Bordwell, F. G.; Van Der Puy, M.; Vanier, N. R. *J. Org. Chem.* **1976**, *41*, 1883–1885.
(7) Bordwell, F. G.; Vanier, N. R., unpublished results.
(8) Bordwell, F. G.; Bartmess, J. E.; Hautala, J. A. *J. Org. Chem.* **1978**, *43*, 3095–3101.

Table I. Equilibrium Acidities of Some Sulfoxonium Cations, *N*-(Phenylsulfonyl)sulfoximines, and Phenyl Alkyl Ketones in Dimethyl Sulfoxide Solution at 25 °C

compd[a]	no.	indicator	pK_{IND}	pK_{obsd}	selected[l] pK_a
$PhS(=O)(=NSO_2Tol\text{-}p)CH_3$	4	9-(PhS)FH[b]	15.4	14.40	
		FMY33[c]	13.8	14.36	14.4
Me_2N^+					
$CH_3S(=O)(=NSO_2Tol\text{-}p)CH_3$	6	9-(*i*-PrS)FH[d]	16.9	16.32	
		9-(PhS)FH[b]	15.4	16.8	16.4
Et_2N^+					
$(CH_3)_2CHS(=O)(=NSO_2Tol\text{-}p)CH(CH_3)_2$	7	CNAH[e]	18.9	18.55	
		9-PhFH[f]	17.9	18.2 ± 0.2	18.3 ± 0.3
Me_2N^+					
$CH_3SO_2CF_3$	8				18.8[m]
$MeCH_2SO_2CF_3$	9				20.4[m]
$Me_2CHSO_2CF_3$	10				21.8[m]
$PhS(=O)(=NSO_2Tol\text{-}p)CH_3$	11	TPPH[g]	25.6	24.49	
		9-MeFH[h]	22.34	24.46	
		9-*t*-BuFH[i]	24.35	24.51	24.5
$PhS(=NSO_2Tol\text{-}p)CH_2CH_3$	12	TPPH[g]	25.6	26.50	
		m-ClPXH[j]	26.6	26.46	26.5
$PhS(=NSO_2Ph)CH_2CH_3$	13	*m*-ClPXH[j]	26.6	28.55	
		PXH[k]	27.9	28.48	28.5
$PhS(=NSO_2Tol\text{-}p)CH(CH_3)_2$					
$PhCOCH_3$	14				24.7[n]
$PhCOCH_2Me$	15				24.4[n]
$PhCOCHMe_2$	16				26.25[n]

[a] The acidic hydrogen atom is in boldface. [b] 9-(Phenylthio)fluorene. [c] 2-(Phenylsulfonyl)-9-phenylfluorene. [d] 9-(Isopropylthio)fluorene. [e] 4-Chloro-2-nitroaniline. [f] 9-Phenylfluorene. [g] 1,3,3-Triphenylpropene. [h] 9-Methylfluorene. [i] 9-*tert*-Butylfluorene. [j] 9-(*m*-Chlorophenyl)xanthene. [k] 9-Phenylxanthene. [l] The values are ±0.05 unless otherwise noted. [m] Reference 5. [n] Reference 8.

Table II. Cyclopropyl Effects on Equilibrium Acidities in Dimethyl Sulfoxide Solution

G	$pK_a(CH_3G)$[a]	pK_a(c-PrG)[a]	ΔpK[b]
$Ph(NMe_2)SO^+$	14.4	20.9 ± 0.3[c]	6.0
$p\text{-}CH_3C_6H_4(NMe_2)SO^+$	~15	20.8	~6
NO_2	17.2	~27[c]	~9[d]
F_3CSO_2	18.8	26.6	7.3[d]
$Ph(NSO_2Ph)SO$	24.5	28.8 ± 0.2[c]	3.8 ± 0.2
PhCO	24.7	28.2	3.0[d]
$PhSO_2$	29.0	>32	>2.5[d]

[a] Values are ±0.05 pK units unless otherwise noted. [b] $\Delta pK = pK_a$(c-PrG) − $pK_a(CH_3G)$, statistically corrected for the number of acidic hydrogen atoms. [c] Decomposition; the pK_a for c-PrNO$_2$ may be high by as much as 1 or 2 units. Error limits are shown for c-PrSO(NMe$_2$)Ph and c-PrSO(NSO$_2$Ph)Ph, which decompose more slowly. [d] Reference 5.

degree of s character in cyclopropane C–H bonds has been revealed by their relatively high kinetic acidities.[9,10] The ultimate effect of forcing these exo bonds to acquire p character is shown by the 13.5 kcal/mol greater strain for methylenecyclopropane than for cyclopropane.[11] Nitro and PhCO functions introduce large strains when attached to the cyclopropyl anion because they demand p–p overlap to form a π bond. As judged from the ΔpK values in Table II, the sulfone functions introduce similar strains when attached to the cyclopropyl anion, presumably because they demand orbital overlap to form a π bond (often called "back-bonding"). The simplest picture of such a π bond is one involving overlap of a p orbital of the first-row element with a d orbital of the second-row element. Antibonding orbitals involving the second-row element provide an alternative mode for electron delocalization.

The most surprising feature of the data is that the ΔpK values for the sulfone-type functions are as large or larger than that for the PhCO function. Quantitative comparisons are difficult to make, however, because the GCH_2^- anions may not be good models for G-c-$C_3H_4^-$ anions; $GC(CH_3)_2^-$ anions might appear to be more appropriate models. Use of the latter models decreases the ΔpK value for the F_3CSO_2 function by 3 units, that for the Ph(NSO$_2$Ph)SO function by 4 units, and that for the PhCO function by only 1.6 units. Furthermore, judging from the 0.5-pK-unit *increase* in acidity for $PhCOCH_2Me$ vs. $PhCOCH_3$, it seems likely that in the absence of steric effects $PhCOCHMe_2$ might be *more* acidic than $PhCOCH_3$ by 1 pK unit. The ΔpK values for c-PrG vs. *i*-PrG for the F_3CSO_2, Ph(NSO$_2$Ph)SO, and PhCO functions would then be 4.8, 0.3, and 4.5 units, respectively. We conclude that the demand for p character from the cyclopropyl group by PhCO may indeed be as large or larger than that of the sulfone groups, as expected, and that no model is available that will allow quantitative comparison. The data show, however, that the Ph(Me$_2$N)SO$^+$, F_3CSO_2, and Ph-

(9) Shatenshtein, A. I. *Adv. Phys. Org. Chem.* **1963**, *1*, 155–201.
(10) Streitwieser, A.; Caldwell, R. A.; Granger, M. R. *J. Am. Chem. Soc.* **1964**, *86*, 3578–3579.
(11) Wiberg, K. B.; Genoglio, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3395–3397.

(NSO_2Ph)SO functions, like the PhCO and NO_2 functions, demand p character from cyclopropyl anions. The structures of these anions will be hybrids wherein the relative degree of p and s character in the cyclopropyl anion orbital will depend on the extent to which the demand for p character by the attached function will be resisted by the strain induced.

Planar vs. Pyramidal Structures for α-Sulfonyl and Related Carbanions. We have seen in the previous section that the similarity of cyclopropyl effects on acidities in substituted cyclopropanes, c-PrG, when G is NO_2, PhCO, F_3CSO_2, $Ph(Me_2N)SO^+$, or $Ph(NSO_2Ph)SO_2$, can be interpreted in terms of a demand for p character from cyclopropyl anions, which suggests that α-sulfonyl carbanions, as well as nitronate ions and enolate ions, have planar structures. This conclusion is supported by (a) X-ray analysis, (b) ^{13}C NMR spectra, (c) recent calculations, (d) acidity data, and (e) stereochemical data.

Analysis of X-ray data on a nitrogen analogue, $Me_2NSO_2NMe_2$, isoelectronic with an α-sulfonyl carbanion, has shown that the nitrogen atom has a planar configuration.[12] X-ray analyses have also shown that the $(MeSO_2)_3C^-$,[13] $C_5H_5N^+C(CN)_2^-$,[14] and $C(CN)_3^-$ anions also have planar or nearly planar structures.[14]

Recent analyses of the ^{13}C NMR spectra of α-sulfinyl carbanions derived from 4-*tert*-butylthiacyclohexane 1-oxide and methyl phenyl sulfoxide indicate that these anions are planar and that the pyramidal structure can be rejected.[15] The spectrum of $PhSO_2CH_2^-$ is interpreted to indicate a structure "intermediate" between sp^2 and sp^3 hybridization.

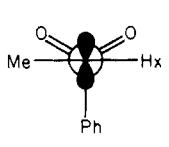
Early calculations suggested that a pyramidal structure was preferred to a planar structure for α-sulfonyl carbanions.[16] The differences were small, however, and probably below the error limits in these minimal basis set calculations. We note in this regard that minimal basis set calculations gave a barrier to inversion of 28.85 kcal/mol for the methide ion, CH_3^-,[17] whereas use of a large and flexible basis set gives a calculated barrier of 1.50 kcal/mol.[18] Since most calculations indicate a very low barrier to inversion for the CH_3^- ion,[18] we can expect any function, G, in the GCH_2^- ion that can provide even a small conjugative overlap with a p orbital to cause this ion to be planar, or nearly so. We have seen in the previous section that α-sulfonyl and α-sulfonimidoyl functions, as well as nitro and carbonyl functions, appear to demand p character of cyclopropyl anions. It follows that GCH_2^- ions where G is NO_2, PhCO, $PhSO_2$, PhSONR, and the like (CN, PhSO, Ph_2PO, etc.) are planar or nearly planar.

Substitution of a phenyl group for a hydrogen atom in a planar GCH_2^- anion would be expected to enhance its stability greatly by delocalization of the negative charge from the p orbital into the π system of the benzene ring. As judged from acidity data, this stabilization for the substitutions, $CH_3^- \rightarrow PhCH_2^-$, $CH_2CN^- \rightarrow PhCHCN^-$, and $CH(CN)_2^- \rightarrow PhC(CN)_2^-$, amounts to ~20, 15, and 10 kcal/mol respectively.[19] (The decrease in the phenyl acidifying effect in this series is caused by resonance saturation.[19]) This stabilization should be ample to ensure a planar structure for these anions. A planar structure for the $PhC(Me)(CN)^-$ and $PhC(Me)(Et)^-$ ions is supported further by stereochemical evidence.[3] The Ar groups in $ArCHCN^-$ and $ArCHSO_2Ph^-$ anions must interact conjugatively with the carbanion in a comparable manner since a plot of $pK_a(ArCH_2CN)$ vs. $pK_a(ArCH_2SO_2Ph)$ for 17 substituents is linear over a range of 9 pK_a units (R^2 = 0.997).[20] If we accept a planar structure for $ArCHCN^-$ anions, it follows that α-sulfonyl carbanions of the type $ArCHSO_2Ph^-$ must also be planar.

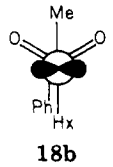
The elegant stereochemical studies of Corey and his students have shown that the maintenance of configuration of chiral α-sulfonyl carbanions is caused by the presence of a barrier to rotation, rather than a barrier to inversion.[21,22] These data establish a planar structure for these α-sulfonyl carbanions and rule out a pyramidal structure.

One of the pieces of evidence presented to establish the absence of barrier to inversion for α-sulfonyl carbanions was the observation that both optically active $PhC^*H(Me)SO_2Ph$ and $HxC^*H(Me)SO_2Ph$ undergo base-catalyzed exchange with deuterated solvent in 2:1 EtOD–D_2O with similar k_{exc}/k_{rac} ratios (44 and 41, respectively) despite a 10^4 difference in exchange rates.[21c] (A high rate of k_{exc}/k_{epim} was also observed for *dl*- and *meso*-$PhCD(Me)SO_2CD(Me)Ph$ isomers.[23]) The failure of the substitution of Ph for Hx to lower the k_{exc}/k_{rac} ratio is inconsistent with a pyramidal structure for the α-sulfonyl carbanion since, as we have mentioned above, the acidity data indicate that this structural change should flatten the anion and increase its stability by over 10 kcal/mol.

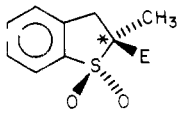
Stereoselective Generation of Chiral α-Sulfonyl Carbanions and Related Carbanions. Acceptance of a planar structure for carbanions of the type $GCHR^-$, where R is alkyl and G is a strong electron-withdrawing group, makes chirality impossible for anions of the type O_2NCHR^-, $PhCOCHR^-$, and $N{\equiv}CCHR^-$, where overlap of the p orbital of the carbanion with the π bonds requires planarity of the anion as a whole. On the other hand, chirality is possible for anions of the type RSO_2CHR^-, $RSONRCHR^-$, Ph_2POCHR^-, etc., since overlap with the carbanion can occur with a set of empty d orbitals on the second-row element to produce a chiral anion, e.g., **18a**,



18a



18b



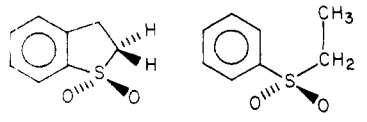
19 (E = H or CO_2H)

in which the p orbital of the carbanion is flanked by the sulfonyl oxygen atoms. Alternatively, overlap with another set of empty d orbitals can produce a diastereomeric achiral anion (**18b**), which is separated from **18a** by a barrier to rotation. The base-catalyzed deuterium exchange with retention of configuration for $HxC^*H(Me)SO_2Ph$ (and like sulfones) shows that carbanion **18a** is

(12) Jordan, T.; Smith, H. W.; Lohr, L. L.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1963**, *85*, 846–851.
(13) Hoogsteen, K. Ph.D. Dissertation, University of Groningen, Groningen, Holland, 1957.
(14) Bugg, C.; Desiderato, R.; Sass, R. L. *J. Am. Chem. Soc.* **1964**, *86*, 3157 and references cited therein.
(15) (a) Lett, R.; Chassaing, G. *Tetrahedron* **1978**, *34*, 2705–2715; (b) Chassaing, G.; Marquet, A. *Ibid.* **1978**, *34*, 1399–1404.
(16) Wolfe, S.; Rauk, A.; Csizmadia, I. G. *J. Am. Chem. Soc.* **1969**, *91*, 1567–1569; Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102–111.
(17) Mezny, P. G.; Kresge, A. J.; Csizmadia, I. G. *Can. J. Chem.* **1976**, *54*, 2526–2533.
(18) Hereld, M.; Lucchese, R. R.; Schaefer, H. F.; Meyer, W. *J. Chem. Phys.* **1977**, *67*, 4071–4075 and references cited therein.
(19) Algrim, D.; Bares, J. E.; Branca, J. C.; Bordwell, F. G. *J. Org. Chem.* **1978**, *43*, 5024–5026.
(20) Branca, J. C. Ph.D Dissertation, Northwestern University, 1979.
(21) (a) Corey, E. J.; Konig, H.; Lowry, T. H. *Tetrahedron Lett.* **1962**, 515–520; (b) Corey, E. J.; Lowry, T. H. *Ibid.* **1975**, 793–801; (c) Corey, E. J.; Lowry, T. H. *Ibid.* **1965**, 803–806.
(22) This conclusion has been accepted by Cram, see: Roitman, J. N.; Cram, D. J. *J. Am. Chem. Soc.* **1971**, *93*, 2225–2231.
(23) Bordwell, F. G.; Phillips, D. D.; Williams, J. M. *J. Am. Chem. Soc.* **1968**, *90*, 426–428.

generated by deprotonation in preference to **18b**. This view is supported by the demonstration that deprotonation or decarboxylation of **19** is accompanied by racemization.[21a,24] Here an achiral, planar carbanion, analogous to **18a**, is precluded by the ring structure.

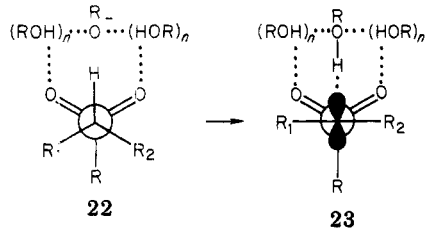
The formation of **18a** in preference to **18b** could be caused, a priori, by a greater stability of this carbanion, a preferred kinetic pathway leading to this carbanion, or a combination of these effects. The observation that the change in structure from $HxC^*H(Me)SO_2Ph$ to $PhC^*H(Me)SO_2Ph$ causes no change in k_{exc}/k_{rac}, despite a large change in carbanion stability, suggests that the stereochemistry is dictated by kinetics rather than by thermodynamics. This conclusion is supported by a comparison of the equilibrium acidities in Me_2SO of **20** and an acyclic analogue (**21**). The cyclic sulfone **20**, which forms an



20 (pK_a = 28.7) **21** (pK_a = 31.0)

achiral carbanion is 2.3 pK_a units *more* acidic than the open-chain analogue **21**, which could form either an achiral or a chiral carbanion. This result indicates that chiral α-sulfonyl carbanions, like **18a**, do *not* have an inherently greater stability than achiral α-sulfonyl carbanions, like **18b**. In fact, the reverse may be true. Firm conclusions concerning small differences in carbanion stabilities in carbanion structures cannot be drawn from acidity measurements, however, because the relative stabilities of the undissociated acids **20** and **21** are unknown and because the analogy is not exact. Nevertheless, these acidity measurements, together with those made on cyclic and acyclic disulfones,[3,21a] show that the difference in stability is not large and point to a kinetically controlled generation of **18a**.

The experiments of Corey and Lowry show that deprotonation, decarboxylation, and dealdolization of chiral acyclic sulfones all occur preferentially from a conformation in which the departing group is flanked by (syn to) the sulfonyl oxygen atoms.[21] This leads to preferential formation of a chiral planar carbanion, analogous to **18a**. For deprotonation by hydroxide or alkoxide ions, RO^-, they suggest a mechanism involving hydrogen bonding to the oxygen atoms of the sulfonyl group and the alkoxide ion, e.g., as in **22** and **23**.



22 **23**

Similar mechanisms can be written for the decarboxylation and dealdolization reactions. Attack of alkoxide ion on a hydrogen atom syn to the sulfonyl oxygen atoms to give a carbanion of type **18a** will also account for the inversion at each chiral carbon atom α to the sulfonyl group observed in the Ramberg–Bäcklund reaction of *dl-erythro-* and *dl-threo*-$PhCH(Me)SO_2C(Br)(Me)Ph$. We previously represented these reactions as proceeding through a mechanism involving α-sulfonyl carbanions with a low barrier to inversion.[25] This pictorialization should now be replaced by one in which the carbanion is depicted as planar.[26]

The reactions used to generate α-sulfonyl carbanions in stereochemical studies have usually been carried out in solvents such as MeOH, aqueous EtOH, and Me_2SO (92%)/MeOH (8%), which are good at dissociating ion pairs. In such instances the preferential generation of chiral α-sulfonyl carbanions in dilute solution is essentially free of counterion effects. However, in poorly dissociating solvents, such as benzene, tetrahydrofuran, and *tert*-butyl alcohol, we can expect cation counterions to play a role in determining the stereoselectivity. For example the k_{exc}/k_{rac} ratios for deuterium exchange with chiral sulfones are usually higher in *t*-BuOH,[3] probably due to counterion effects. Furthermore, anions containing several electron-donor sites, such as those derived from β-diketones and certain β-disulfones, will form chelates with K^+ and much stronger chelates with Li^+ that remain at least partly associated even in good dissociating solvents such as Me_2SO and *N*-methylpyrrolidin-2-one.[28] It is not surprising to find, therefore, that cations are often highly important in directing the stereochemical course of anion reactions.

Factors Controlling the Stereoselective Generation and Reactions of Carbanions. The extensive studies on the generation and reactions of enolate ions have shown that the stereochemistry of their reactions is controlled by stereoelectronic effects, steric effects, and cation effects. The stereoelectronic effect dictates that in the generation of enolate ions from cyclohexanones the axial proton be removed selectively by base, since this will provide a better alignment of the p orbital of the developing carbanion with the π bond of the carbonyl group.[29] This stereoelectronic control may be appreciable in the absence of steric effects,[30] but for many cycloalkanones it is counterbalanced by steric hindrance to attack by the base, and the net effect is small.[31,32] The recent demonstration that the stereochemistry of aldol condensations between *E* or *Z* enolate ions and carbonyl compounds can be completely reversed by changing the cation from Li^+ to R_4N^+ illustrates the important role that cations can play.[33] In this instance the same stereochemical result is observed with Li^+ in either THF or HMPA, presumably because the strong chelating effect of Li^+ is retained even in the dipolar nonhydroxylic solvent.[28]

With certain fluorenyl anions the effect of the counterion may change with solvent. For example, the stereochemistry of the amine-catalyzed deuterium exchange of 2-(*N*,*N*-dimethylcarbamoyl)-9-methylfluorene-9-*d* changes from retention to racemization to inversion as the solvent

(24) Cram, D. J.; Whitney, T. A. *J. Am. Chem. Soc.* **1967**, *89*, 4651–4661.

(25) Bordwell, F. G.; Doomes, E.; Corfield, P. W. R. *J. Am. Chem. Soc.* **1970**, *92*, 2581–2583; Bordwell, F. G.; Doomes, E. *J. Org. Chem.* **1974**, *39*, 2526–2531.

(26) Planar α-sulfonyl carbanions are presumably also formed in the stereoselective debrominations of *dl*- and *meso*-$PhCHBrSO_2CHBrPh$ by Ph_3P in benzene,[27] but in these Ramberg–Bäcklund reactions, the stereochemical course must be directed in a somewhat different manner. Ion pairing involving the Ph_3PBr^+ cation and the sulfonyl oxygen atoms may provide the directing force here.

(27) Bordwell, F. G.; Jarvis, B. B. *J. Am. Chem. Soc.* **1973**, *95*, 3585–3594.

(28) Bordwell, F. G.; Branca, J. C.; Hughes, D. L.; Olmstead, W. N. *J. Org. Chem.*, **1980**, *45*, 3305–3313.

(29) Corey, E. J.; Sneen, R. A. *J. Am. Chem. Soc.* **1956**, *78*, 6269–6278.

(30) Fraser, R. R.; Deslongchamps, P. *J. Am. Chem. Soc.* **1978**, *100*, 657–659.

(31) Bordwell, F. G.; Scamehorn, R. G. *J. Am. Chem. Soc.* **1968**, *90*, 6749–6751.

(32) House, H. O. "Modern Synthetic Reactions", W. A. Benjamin, Menlo Park, CA, 1972, pp 586–595.

(33) Kleshchick, W. A.; Buse, C.; Heathcock, C. M. *J. Am. Chem. Soc.* **1977**, *99*, 247–251.

is changed from THF to Me_2SO to MeOH.[34] In THF, internal return from the tight RNH_2D^+[fluorenyl]$^-$ ion pair leads to retention. In the dipolar nonhydroxylic solvent Me_2SO, dissociation of the ion pair leads to racemization. In the hydroxylic solvent MeOH, proton donation from the solvent is faster than internal return of hydrogen from RNH_2D^+, leading to net inversion. These and many other examples show that stereoselectivity in the generation and reactions of planar carbanions is dictated by a combination of stereoelectronic and steric effects and that the latter may be strongly dependent on the structure of the base, the nature of the counterion, and the nature of the solvent.

The stereoselective generation and reactions of α-sulfonyl, α-diphenylphosphonyl, and the like planar carbanions will be subject to control by most of the factors enumerated for planar enolate and fluorenyl ions. In addition, these anions may be chiral (e.g., **18a** and **23**) or achiral (e.g., **18b**). Stereoelectronic control is expected to play a minor role, however, since d orbitals are available for overlap with the developing p orbital for several different steric approaches by the base. The superior ability of sulfonyl-like functions, SO_2G (G = R, Ar, NRAr, OR), to promote the generation of chiral α-carbanions by base-catalyzed deprotonation, as compared to Ph_2PO, $(RO)_2PO$, and like functions, apparently depends on the preferred kinetic pathway provided by the two oxygen atoms attached to sulfur. Evidently the single, more strongly basic oxygen atom in sulfinyl functions, e.g., PhSO, is unable to play this role in hydroxylic solvents.[3] However, in weakly dipolar solvents, such as THF, relatively high degrees of stereoselectivity have been achieved for reactions of electrophiles with the lithio derivatives of the carbanions generated from benzyl methyl sulfoxide[35] and *cis*- and *trans*-4-*tert*-butylthiacyclohexane 1-oxides.[36] Convincing evidence has been presented to show that in these instances chelation of Li^+ with the oxygen atom of the sulfoxide is important in determining the stereochemistry.

Experimental Section

The preparations of the following substances have been described previously: *N*,*S*-dimethyl-*S*-phenylsulfoximine (**1**),[37] (dimethylamino)methylphenyloxosulfonium tetrafluoroborate (**4**),[37] (diethylamino)dimethyloxosulfonium tetrafluoroborate (**6**),[38] *S*-methyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximine (**11**),[39] cyclopropyl(dimethylamino)phenyloxosulfonium tetrafluoroborate (**17**),[40] cyclopropyl(dimethylamino)-*p*-tolyloxosulfonium tetrafluoroborate,[40] and *S*-isopropyl-*S*-phenyl-*N*-*p*-tolylsulfoximine (**13**).[41]

***N*-(Phenylsulfonyl)sulfoximines.** The sulfide (0.1 mol) and Chloramine-B (the sodium salt of *N*-chlorobenzenesulfonamide, 0.11 mol) were dissolved in 30 mL of methanol, and 1 mL of acetic acid in 5 mL of methanol was added slowly. The reaction mixture was warmed to 50 °C and maintained at that temperature until monitoring by thin-layer chromatography showed formation of the sulfilimine to be complete. The reaction mixture was poured into cold dilute aqueous sodium hydroxide; the precipitated sulfilimine was collected, washed with water, and recrystallized from methanol–water. The following *S*-alkyl-*S*-phenyl-*N*-(phenylsulfonyl)sulfilimines were prepared: *S*-ethyl (mp ~23 °C), *S*-cyclopropyl (mp 122–123.5 °C).

The above sulfilimines were oxidized with basic hydrogen peroxide in methanol[41] to yield the desired *S*-alkyl-*S*-phenyl-*N*-(phenylsulfonyl)sulfoximine: *S*-ethyl (mp 72–73.5 °C), *S*-cyclopropyl (mp 105–106 °C).

(Dimethylamino)diisopropyloxosulfonium tetrafluoroborate (7) was prepared by methylation of *S*,*S*-diisopropylsulfoximine with trimethyloxonium tetrafluoroborate in dichloromethane in the presence of sodium carbonate.[37] The product had the following: mp 136.5–137.5 °C; ^1H NMR ($CDCl_3$) δ 1.5 (d, 6, CCH_3), 1.62 (d, 6, CCH_3), 3.2 (s, 6, NCH_3), 4.68 (heptet, 2, CH).

Equilibrium acidity measurements in dimethyl sulfoxide solution were carried out by the method originally described[4] but by using a modified method for preparing the stock base, $CH_3SOCH_2^-K^+$, from KH and CH_3SOCH_3.[42]

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Registry No. **1**, 30004-67-2; **2**, 3112-85-4; **3**, 1193-82-4; **4**, 21077-81-6; **6**, 36501-44-7; **7**, 74195-10-1; **8**, 421-82-9; **9**, 13003-57-1; **10**, 57964-42-8; **11**, 42153-74-2; **12**, 74195-11-2; **13**, 69780-68-3; **14**, 98-86-2; **15**, 93-55-0; **16**, 611-70-1; **17**, 33381-21-4; cyclopropyl(dimethylamino)-*p*-tolyloxosulfonium tetrafluoroborate, 50320-44-0; nitrocyclopropane, 13021-02-8; cyclopropyl trifluoromethyl sulfone, 57964-43-9; *S*-cyclopropyl-*S*-phenyl-*N*-(phenylsulfonyl)sulfoximine, 74195-12-3; cyclopropyl phenyl ketone, 3481-02-5; cyclopropyl phenyl sulfone, 17637-57-9; ethyl phenyl sulfide, 622-38-8; cyclopropyl phenyl sulfide, 14633-54-6; Chloramine-B, 127-52-6; *S*-ethyl-*S*-phenyl-*N*-(phenylsulfonyl)sulfilimine, 29723-62-4; *S*-cyclopropyl-*S*-phenyl-*N*-(phenylsulfonyl)sulfilimine, 74195-13-4; *S*,*S*-diisopropylsulfoximine, 74195-14-5; trimethyloxonium tetrafluoroborate, 420-37-1.

(34) Cram, D. J.; Gosser, L. *J. Am. Chem. Soc.* **1963**, *85*, 3890–3891.
(35) Biellman, J. F.; Vicens, J. J. *Tetrahedron Lett.* **1978**, 467–470.
(36) Chassaing, G.; Lett, R.; Marquet, A. *Tetrahedron Lett.* **1978**, 471–474.
(37) Johnson, C. R.; Haake, M.; Schroeck, C. W. *J. Am. Chem. Soc.* **1970**, *92*, 6594–6598.
(38) Johnson, C. R.; Rogers, P. E. *J. Org. Chem.* **1973**, *38*, 1793–1797.
(39) Johnson, C. R.; Kirchhoff, R. A.; Reischer, R. J.; Katikar, G. F. *J. Am. Chem. Soc.* **1973**, *95*, 4287–4291.
(40) Johnson, C. R.; Janiga, E. R. *J. Am. Chem. Soc.* **1973**, *95*, 7692–7700.
(41) Johnson, C. R.; Kirchhoff, R. A. *J. Org. Chem.* **1979**, *44*, 2280–2284.
(42) Olmstead, W. N.; Margolin, Z.; Bordwell, F. G., *J. Org. Chem.* **1980**, *45*, 3295–3299.