R-I-*d*, $[\alpha]^{25}_{546}$ +15.1 ± 0.4° (*c* 6.5 chloroform), m.p. 45.5-46.5°. Repeated oxidation and chromatography of the above samples did not alter their properties. The infrared spectra of the sulfone was completely free of the sulfoxide absorption at 9.6 μ.

A mixture composed of 40% of optically pure (−)-*R*-*R*-III-*d* and 60% of optically pure (−)-*S*-*R*-III-*d* was oxidized to sulfone by the above procedure. The product was 80% racemic, a fact which demonstrates that the diastereomer ratio of sulfoxides can be measured by oxidation to sulfone and examination of the optical properties thereof.

Solvents.—Deuterated *tert*-butyl alcohol (99% OD by combustion and falling drop method) was prepared as before[22] and stored over Linde 4A Molecular Sieves. Non-deuterated *tert*-butyl alcohol was purified by careful fractional distillation and stored over Molecular Sieves. The basic solutions of *tert*-butyl alcohol were prepared by reaction of a weighed amount of clean potassium metal with the solvent in a dry, pure nitrogen atmosphere. Dimethyl sulfoxide (J. T. Baker analyzed reagent) was carefully distilled and stored over Molecular Sieves. The basic solutions of dimethyl sulfoxide–methanol were prepared by adding clean potassium metal to pure methanol at low temperature, and adding the resulting solution to dimethyl sulfoxide. Karl Fischer titrations of all solvents demonstrated the presence of less than 0.05% water. Solutions of potassium *tert*-butoxide in dimethyl sulfoxide were prepared by adding carefully sublimed, pure potassium *tert*-butoxide to dimethyl sulfoxide. Final base concentrations were obtained by titration in aqueous solutions with standard acid.

Kinetics.—Kinetic runs were all carried out at 60.0 ± 0.3° on 0.17 *M* solutions of substrate in basic solutions of *tert*-butyl alcohol or dimethyl sulfoxide under pure dry nitrogen. Sealed ampoules containing 0.20 g. of sulfoxide were used for each point. At appropriate times the ampoules were removed, opened, and the contents were shaken with 25 ml. of pentane and 25 ml. of water. The pentane layer was washed with salted water, dried, evaporated, and the residue was warmed under vacuum (wt. 0.15 to 0.20 g.). In representative runs the aqueous extracts were titrated with standard acid to ensure that base was not lost during the run. Each sample of material was oxidized directly to sulfone by the above procedure. The total sulfone sample was homogenized and analyzed for deuterium, and its optical rotation was determined. Analysis for deuterium content at the 2-octyl position of the sulfone was made by the previously reported method.[3b] Standard samples of known deuterium content were always used for comparison purposes. Rotations of sulfone were taken at λ 546 mμ in a 1-dm. tube in chloroform at concentrations of 6.5 g. per 100 ml. A Zeiss circular scale polarimeter was used, and observed rotations varied between 0.4 and 1.1°.

Calculations of the pseudo-first-order rate constants for epimerization were based on the epimer equilibration rotation of $[\alpha]^{25}_{546}$ ± 3.4°, depending on the starting material. The assumption was made that the point of epimeric equilibrium for the diastereomeric sulfoxides was the same in *tert*-butyl alcohol as in dimethyl sulfoxide. Pseudo-first-order rate constants for the exchange reactions were calculated based on a potential maximum change of deuterium content of 100% for III-*h* and 98.5% for III-*d*. Pseudo-first-order rate constants for the epimerization were computed based on a potential maximum change in specific rotation for the sulfone of 11.1° when (−)-*R*-*R*-III-*h* was starting material, 11.7° when (−)-*R*-*R*-III-*d* was used, and 18.5° when (+)-*R*-*S*-III-*d* was employed. The experimental details and results are recorded in Table II.

Attempts were made to racemize and effect base-catalyzed deuterium–hydrogen exchange with (−)-2-octyl-2-*d* phenyl sulfide. No exchange or racemization was observed under the following conditions: dimethyl sulfoxide, 0.9 *M* in potassium *tert*-butoxide at 60° for 142 hr. (20% recovery of sulfide unchanged optically or isotopically). Both thiophenol and diphenyl disulfide were produced.

Equilibration Experiments.—The equilibration runs were carried out under the conditions reported in Table I. The sulfoxide product was isolated as in the kinetic runs, oxidized to sulfone by the above reported procedure, and the rotation of sulfone was taken. The results are reported in Table I. Sulfoxide from run 1 was divided into two parts. The first part was oxidized directly to sulfone which was analyzed. The second part was subjected to the same epimeric equilibrating conditions again. The sulfoxide was reisolated, and oxidized to the sulfone. The rotations of the two samples of sulfone were identical.

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[22] D. J. Cram and B. Rickborn, *J. Am. Chem. Soc.* **83**, 2178 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES, LOS ANGELES 24, CALIF.]

Electrophilic Substitution at Saturated Carbon. XVIII. Carbon as Leaving Group in Generation of Optically Active α-Sulfonylcarbanions[1,2]

BY DONALD J. CRAM AND ALAN S. WINGROVE

RECEIVED OCTOBER 9, 1962

The base-catalyzed decarboxylation of optically pure (+)-2-benzenesulfonyl-2-methyloctanoic acid ((+)-I) and cleavage of optically pure (−)-3-benzenesulfonyl-2,3-dimethyl-2-nonanol ((−)-II) has been studied in a variety of solvents. Both compounds gave (+)-2-octyl phenyl sulfone ((+)-III) in from 96 to 100% optical purity, and the reactions are presumed to occur with retention of configuration. Hydrogen–deuterium isotope effects for the proton-capture process were measured for the carbanion generated in the decarboxylation reaction and were found to vary from $k_{\mathrm{H}}/k_{\mathrm{D}} = 1.0$ in ethylene glycol–potassium ethylene glycoxide to 1.8 in *tert*-butyl alcohol–tetramethylammonium hydroxide. A survey of available data suggests that a variety of configurations which range from trigonal to tetrahedral are available to carbanions stabilized by d-orbital containing groups.

Through a determination of the relative rates of base-catalyzed hydrogen–deuterium exchange and racemization of optically active 2-octyl phenyl sulfone, the 2-benzenesulfonyl-2-octyl anion would appear asymmetric.[3] Similar studies applied to optically active diphenyl-2-octylphosphine oxide and 2-octyl phenyl sulfoxide[4] led to the conclusion that the low degree of stereospecificity observed in the exchange reactions of these systems was due only to asymmetric solvation. Of the three d-orbital carbanion stabilizing groups, only the sulfone group conferred asymmetric properties on the anion. Detailed discussion of the causes of the differences between these three carbanions was deferred to this paper.

The present study was undertaken to determine if the 2-benzenesulfonyl-2-octyl anion generated with carbon as a leaving group would exhibit the same stereochemical properties as that anion generated with hydrogen or deuterium as leaving group.[5] Accordingly, optically pure (+)-2-benzenesulfonyl-2-methyloctanoic acid ((+)-I) and (−)-3-benzenesulfonyl-2,3-dimethyl-2-nonanol ((−)-II) were prepared and subjected to base-catalyzed cleavage reactions to give 2-octyl phenyl sulfone (III).

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[1] The authors wish to thank the National Science Foundation for a grant used in support of this work.

[2] Part of the results of this investigation appeared in preliminary form; D. J. Cram and A. S. Wingrove, *J. Am. Chem. Soc.*, **84**, 1496 (1962).

[3] (a) D. J. Cram, W. D. Nielsen and B. Rickborn, *ibid.*, **82**, 6415 (1960); (b) D. J. Cram, D. A. Scott and W. D. Nielsen, *ibid.*, **83**, 3696 (1961); (c) E. J. Corey and E. T. Kaiser, *ibid.*, **83**, 490 (1961); (d) H. L. Goering, P. T. Towns and B. Dittmar, *J. Org. Chem.*, **27**, 736 (1962).

[4] (a) D. J. Cram, R. D. Partos, S. H. Pine and H. Jager, *J. Am. Chem. Soc.*, **84**, 1742 (1962); (b) D. J. Cram and R. D. Partos, *ibid.*, **85**, 1093 (1963); (c) D. J. Cram and S. H. Pine, *ibid.*, **85**, 1096 (1963).

[5] That some stereospecificity would be observed is suggested by previous work [J. E. Taylor and F. H. Verhoek, *ibid.*, **81**, 4537 (1959)] in which optically active 2-methyl-2-benzenesulfonylbutyric acid was decarboxylated at high temperature to give optically active 2-butyl phenyl sulfone of undetermined optical purity.

TABLE I

RESULTS OF BASE-CATALYZED DECARBOXYLATION OF (+)-2-BENZENESULFONYL 2-METHYLOCTANOATES AT 90 ± 0.2° ((+)-I)

Run	Solvent	Base Nature	 Concn., *N*	Subst. concn., *N*	Time, hr.	Yield, %	Net steric course, %[a]
1	$(CH_3)_3COH$[b]	$(CH_3)_3COK$	0.17	0.20	166	72	97 ret.
2	$(CH_3)_3COH$[b]	$(CH_3)_3COK$	.17	.20	1104	99	98 ret.
3	$HOCH_2CH_2OH$	$HOCH_2CH_2OK$	.17	.20	103	45	98 ret.
4	CH_3OH[b]	CH_3OK	.17	.20	171	86	98 ret.
5	H_2O[c]	HOK	.034	.04	437	10	98 ret.
6	$(CH_3)_2SO$[b]	CH_3OK	.17	.20	148	83	98 ret.
7	$(CH_3)_2SO$[d]	$(CH_3)_4NOH$	.17	.20	133	84	98 ret.

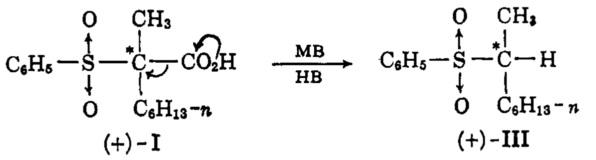
[a] ±3%. [b] White residue present during run, possibly a carbonate. [c] Reaction was heterogeneous. [d] Brown needles present during run, possibly a carbonate.

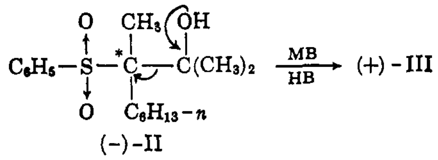
TABLE II

RESULTS OF BASE-CATALYZED CLEAVAGE OF 0.2 *M* SOLUTIONS OF (−)-3-BENZENESULFONYL-2,3-DIMETHYL-2-NONANOL ((−)-II)

Run	Solvent	Base Nature	 Concn., *N*	Temp., °C.	Time, hr.	Yield, %	Obsd. net steric course, %	Corrected net steric course, %
8	$(CH_3)_3COH$	$(CH_3)_3COK$	0.093	25	15.5	38	97% ret.	~100% ret.
9	$HOCH_2CH_2OH$	$HOCH_2CH_2OK$	.059	90	24	61	96% ret.	98% ret.
10	$(CH_3)_2SO$[a]	CH_3OK	.062	25	15.5	48	100% rac.	...[b]

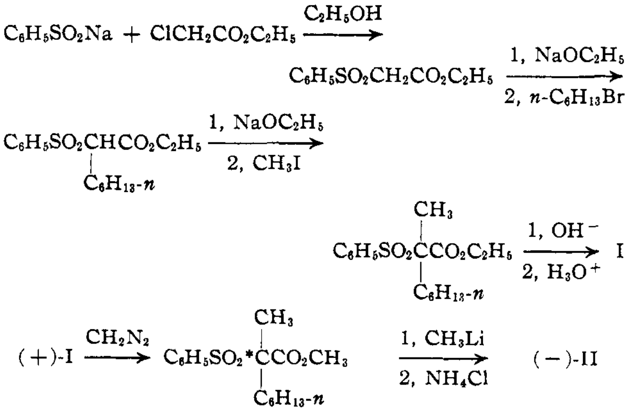
[a] 5% by weight methanol. [b] No correction possible—see Discussion.





Results

Starting Materials.—The synthesis of 2-benzenesulfonyl-2-methyloctanoic acid (I) is formulated. The solid racemic acid was resolved with 4 recrystallizations of its quinine salt from absolute ethanol. Additional recrystallizations (2) of the salt did not change the rotation of the acid made from the salt. This enantiomeric acid could not be induced to crystallize. Its ester was converted to *tert*-alcohol, (−)-II, at −30 to −40° to avoid side reactions. The preparation and maximum rotation of 2-octyl phenyl sulfone has been reported.[3b]



$$C_6H_5SO_2Na + ClCH_2CO_2C_2H_5 \xrightarrow{C_2H_5OH} C_6H_5SO_2CH_2CO_2C_2H_5 \xrightarrow[2,\ n\text{-}C_6H_{13}Br]{1,\ NaOC_2H_5}$$

$$C_6H_5SO_2\underset{\substack{|\\ C_6H_{13}\text{-}n}}{C}HCO_2C_2H_5 \xrightarrow[2,\ CH_3I]{1,\ NaOC_2H_5} C_6H_5SO_2\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ C_6H_{13}\text{-}n}}{C}}CO_2C_2H_5 \xrightarrow[2,\ H_3O^+]{1,\ OH^-} \text{I}$$

$$(+)\text{-I} \xrightarrow{CH_2N_2} C_6H_5SO_2{}^*\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ C_6H_{13}\text{-}n}}{C}}CO_2CH_3 \xrightarrow[2,\ NH_4Cl]{1,\ CH_3Li} (-)\text{-II}$$

Decarboxylation Experiments.—The free acid (+)-I was demonstrated to be stable at 90° in *tert*-butyl alcohol, methanol, ethylene glycol and dimethyl sulfoxide but underwent decarboxylation at this temperature in the presence of base. Decarboxylations were carried out in these solvents as well as in water in the presence of less than an equivalent amount of base. The product of the reaction, (+)-III, was optically stable under the conditions of its formation as long as some of the starting acid was present. Potassium cations were employed in all runs except one which was carried out in dimethyl sulfoxide with tetramethylammonium cation. The results of these experiments are summarized in Table I.

Cleavage Experiments.—Stronger base was required for the cleavage than the decarboxylation reaction. In *tert*-butyl alcohol the reaction occurred at 25° with potassium *tert*-butoxide as base, conditions under which the product was estimated to have racemized not more than 3%. This estimate was based on the value of the rate constant for racemization of (+)-III under the conditions of the experiment.[3b] In ethylene glycol at 90° with potassium ethylene glycoxide as base the cleavage occurred under conditions where the product once formed could have racemized a maximum of 2%. This estimate was also based on the known rate constant for racemization.[3b] In dimethyl sulfoxide (5% by weight in methanol) at 25° with potassium methoxide as base, cleavage occurred, but only at a base concentration at which the product once formed would have racemized. This conclusion was drawn from the known rate constant for the racemization reaction.[3b] Table II records the results. As expected, racemic III was obtained in dimethyl sulfoxide from (−)-II (run 10).

Isotope Effects for Carbanion Capture in Decarboxylation Reaction.—Three decarboxylations were carried out in solvent mixtures, 50 mole % deuterated-50 mole % non-deuterated at oxygen. Two runs were made in *tert*-butyl alcohol, one with potassium and one with tetramethylammonium cation, and one run was made in ethylene glycol with potassium cation. Table III records the results. The run (12) made with tetramethylammonium cation was complicated by several factors: (1) The tetramethylammonium hydroxide employed was difficult to obtain free of water. (2) This base decomposes into methanol and trimethylamine at 81°, being 66% complete in *tert*-butyl alcohol after 6 hr.[6] (3) Possible exchange reactions might occur between the methyl groups of the base and solvent, thereby diluting the solvent.[7] These variables were controlled as follows. A run was made in which the

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(6) D. J. Cram, J. L. Mateos, F. Hauck, A. Langemann, K. R. Kopecky, W. D. Nielsen and J. Allinger, *J. Am. Chem. Soc.*, **81**, 5774 (1959).

(7) W. E. Doering and A. K. Hoffman, *ibid.*, **77**, 521 (1955), observed that the rate constant of exchange of tetramethylammonium iodide with sodium deuteroxide in heavy water was 7×10^{-9} sec.$^{-1}$ at 100°.

TABLE III

ISOTOPE EFFECTS FOR PROTON CAPTURE OF CARBANIONS PRODUCED IN BASE-CATALYZED DECARBOXYLATION OF (+)-2-BENZENESULFONYL-2-METHYLOCTANOIC ACID ((+)-I) AT 90 ± 0.2°

Run	Solvent[a]	Base Nature	Base Concn., N	Time, hr.	Yield, %	% D in (+)-III[b]	k_H/k_D
11	$(CH_3)_3COH(D)$	$(CH_3)_3COK$	0.17	130	88	43	1.3
12	$(CH_3)_3COH(D)$	$(CH_3)_4NOH$	.144	45	60	35	1.8
13	$(D)HOCH_2CH_2OH(D)$	$(D)HOCH_2CH_2OK$	.17	130	44	50	1.0

[a] Solvent was 50 mole % O–D in each case, prepared by mixing 99% O-deuterated solvent with ordinary solvent. [b] ±1%.

TABLE IV

COMPARISON OF RATIOS OF RATE CONSTANTS FOR ISOTOPIC EXCHANGE (k_e) TO RATE CONSTANTS FOR RACEMIZATION (k_α) IN BASE-CATALYZED HYDROGEN–DEUTERIUM EXCHANGE REACTIONS OF 2-OCTYL PHENYL SULFONE, 2-OCTYL PHENYL SULFOXIDE AND DIPHENYL-2-OCTYLPHOSPHINE OXIDE

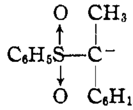
Compound	Solvent	T, °C.	k_e/k_α
Sulfone	$(CH_3)_3COH(D)$	25	73–1980[a]
Sulfoxide	$(CH_3)_3COH(D)$	60	1.2–3.6[b]
Phosphine oxide	$(CH_3)_3COH$	100	3.3[c]
Sulfone	$(CH_3)_2SO$[c]	25	10
Sulfoxide	$(CH_3)_2SO$[d]	60	0.58–1.4[b]
Phosphine oxide	$(CH_3)_2SO$[e]	75	1[f]

[a] Data taken from ref. 3b. [b] Data taken from ref. 4c; results varied with diastereomer used. [c] 8% by weight in methanol. [d] 1.2 M in methanol. [e] 4% by weight in methanol. [f] Data taken from ref. 4b.

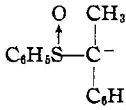
conditions of run 12 were duplicated except that the temperature was held at 25° where no decarboxylation occurred. The solvent was recovered after run 12 and after the control run, purified and analyzed for deuterium content. The control run indicated the presence of 57% deuterated *tert*-butyl alcohol, and the solvent after run 12 indicated 53%. The slight increased concentration of deuterium in solvent probably reflects selective loss of protonated solvent (solvation of solutes) during purification. As expected, ordinary alcohol exhibited higher solvation energy than deuterated material.

Discussion

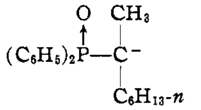
In the preceding two papers, evidence was obtained that the phenylsulfinyl[4c] and diphenylphosphinoxy[4b] carbanions did not exhibit intrinsic configurational stability as did the phenylsulfonyl carbanion.[3] Evidence was produced that all three systems were subject to asymmetric solvation effects particularly in hydroxylic solvents of low dielectric constant. Differences in the relative importance of inductive and d-orbital multiple bonding for the three systems did not provide a satisfactory explanation for the difference in symmetry properties of their three anions.[4c] Differences in the abilities of the three anions to protonate on oxygen were considered. Discussion of other possible explanations was reserved for this paper and are found in the next section. Subsequent sections treat the magnitude of the energy barrier for sulfonyl carbanion racemization, effects of differences in leaving group on the fate of the sulfonyl carbanion, steric and ring confinement effects on the configuration of the sulfonyl carbanion, asymmetric solvation effects, and isotope effects in proton capture by carbanions.


$$C_6H_5\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-\overset{\overset{CH_3}{|}}{\underset{\underset{C_6H_{13}\text{-}n}{|}}{C^-}}$$

Phenylsulfonyl carbanion


$$C_6H_5\overset{\overset{O}{\uparrow}}{S}-\overset{\overset{CH_3}{|}}{\underset{\underset{C_6H_{13}\text{-}n}{|}}{C^-}}$$

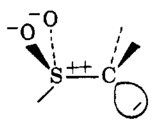
Phenylsulfinyl carbanion


$$(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}-\overset{\overset{CH_3}{|}}{\underset{\underset{C_6H_{13}\text{-}n}{|}}{C^-}}$$

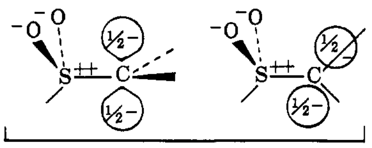
Diphenylphosphinoxy carbanion

Differences in Configurational Stability of Sulfonyl, Sulfinyl and Phosphinoxy Carbanions.—Table IV compares the stereochemical outcome of hydrogen–deuterium exchange reactions of the sulfone and the two oxides. One possible explanation for the differences in the stereochemical course of the reaction of the sulfone and the two oxides makes use of electrostatic inhibition of pyramidal carbanion inversion. In the absence of stabilizing groups, carbanions are undoubtedly pyramidal and possess a very low activation energy for inversion. Saturated amines serve as isoelectronic models for carbanions in providing this conclusion.

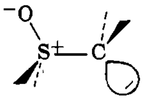
If anion stabilization by p–d overlap has neither strict configurational nor conformational requirements,[8] other effects such as solvation, steric or electrostatic, might tend to preserve the normal pyramidal geometry. The electrostatic effect particularly would tend to inhibit anion inversion. If the rate of proton capture was faster than the rate of inversion, the exchange reaction would occur with retention of configuration. The sulfone has two negative oxygens and each of the two oxides has only one. The oxygen–carbanion repulsions might be enough greater in the sulfone than in the two oxides to provide for the observed stereochemical differences in the systems. Negative charge is much more concentrated in passing from the ground to the transition state for carbanion inversion (trigonal geometry) in the sulfone than in the two oxide systems.



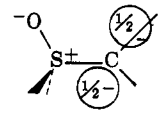
Most stable conformation for the ground state (approximation)



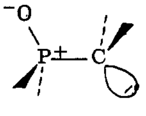
Possible transition states for inversion



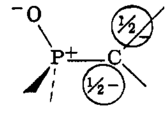
Most stable conformation for the ground state



Transition state for inversion



Most stable conformation for ground state



Transition state for inversion

Electrostatic inhibition of inversion should be sensitive to the dielectric constant of the medium, since carbanion–solvent electrostatic interactions should seriously affect the magnitude of the intramolecular interactions. The electrostatic barrier to inversion should be greater the lower the dielectric constant of the medium, an expectation compatible with the observed higher stereospecificity associated with solvents of low dielectric constant.

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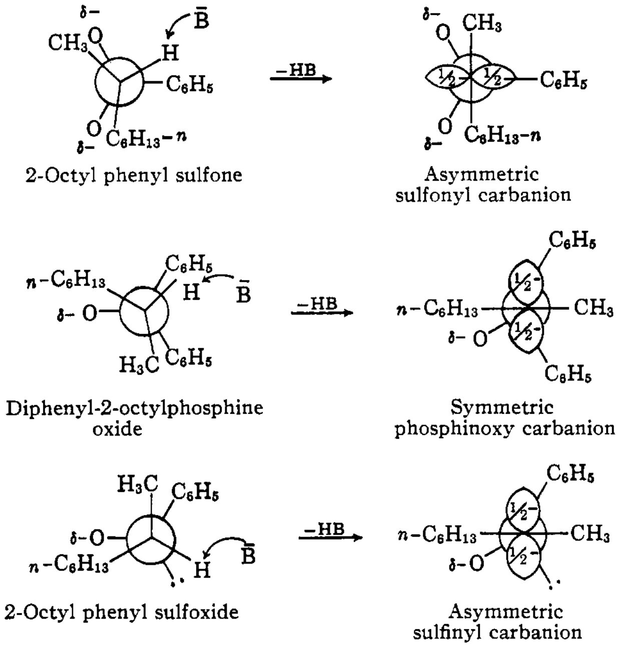
(8) (a) W. E. Doering and L. K. Levy, *J. Am. Chem. Soc.*, **77**, 509 (1955); (b) H. E. Zimmerman and B. S. Thyogarajan, *ibid.*, **82**, 2505 (1960); (c) R. Breslow and E. Mohacsi, *ibid.*, **83**, 4100 (1961); (d) S. Oae, W. Tagaki and A. Ohno, *ibid.*, **83**, 5036 (1961); (e) T. Jordan, W. Smith and W. N. Lipscomb, *Tetrahedron Letters*, **2**, 37 (1962).

A second possible explanation for the differences in stereochemistry of the hydrogen–deuterium exchange reactions of sulfone and the two oxides makes use of *electrostatic inhibition of planar carbanion rotation.* If the three carbanions are trigonal because of enhanced p–d overlap in such a geometry, the sulfonyl carbanion could possess different symmetry properties than the other two anions. A number of conditions would have to be fulfilled before such an explanation applied: (1) The sulfonyl anion would have to be formed largely from one particular conformation (see formulas). Pole–dipole interactions would tend to be minimized in one particular transition state which would lead to an asymmetric rotamer. (2) This rotamer would have to capture a proton or deuteron faster than rotation occurred. The barrier to rotation would be both electrostatic and steric in character. (3) Proton (deuteron) capture would have to occur from the side from which the leaving group became detached.

Application of condition 1 to diphenyl-2-octylphosphine oxide leads directly to a symmetrical rotamer for the carbanion (see formulas), from which only racemic product could arise. Under the same circumstances, 2-octyl phenyl sulfoxide would produce an asymmetric anion, but preferential proton capture from one or the other face of the anion would only be the result of asymmetric induction effects from the adjacent asymmetric sulfur atom.



2-Octyl phenyl sulfone

Asymmetric sulfonyl carbanion

Diphenyl-2-octylphosphine oxide

Symmetric phosphinoxy carbanion

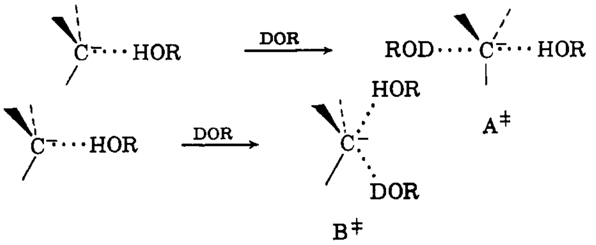
2-Octyl phenyl sulfoxide

Asymmetric sulfinyl carbanion

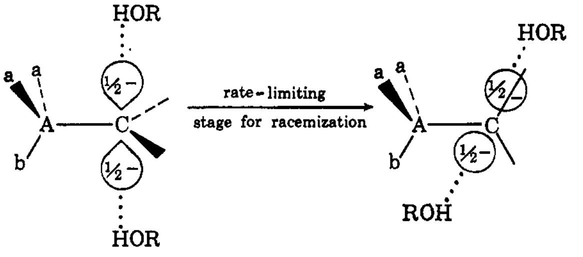
Magnitude of Energy Barrier for Sulfonyl Carbanion Racemization.—If k_f is the rate constant for proton capture from the front (side of leaving group), and k_b is the rate constant for proton capture from the back (side remote from leaving group), then the energy barrier to sulfonyl carbanion configurational equilibration must be large enough to provide a factor of at least 20 for k_f/k_b. In hydroxylic solvents such as methanol, both of these rate constants involve processes in which one hydrogen-bonded carbanion is exchanged for a second, in one case with, and the other case without, change of configuration. Others have collected and correlated data[9] that suggest that the rate constants for proton capture from water by carbanions derived from substances such as dimethyl sulfone, acetamide and acetonitrile are all in the neighborhood of 2 × 10^{13} l./m. min. at 25°[10] and are diffusion controlled. Such a value for k_f provides a value for k_b of about 10^{10} sec.$^{-1}$ in methanol at 25°.[11] Use of eq. 1, coupled with the assumption that the transmission coefficient (κ) is equal to unity for change of configuration, provides an activation energy for configurational change of the carbanion ($\Delta E^{\ddagger}$) of about 4 kcal./mole. This activation energy as calculated includes any difference in solvation energy in the transition states for configurational change on the one hand and for exchange of one hydrogen bond for another without change of configuration on the other. The energy of breaking a hydrogen bond is of the same order of magnitude as the above-calculated value of $\Delta E^{\ddagger}$ for configuration alteration.

$$k_b = \kappa(kT/h)e^{-\Delta E\ddagger/RT}$$

If the transition state for configurational alteration involves inversion of a non-flat carbanion, the transition state for inversion ($A^{\ddagger}$) is probably less hydrogen bonded than that for simple exchange ($B^{\ddagger}$). For this case, $\Delta E^{\ddagger}$ as estimated above includes desolvation energy of the transition state.



If the carbanion is planar and owes its asymmetry to electrostatic and steric inhibition of conformational equilibration, the transition state for conformational equilibration ($C^{\ddagger}$) is expected to be as hydrogen bonded as the ground state. For this case, $\Delta E^{\ddagger}$ as estimated would involve little change in solvation energy associated with the rate-limiting process of racemization by rotation about a carbon–sulfur or carbon–phosphorus bond.



Asymmetric

Symmetric $C^{\ddagger}$

Proton *vs.* Carboxyl-leaving Groups in Generation of Sulfonyl Carbanions.—The data of Tables I and II indicate very high stereospecificity for both the decarboxylation and reverse condensation reactions to give 2-octyl phenyl sulfone. In fact, the stereospecificity is too high to be in a range which allows solvent effects to be studied (k_f/k_b ~ 50 for all solvents and both types of reactions). The experimental uncertainty is such as to allow the value of the ratio to be as low as 20 and as high as infinity. The results in various solvents are within experimental error of one another. With proton or deuteron as leaving group, the same ratio was found to vary between 20 and almost 4000,[3b] so the results indicate that no difference

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[9] R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2441 (1953).

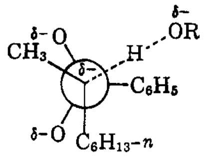
[10] M. Eigen and J. Schoen [*Z. Elektrochem.*, **59**, 483 (1955); *Z. physik. Chem.* (Frankfurt), **3**, 126 (1955)] have reported that $k = 3 \times 10^{10}$ l./m. sec. for the reaction $H_3ND^+ + OH^- \xrightarrow[k]{} H_3N + DOH$. See also M. T. Emerson, E. Grunwald, M. L. Kaplan and R. A. Kromhout, *J. Am. Chem. Soc.*, **82**, 6307 (1960).

[11] In methanol at 100°, k_e/k_α = 10,[3b] and this ratio is presumed not to change much in passing to 25°.

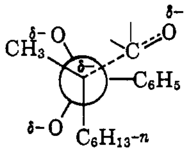
was detected between hydrogen and carbon as leaving group. To the extent data are available, the stereospecificity seems independent of the leaving group.

For the hydrogen–deuterium exchange reaction, the principle of microscopic reversibility requires that, aside from isotope effects, proton or deuteron capture occurs from the same side of a flat asymmetric anion from which a deuteron or proton departed. With carbon as leaving group, the principle of microscopic reversibility does not apply. Thus the stereospecific capacities of the sulfonyl carbanion are independent of the applicability of the principle of microscopic reversibility to the reaction.

To the extent that reaction occurs from a particular conformation, the selectivity would probably depend on repulsion between like charges in the transition states in question. Charge distribution in transition state D‡ with hydrogen as leaving group should not be very different from E‡ with carbon as leaving group.

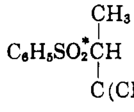


D‡



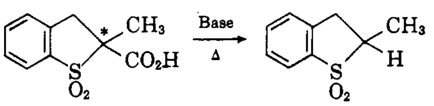
E‡

Steric and Ring Confinement Effects on Configuration of the Sulfonyl Carbanion.—In a recent communication, the stereochemistry of two new sulfonyl carbanions was examined.[12] The relative rates of base-catalyzed hydrogen–deuterium exchange and of racemization of IV were examined in 2:1 ethanol–water, and k_e/k_α was found to be 59 as compared to 42 observed for 2-octyl phenyl sulfone (III) in the same solvent.[3c] The authors claim this result "excludes" the possibility that the α-sulfonyl carbanion has a pyramidal bonding arrangement. This conclusion rests on the expectation that if the carbanion was pyramidal, the greater B-strain in that from IV over that from III should provide $[k_e/k_\alpha]_{IV} \ll [k_e/k_\alpha]_{III}$. The possibility exists that steric effects would operate in a direction exactly opposite to the above expectation.[12] If steric effects on solvation of the anion in ethanol–water are greater than B-strain effects, the electrostatic advantage of a pyramidal anion would be buttressed by substitution of the *tert*-butyl for the *n*-hexyl group, and $[k_e/k_\alpha]_{IV}$ might be greater than $[k_e/k_\alpha]_{III}$, as is observed. For the anions from both III and IV, steric inhibition of solvation would be less for the pyramidal than for the trigonal configuration, but the effect would be greater for the anion derived from the compound which contains the *tert*-butyl group (IV) than for that with the *n*-hexyl group (III).



$C_6H_5SO_2\overset{*}{C}H(CH_3)C(CH_3)_3$

IV



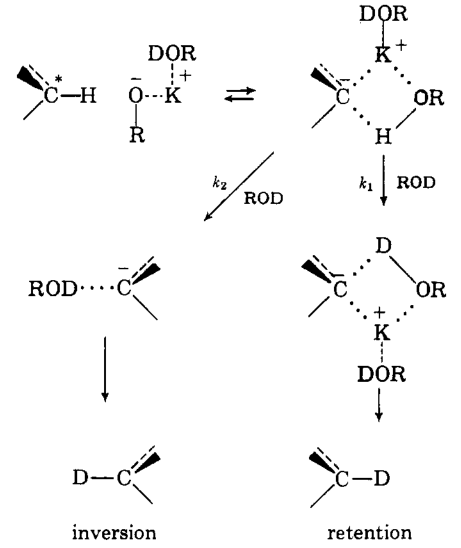
V VI

In a more striking observation,[12] optically active V was found to decarboxylate to ultimately produce racemic VI. The conclusion was reached that the carbanion of VI was planar and symmetric, and therefore that the open-chain carbanions from III and IV were also flat, but asymmetric due to conformational restrictions. This experiment, although very interesting, does not in our opinion rule out non-planar open-chain α-sulfonyl carbanions. The carbanion derived from VI could well be planar since the conformational restriction of the ring system destroys the electrostatic driving force for a pyramidal anion. In fact, pole–dipole repulsions in the anion of VI could be minimized with a trigonal hybridization. The fact that carbanions incorporated in ring systems exhibit different stereochemical behavior from that of their open-chain counterparts has been demonstrated for the α-cyano carbanion.[13] The forced pyramidal character of the three-membered ring anion was not used to infer that the open-chain α-cyano carbanion was also pyramidal.[13]

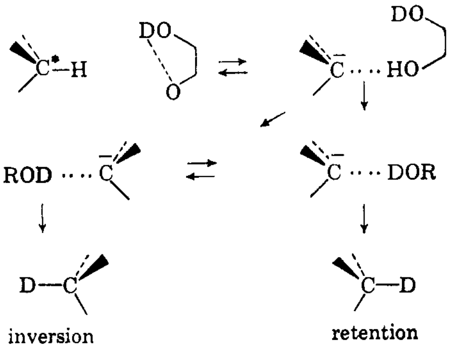
Asymmetric Solvation Effects.—The term "asymmetric solvation" used here and elsewhere refers to the

CHART I

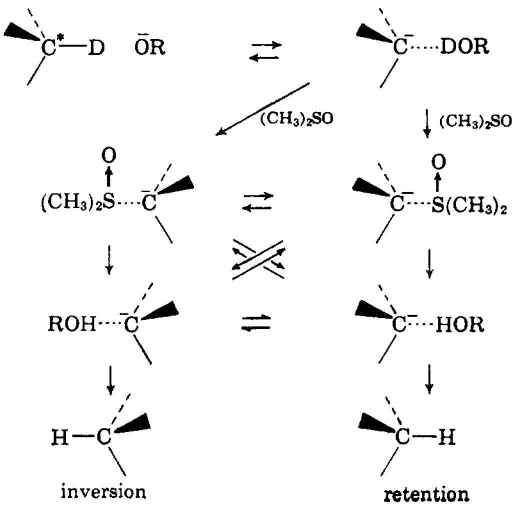
Exchange in *tert*-butyl alcohol, R = $(CH_3)_3C$



Exchange in ethylene glycol, R = $DOCH_2CH_2$



Exchange in dimethyl sulfoxide, R = CH_3



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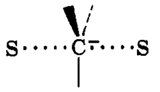
(12) E. J. Corey, H. König and T. H. Lowry, *Tetrahedron Letters*, **12**, 515 (1962).

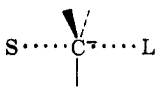
contribution which solvation makes to raising the energy of the transition state for racemization of an asymmetric species. The term applies equally well to solvated trigonal as to solvated tetrahedral carbanions. Operationally, asymmetric solvation effects are detected when large differences in stereospecificity accompany changes in anion-solvating ability of the solvent. All systems studied thus far which give stereospecific electrophilic substitution reactions exhibit asymmetric solvation effects.

Potential roles which asymmetric solvation might play in determining the stereochemistry of pyramidal carbanions are outlined in Chart I. In non-dissociating solvents such as *tert*-butyl alcohol, $k_1 \gtrsim k_2$ because the anion is stabilized configurationally by the hydrogen bond to the leaving group.[14] Isotopically labeled solvent is held at the front of the carbanion by the metal cation, and exchange of one hydrogen bond for another is facilitated. In dissociating dihydric solvents such as ethylene glycol, exchange of one hydrogen bond for a second is facilitated by the bifunctional character of the glycol. However, the solvent-orienting ability of the metal cation is lost. In non-proton donating but dissociating solvents such as dimethyl sulfoxide, the life of the carbanion is extended by solvation with sulfoxide molecules, which are non-proton donating. For all d-orbital-containing systems studied to date, *tert*-butyl alcohol > ethylene glycol > dimethyl sulfoxide in providing net retention in the exchange reaction. Dimethyl sulfoxide as solvent probably provides the best medium to distinguish intrinsic carbanion asymmetry from asymmetric solvation effects, since this solvent preserves the life of the anion long enough to allow the leaving group and its solvating molecules to leave the environment of the carbanion.

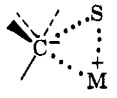
Asymmetric solvation of the 2-phenyl-2-butyl anion provides an interesting basis of comparison for that of the phosphine oxide and sulfoxide systems. Delocalization of charge of a benzyl anion is expected to be most complete in a planar configuration. Solvation effects might enhance or oppose a planar configuration for a benzyl anion, depending on whether solvation occurs from both or only one face of the ion. Solvation from two faces should stabilize a trigonal geometry, whereas solvation from only one side should oppose a planar configuration and induce slight pyramidal character in a species which is itself intrinsically planar. The extent of deformation would depend on solvation energies as well as on whether an ion-pair or a free anion was involved. These models have been employed to explain the three types of stereochemical results obtainable by solvent variation in reactions which generate the 2-phenyl-2-butyl anion.[15]



Flat carbanion
symmetrically
solvated from
both faces; stereochemical
fate, racemization



Flat carbanion
asymmetrically
solvated from
both faces; stereochemical
fate, inversion



Near-planar carbanion
asymmetrically
solvated from
one face; stereochemical
fate, retention

Table V compares the effects of solvent variation on the stereochemical outcome of base-catalyzed hydrogen–deuterium exchange reactions of diphenyl-2-octylphosphine oxide and 2-phenylbutane. In *tert*-butyl alcohol and dimethyl sulfoxide the results are comparable, but differ slightly in the glycols with the oxide giving slight retention and the hydrocarbon inversion. Of the two anions, the 2-phenyl-2-butyl seems the more adaptable to an inversion mechanism. This difference between the two anions provides some support for the thesis that a non-planar carbanion is derived from the phosphine oxide in glycol as solvent.

TABLE V

RATIOS OF RATES OF ISOTOPIC EXCHANGE (k_e) TO RATE OF RACEMIZATION (k_α) IN BASE-CATALYZED HYDROGEN–DEUTERIUM EXCHANGE REACTIONS OF 2-PHENYLBUTANE AND DIPHENYL-2-OCTYLPHOSPHINE OXIDE

Carbanion-stabilizing substituent	T, °C.	Solvent	k_e/k_α
$PO(C_6H_5)_2$[a]	100	$(CH_3)_3COH$	3.3
C_6H_5[b]	~215	$(CH_3)_3COH$	2.3–13
$PO(C_6H_5)_2$[a]	175	$HOCH_2CH_2OH$	1.3
C_6H_5[b]	~260	$(HOCH_2CH_2)_2O$	0.7–0.9[c]
$PO(C_6H_5)_2$[a]	75	$(CH_3)_2SO$[d]	~1
C_6H_5[b]	84	$(CH_3)_2SO$[e]	~1

[a] Data taken from ref. 4b. [b] Data taken from ref. 15b. [c] Values are crude. [d] 4% by weight in methanol. [e] 1.35 M in *tert*-butyl alcohol.

In view of the wide range of solvent, substituent and ring confinement effects on the stereochemical behavior of carbanions stabilized by d-orbital-containing substituents, *we conclude that a variety of configurations which range from sp^2 to sp^3 is available to the ions. No single configuration is demanded by the data.* We are actively continuing our survey of the stereochemical behavior of carbanions stabilized by different d-orbital-containing substituents.

Isotope Effects for Proton Capture by Carbanions.—The data of Table III indicate that, in the decarboxylation of acid I, the carbanion generated exhibits an isotope effect for proton *vs.* deuteron capture in *tert*-butyl alcohol. When the potassium salt of the acid was employed, $k_H/k_D = 1.3$, whereas with the tetramethylammonium salt, $k_H/k_D = 1.8$. In ethylene glycol, $k_H/k_D = 1.0$ with the potassium salt.

With anions whose conjugate acids differ in pK_a from those of the proton donor by many units, proton capture is probably close to diffusion controlled (see last section). It is therefore not surprising that these isotope effects are not large. In decarboxylation of sodium trinitrobenzoate in water and deuterium oxide, $k_H/k_D = 1$ for the solvent isotope effect.[16] In competitive proton capture by highly reactive organometallic reagents in water–heavy water and methanol–deuterated methanol, k_H/k_D was found to range from 0.84 to 1.16.[17] On the other hand, the surprisingly large isotope effect of $k_H/k_D = 5.5$ was calculated for the rate of proton *vs.* deuteron capture by acetone anion in 50% deuterated water[18] in spite of the fact that the rate

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(13) (a) H. M. Walborsky, A. A. Youssef and J. M. Motes, *J. Am. Chem. Soc.*, **84**, 2465 (1962); (b) D. J. Cram, B. Rickborn, C. A. Kingsbury and P. Haberfield, *ibid.*, **83**, 3678 (1961).

(14) The fact that negative carbon forms strong hydrogen bonds with hydroxylic solvents is now well established [L. L. Ferstandig, *ibid.*, **84**, 1323, 3553 (1962)].

(15) (a) D. J. Cram, J. L. Mateos, F. Hauck, A. Langemann, K. R. Kopecky, W. D. Nielsen and J. Allinger, *ibid.*, **81**, 5774 (1959); (b) D. J. Cram, C. A. Kingsbury and B. Rickborn, *ibid.*, **83**, 3688 (1961); (c) D. J. Cram and J. S. Bradshaw, *ibid.*, **85**, 1108 (1963).

(16) R. E. Glick, *Chem. Ind.* (London), 716 (1955).

(17) K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

(18) Y. Pocker, *Chem. Ind.* (London), 1383 (1959).

is probably close to diffusion controlled ($k = 3 \times 10^{12}$ l./m. min.).[9]

The present results suggest a number of tentative conclusions. In ethylene glycol, the starting salt was probably dissociated, and no isotope effect was observed. In *tert*-butyl alcohol, the salt was undoubtedly associated since an isotope effect was observed whose magnitude varied with the nature of the cation. The carbanion must have been part of an ion-pair in the reaction with *tert*-butyl alcohol. Just as water is a stronger solvator of ionic species than deuterium oxide,[19] ordinary *tert*-butyl alcohol is probably a stronger solvator of ionic species than deuterated *tert*-butyl alcohol. If the carbanion reacted faster with the solvent which solvated the ion pair than with the solvent in general (as is probably the case), the isotope effect is thermodynamic rather than kinetic in nature, and the anion would favor protium over deuterium, as was observed.

Experimental

Ethyl 2-Benzenesulfonyloctanoate.—Ethyl benzenesulfonylacetate was prepared[20] in 75% yield, m.p. 42–43°, reported[20] 42–43°. A solution of 35.8 g. of sodium in 1 l. of absolute ethanol was prepared, and 355 g. of ethyl benzenesulfonylacetate was added with stirring. The mixture was warmed until homogeneous. Over a period of several hours, 257 g. of 1-bromohexane was added dropwise. The mixture was then held at reflux for 6 hr., was stirred at 25° for 10 hr., and 900 ml. of ethanol was distilled from the mixture. The viscous residue was shaken with 1 l. of ice-water and 500 ml. of ether. The water layer was extracted with three 500-ml. portions of ether and the combined ether layers washed with three 300-ml. portions of water. The solution was dried, the ether was evaporated at reduced pressure, and the residue was distilled through a 100-cm. column of wire gauze; b.p. 164–165° (0.5 mm.), wt. 375 g. (78%, colorless oil), n^{25}_{D} 1.5022.

Anal. Calcd. for $C_{16}H_{24}SO_4$: C, 61.51; H, 7.74. Found: C, 61.34; H, 7.82.

Ethyl 2-Methyl-2-benzenesulfonyloctanoate.—A solution of 28.0 g. of sodium in 1500 ml. of absolute ethanol was prepared, and 375 g. of ethyl 2-benzenesulfonyloctanoate was added dropwise with stirring. The mixture was warmed somewhat to overcome the resistance to stirring by the curdy precipitate. Methyl iodide (179 g.) was then added slowly, and the precipitate dissolved. After the mixture became homogeneous it was cooled to 25° for addition of the remaining halide. After addition was complete, the mixture was stirred at 25° for 10 hr., and 1300 ml. of ethanol was distilled at atmospheric pressure. The oily residue was added to 1500 ml. of ice-water, and the mixture was extracted with three 750-ml. portions of ether. The combined ether extracts were washed with water, dried, and evaporated under reduced pressure. The residue was distilled, the product being collected at b.p. 174–176° (0.5 mm.), wt. 328 g. (84% as light yellow oil), n^{25}_{D} 1.5044.

Anal. Calcd. for $C_{17}H_{26}SO_4$: C, 62.54; H, 8.03. Found: C, 62.82; H, 8.02.

2-Methyl-2-benzenesulfonyloctanoic Acid (I).—A mixture of 400 ml. of 95% ethanol, 29 g. of potassium hydroxide and 77.7 g. of the above ester was brought to reflux for 10 min. Water, 500 ml., was added, and the resulting mixture was cooled to 0° and poured onto 350 ml. of *concd.* hydrochloric acid at 0°. The cold mixture was extracted with three 300-ml. portions of ether, the ether was washed with three 100-ml. portions of cold water, dried and evaporated at reduced pressure. The crude acid, wt. 68 g. (97%), was recrystallized twice from carbon tetrachloride to give 60 g. of white powder, m.p. 97–98°.

Anal. Calcd. for $C_{15}H_{22}SO_4$: C, 60.37; H, 7.43. Found: C, 60.67; H, 7.58.

(+)-2-Methyl-2-benzenesulfonyloctanoic Acid ((+)-I).—A solution of 86.5 g. of I and 94 g. of quinine in 200 ml. of absolute ethanol was prepared, and after 30 min. the salt separated. The mixture was heated to reflux, and sufficient absolute ethanol was added to effect solution (2100 ml.). The solution was cooled to 25°, and after 3 days white needles separated. A small portion of this salt was converted to acid, which exhibited $[\alpha]^{29}_{546}$ +12.1° (*c* 8.4, chloroform). Five additional recrystallizations of the salt gave acid, $[\alpha]^{29}_{546}$ +15.6° (*c* 8.4, chloroform). Two additional recrystallizations of the salt provided no change in rotation of the derived acid. After the four crystallizations, 35 g. (19%) of the quinine salt was obtained. An additional 7 g. was obtained by fractional recrystallizations of salt from the mother liquors. Thus 42 g. (23%) of optically pure salt was obtained. This material was shaken with 300 ml. of 6 *N* sulfuric acid and 500 ml. of ether, and the aqueous layer was extracted with ether. The combined ether extracts were washed with water, dried, and evaporated to give 19.8 g. of optically pure acid as an oil, $[\alpha]^{29}_{546}$ +15.6° (*c* 8.4, chloroform).

Attempts to obtain (−)-I from the mother liquors failed. Use of cinchonidine gave salt whose acid became more positive on successive recrystallizations.

(−)-3-Benzenesulfonyl-2,3-dimethyl-2-nonanol ((−)-II).—The methyl ester (14 g.) of (+)-I was prepared in 63% yield from 20.1 g. of (+)-I and diazomethane prepared from 12 g. of N-methyl-N-nitrosourea by the usual method.[21] This ester exhibited $[\alpha]^{29}_{546}$ +22.7 (*c* 9.1, chloroform). A solution of methyllithium was prepared from 1.82 g. of lithium wire containing 0.8% by weight of sodium, 19.2 g. of methyl iodide and 75 ml. of anhydrous ether under an atmosphere of dry nitrogen at −30 to −40°. The above ester, 13.5 g. dissolved in 50 ml. of anhydrous ether, was added dropwise over a 2-hr. period to the stirred organometallic solution maintained at −30 to −40°. The mixture was stirred for an additional hour and hydrolyzed by dropwise addition of 30 ml. of cold, saturated ammonium chloride solution. The mixture was shaken with 500 g. of ice, 200 g. of ammonium chloride and 300 ml. of pure ether. The aqueous layer was extracted with two 300-ml. portions of ether. The combined ether extracts were washed with water, dried and evaporated under reduced pressure to give 13.5 g. of an oil, which exhibited infrared bands at 3500 cm.$^{-1}$ (O–H stretch) and 1700 cm.$^{-1}$ (ketone carbonyl). This material was subjected to chromatographic separation on 300 g. of activated neutral alumina. The column was washed with 9.5 l. of 5% ether–95% pentane, and 5 l. of 25% ether–75% pentane eluted 7.9 g. of an oil which exhibited an infrared band at 1700 cm.$^{-1}$ and a rotation of $[\alpha]^{28}_{546}$ −25.4° (*c* 9.3, chloroform). This material was undoubtedly 3-benzenesulfonyl-3-methyl-2-nonanone. With 1 l. of ether, 4.0 g. of additional oil was washed from the column; its infrared spectrum indicated it to be about 90% ketone and 10% desired alcohol, (−)-II. The next 250 ml. of ether contained only (−)-II, wt. 1.4 g. (10%), infrared peak at 3500 cm.$^{-1}$, $[\alpha]^{28}_{546}$ −30.6° (*c* 9, chloroform). This colorless oil could not be induced to crystallize and was analyzed after being film dried at 60° under vacuum.

Anal. Calcd. for $C_{17}H_{28}SO_3$: C, 65.34; H, 9.03. Found: C, 65.16; H, 8.91.

The ketone and ketone–alcohol mixtures were recycled to give additional alcohol, and the total yield of alcohol ultimately amounted to 75%.

Solvents, Bases and Gases.—Dry commercial nitrogen (> 99.5% pure) was passed through two 2 × 20 cm. tubes of copper turnings heated at 300°, then through a washing tower of concd. sulfuric acid, and finally through four 2 by 25 cm. tubes containing calcium chloride, calcium sulfate, ascarite and potassium hydroxide, respectively.

Eastman Kodak Co. white label *tert*-butyl alcohol (1.5 l.) and 150 g. of molecular sieves (Linde, Type 4A, pellets) were allowed to stand for 2 days, and the molecular sieves were replaced with a fresh 150 g. of material. The alcohol was then fractionally distilled through a 100-cm. glass helices column, a middle 850-ml. cut being taken, b.p. 82–82.5°, which was stored under pure nitrogen. This alcohol contained less than 0.01% water by Karl Fischer titration.

Eastman Kodak Co. white label ethylene glycol was similarly purified and stored, b.p. 90° (9.5 mm.), and contained less than 0.01% water.

Dimethyl sulfoxide, J. T. Baker analyzed, was similarly purified and stored, b.p. 74° (9.5 mm.), and contained less than 0.01% water.

Methanol, J. T. Baker analyzed, was refluxed over and distilled from magnesium turnings, the center fraction being collected at 63° and stored under pure nitrogen.

A 10% aqueous solution of Eastman Kodak Co. white label tetramethylammonium hydroxide was decolorized with Norit, and the water was removed under reduced pressure. The white crystalline residue was dried at 0.1 mm. to give a white powder which contained about 3 moles of water (Karl Fischer titration). A 1.23-g. sample of this material was dissolved in 25 ml. of pure *tert*-butyl alcohol, and the water was removed with molecular sieves. Titrations for water before and after indicated that the molecular sieves had removed the water. The solution was titrated for tetramethylammonium hydroxide to a phenolphthalein end-point with standard acid, and for trimethylamine to a brom cresol blue end-point. The results demonstrated the base to be $(CH_3)_4NOH \cdot 0.072(CH_3)_3N$.

Deuterated ethylene glycol (1.98 atoms of deuterium per molecule) and *tert*-butyl alcohol (0.99 atom of deuterium per mole-

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(19) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p. 199.

(20) W. C. Ashley and R. L. Shriner, *J. Am. Chem. Soc.*, **54**, 4410 (1932).

(21) A. Vogel, "Practical Organic Chemistry," Longmans Green and Co., Ltd., London, 1948, p. 969.

cule) were prepared and analyzed as previously.[22] These solvents were dry to Karl Fischer reagent.

Representative Decarboxylation of (+)-2-Benzenesulfonyl-2-methyloctanoic Acid ((+)-I) (Run 1).—Into a 5.0-ml. volumetric flask was weighed 0.298 g. of optically pure (+)-I, and the flask was filled to the mark with dry *tert*-butyl alcohol. In a dry ampoule was placed 0.059 g. of J. T. Baker analyzed potassium carbonate, and the solution of acid was added. The ampoule was flushed with pure, dry nitrogen, sealed, and placed in a constant temperature bath at 90°. A white solid, probably some carbonate, was present during the reaction. After 166 hr., the ampoule was opened, and the contents were shaken with 75 ml. of 67% pure pentane–33% pure ether and 75 ml. of water. The aqueous layer (*p*H 6) was extracted with an additional 25-ml. portion of the pentane–ether mixture. The organic layers were combined, washed with 25 ml. of 5% sodium hydroxide solution, and with three 75-ml. portions of water. The organic layer was dried and evaporated under reduced pressure to give 0.182 g. of 2-octyl phenyl sulfone (III) as an oil, which solidified on standing, m.p. 42–43°, $[\alpha]^{25}_{546}$ +12.8° (*c* 5.3, chloroform). The infrared spectrum of this material was identical with that of authentic III.[3b] Runs 2–7 were similarly conducted.

In a control experiment with 0.100 g. of optically pure III, 92% of III of unchanged rotation was recovered when the substance was submitted to the above isolation procedure.

Stability of (+)-2-Benzenesulfonyl-2-methyloctanoic Acid in Various Solvents in the Absence of Base.—A solution of 0.298 g. of optically pure (+)-I in 5 ml. of *tert*-butyl alcohol was heated at 90° for 170 hr., and the product was put through the same isolation procedure as in run 1. The ether–pentane extracts contained no III. The aqueous phase was acidified with hydrochloric acid and extracted with two 75-ml. portions of ether. The ether layer was washed with water, dried, and evaporated under reduced pressure. The recovered acid, 0.250 g. (84%), possessed the same rotation and infrared spectrum as the starting material. Similar results were obtained in methanol, ethylene glycol and dimethyl sulfoxide.

Optical Stability of (+)-2-Octyl Phenyl Sulfone ((+)-III) under Conditions of its Formation (Control for Run 2).—Sulfone (+)-III, 0.298 g., was mixed with 5 ml. of *tert*-butyl alcohol and 0.059 g. of potassium carbonate in an ampoule sealed under nitrogen. The ampoule was heated at 90° for 46 days. The product was isolated in 98% yield and exhibited a rotation equal to that of run 1 which involved a reaction time of only 166 hr.

Representative Cleavage Reaction of (−)-3-Benzenesulfonyl-2,3-dimethyl-2-nonanol ((−)-II) (Run 8).—To 25 ml. of pure *tert*-butyl alcohol under a nitrogen atmosphere was added 0.0975 g. of freshly cut potassium (cut under pentane and weighed under cyclohexane). After solution was complete, an aliquot of the solution (0.093 *M*) was titrated for base to a phenolphthalein end-point. To a clean, dry 10-ml. flask was added 0.316 g. of optically pure (−)-II, and the flask was flushed with pure nitrogen. The flask was closed with a serum cap, and 5.0 ml. of the basic solution was added with a clean syringe. The mixture became homogeneous and was then transferred to an ampoule with a syringe, where it was further flushed with nitrogen, sealed, and placed in a 25° bath. After 15.5 hr., the contents of the ampoule were shaken with 25 ml. of water and 50 ml. of pure ether. The aqueous phase was extracted with ether and the combined ether layers were washed with water, dried and evaporated under reduced pressure to give 0.119 g. of an oil. This material was chromatographed on a 1 by 25 cm. column of 15 g. of activated neutral alumina. Elution of the column with 60% ether–40% pentane gave 0.095 g. of product in the first 125-ml. fraction, m.p. 42°. This substance ((+)-III) gave $[\alpha]^{26}_{546}$ +12.9° (*c* 5.1, chloroform) and exhibited an infrared spectrum identical with that of authentic (+)-III.

Corrections Applied to Runs 8, 9 and 10 for Racemization of Product Once Formed.—For run 8, the rate constant, $k_{\alpha}^{\mathrm{obs}} = 3.9 \times 10^{-6}$ sec.$^{-1}$ was employed, which was obtained[3b] at 25° with a 0.375 *M* solution of (+)-III in 0.098 *M* potassium *tert*-butoxide in *tert*-butyl alcohol (run 20).[3b] The product once formed was estimated to have racemized about 3% in run 8.

For run 9, the rate constant $k_{\alpha}^{\mathrm{obs}} = 8 \times 10^{-7}$ sec.$^{-1}$ was used, which was obtained at 100° at 0.375 *M* substrate and 0.06 *M* potassium ethylene glycoxide in ethylene glycol (run 15).[3b] The product once formed was estimated to have racemized about 2% in run 9.

For run 10, the rate constant, $k_{\alpha}^{\mathrm{obs}} = 6 \times 10^{-5}$ sec.$^{-1}$ was used, which was obtained at 25° for 0.375 *M* of (+)-III in dimethyl sulfoxide–8% methanol and 0.20 *M* in potassium methoxide (run 11).[3b] Under the conditions of run 10, the product once formed would completely racemize even if it were originally optically active.

The conditions of time, temperature and base concentration were minimal for runs 8–10, as shown by preliminary experiments.

Decarboxylations of (+)-2-Benzenesulfonyl-2-methyloctanoic Acid ((+)-I) in Equivalent Amounts of Deuterated and Nondeuterated Solvents. Run 11.—In a 5.0-ml. volumetric flask were placed 0.298 g. of (+)-I, 2.032 g. of *tert*-butyl alcohol and 2.033 g. of *tert*-butyl alcohol-OD. This mixture was added to an ampoule containing 0.059 g. of dry potassium carbonate. The ampoule was flushed with nitrogen, sealed and heated at 90° for 130 hr. Product (0.225 g. or 88%) was isolated and the deuterium content determined by the same infrared method used previously[3b] was found to be 43 ± 1%.

Run 12.—A solution of 0.356 g. of $(CH_3)_4NOH \cdot 0.027(CH_3)_3N$ in 10.0 ml. of *tert*-butyl alcohol was diluted with 9.856 g. of *tert*-butyl alcohol-OD. The total volume was 25.0 ml. and the base concentration 0.144 *M*. To each of 2 ampoules was added 5.0 ml. of the solution and 0.298 g. of (+)-I. Both tubes were flushed with nitrogen and sealed. One tube was heated at 90° for 45 hr., and the other was shaken at 25° for 5 hr. to ensure homogeneity. The tubes were then opened; a small sample was withdrawn from each and the *tert*-butyl alcohol distilled under reduced pressure at 25°. These materials were analyzed for deuterium by combustion and falling drop method. The solvent from the ampoule which was not heated gave 57.1% of one atom of deuterium per molecule, and that from the ampoule which was heated gave 53.4% of one atom of deuterium per molecule. The remainder of the solution from the ampoule which was heated was treated as in run 1, and the (+)-III recovered (0.180 g., 60%) was analyzed for deuterium by combustion and falling drop method and found to contain 38.5% of one atom of deuterium per molecule.

Run 13 was conducted as was run 11, except that ethylene glycol was substituted for *tert*-butyl alcohol. Results are recorded in Table III.

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[22] D. J. Cram and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 2178 (1961).