method to be 45% deuterated. The values below are all in good agreement with one another except for run 3. Combustion analysis of the product from run 3 indicated 135% deuterated which demonstrated ring deuteration. The infrared spectrum of this sample confirmed this conclusion. Ring deuteration interfered slightly with deuterium analysis at the 2-octyl position, and explains the 8% spread in analytical data for run 3.

Run	Exchange, %		Run	Exchange, %	
	10.98 μ	14.29 μ		10.98 μ	14.29 μ
1	69	72	5	67	65
2	48	46	6	63.5	62
3	37.5	29.5	7	17	15
4	41	44	8	42	42.5

# Electrophilic Substitution at Saturated Carbon. XVII. Stereochemistry of Carbanions Stabilized by Sulfoxide Group[1,2]

BY DONALD J. CRAM AND STANLEY H. PINE

Two diastereometrically related isomers of 2-octyl phenyl sulfoxide were prepared in an optically pure state. The kinetics of base-catalyzed hydrogen–deuterium exchange and of epimeric equilibrium were studied in tert-butyl alcohol-OD. The same isomers deuterated in the 2-octyl position were also prepared, and similarly studied in tert-butyl alcohol and 1.2 M methanol in dimethyl sulfoxide. The position of epimeric equilibrium between the two diastereomers was determined, and configurational assignments were made. The ratios of rate constants for exchange (k_e) and for epimerization (k_α) varied between extremes of 3.6 and 0.6, depending on which diastereomer and what solvent was employed. In tert-butyl alcohol, net retention of configuration was observed for both diastereomers $(k_e/k_\alpha = 1.2$ to 3.6). In dimethyl sulfoxide, one diastereomer gave small net retention and the other net inversion $(k_e/k_\alpha = 0.6$ to 1.4). These results are attributed to asymmetric solvation of carbanions which are intrinsically asymmetric only because of the asymmetric center at sulfur. Sulfur was found to maintain configuration under the conditions of these experiments. Attempts to effect base-catalyzed hydrogen–deuterium exchange of 2-octyl phenyl sulfide failed.

Previous investigations in this series[3] established that the carbanion derived from optically active 2-octyl phenyl sulfone (I) was asymmetric. However, the carbanion generated from optically active diphenyl-2-octylphosphine oxide (II) by proton abstraction did not itself exhibit any asymmetric properties.[4]

The present study was initiated as part of a survey of the effect of d-orbital containing groups on carbanion stereochemistry. The 2-octyl phenyl sulfoxide system (III) was selected since it resembles the phosphine oxide II from an electrostatic point of view, but the sulfone I in the sense that the sulfone and sulfoxides are different oxidation states of sulfur.
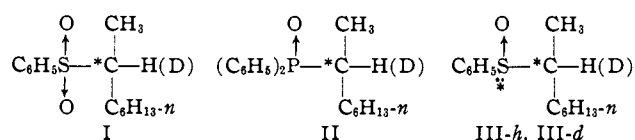
Unlike I or II, sulfoxide III contains two asymmetric centers, one at sulfur and one at carbon. The rate constants for base-catalyzed hydrogen isotope exchange (k_e) and for epimeric equilibration at carbon (k_α) were measured. The ratio k_e/k_α was then used to determine the stereochemical course of electrophilic substitution at saturated carbon.

Preparation, Equilibration and Relative Configurations of Diastereomers of Sulfoxide III.—Optically pure (−)-2-octyl phenyl sulfide[5] was oxidized with tert-butyl hydroperoxide,[6] and the resulting diastereomers were separated by careful chromatography on silica gel followed by fractional crystallization. The two diastereomers differed in both their signs and magnitudes of rotation. The substance, m.p. 20.0–

21.5°, exhibited $[\alpha]^{25}_{546} -192°$ (c 2 95% ethanol), and its isomer gave m.p. −3.7 to −2.2°, $[\alpha]^{27}_{546} +173°$ (c 2 95% ethanol). From optically pure (−)-2-octyl-2-d phenyl sulfide[3b] was similarly obtained two of the isomers of III-d: m.p. 20.0–21.8°, $[\alpha]^{25}_{546} -189°$ (c 2 95% ethanol) and m.p. −1.0 to +1.0°, $[\alpha]^{25}_{D} +173°$ (c 2 95% ethanol). As expected, the effect of deuterium at the 2-octyl position has an indistinguishable effect on the rotation of these compounds.

In the oxidation of sulfide to sulfoxide the configuration at carbon was unaltered, and therefore the diastereomers obtained differ only in their configurations at sulfur.[7] The configuration of 2-octanol has been determined,[8] and (+)-2-octanol was found to have the S- and (−)-2-octanol the R-configuration.[9] Conversion of (+)-2-octanol to (−)-2-octyl phenyl sulfide occurs with inversion,[5] and so the absolute configurations at carbon of the diastereomers obtained from this isomer are both assigned as R.

Others have studied asymmetric induction in the oxidation of asymmetric sulfides to sulfoxides.[10] Application of the principles of steric control of asymmetric induction[11] to the oxidation of (−)-R-2-octyl phenyl sulfide leads to the structure (−)-(R)-2-octyl phenyl sulfoxide-(R) for the higher melting isomer, which was produced in excess of (+)-(R)-2-octyl phenyl sulfoxide-(S) by a factor of 1.6. This conclusion is based on the reasonable assumption that the peroxide attacks the electron pair on sulfur which is distributed between hydrogen and n-hexyl when the molecule is in its most stable conformation.

(7) If the rotational contribution of each asymmetric center is additive, the sulfoxide contribution to the rotation is ±182° and that of carbon is ±10°. The predominant rotational contribution of the sulfoxide function is striking.

(8) (a) P. A. Levene, A. Walti and H. L. Haller, J. Biol. Chem., 71, 465 (1926); (b) K. Wiberg, J. Am. Chem. Soc., 74, 3891 (1952); (c) W. E. Doering and R. W. Young, ibid., 74, 2997 (1952).

(9) R. S. Cahn, C. K. Ingold and V. Prelog, Experientia, 12, 81 (1956).

(10) (a) T. Lavine, J. Biol. Chem., 169, 477 (1947); (b) A. Mayr, E. Montanari and M. Tramontini, Gazz. chim. ital., 90, 739 (1960); (c) K. Balenovic, N. Bregant and D. Francetic, Tetrahedron Letters, 6, 20 (1960); (d) C. A. Kingsbury and D. J. Cram, J. Am. Chem. Soc., 82, 1810 (1960); (e) K. Balenovic, I. Bregoved, D. Francetic, I. Monkovic and V. Tomasic, Chem. Ind. (London), 469 (1961).

(11) (a) D. J. Cram and F. A. Abd Elhafez, J. Am. Chem. Soc., 74, 5828 (1952); (b) D. J. Cram and D. R. Wilson, ibid., in press, and intermediate papers.

(1) This work was supported by a grant from the National Science Foundation.

(2) Some of the results of this paper appeared in preliminary form: D. J. Cram, R. D. Partos, S. H. Pine and H. Jäger, J. Am. Chem. Soc., 84, 1742 (1962).

(3) (a) D. J. Cram, W. D. Nielson and B. Rickborn, ibid., 82, 6415 (1960); (b) D. J. Cram, D. A. Scott and W. D. Nielsen, ibid., 83, 3696 (1961); (c) D. J. Cram and A. S. Wingrove, ibid., 84, 1496 (1962).

(4) (a) D. J. Cram and D. Partos, ibid., 85, 1093 (1963); (b) D. J. Cram and A. S. Wingrove, ibid., 85, 1100 (1963).

(5) J. Kenyon, H. Phillips and V. P. Pittman, J. Chem. Soc., 1072 (1935).

(6) L. Bateman and K. R. Hargrave, Proc. Roy. Soc. (London), A224, 389 (1954).

Favored

$(-)$-(R)-2-octyl phenyl sulfide

$(CH_3)_3CO_2H$

$(+)$-(R)-2-octyl phenyl
sulfoxide-(S), 1

$+$

$(-)$-(R)-2-octyl phenyl
sulfoxide-(R), 1.6
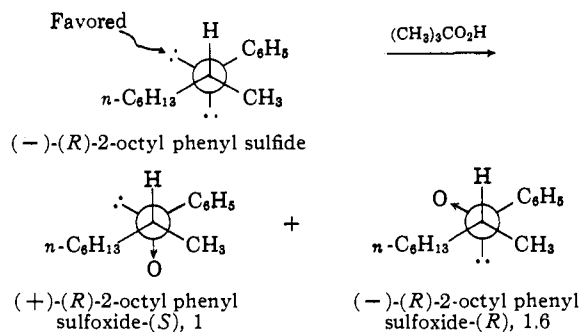
Epimeric equilibration of several isomers of III with potassium *tert*-butoxide in dimethyl sulfoxide at 60° produced sulfoxide which was oxided to sulfone I, and analyzed polarimetrically, with optically pure sulfone as standard. Control experiments demonstrated that oxidation of known mixtures of the diastereomeric sulfoxides produced sulfone whose rotation accurately measured the ratios of the diastereomeric starting materials. That epimerization at sulfur did not occur during the base-catalyzed epimerization at carbon was demonstrated by the fact that once equilibrium was reached, the rotation of sulfone ultimately obtained did not change with extended times for the equilibration.[12] Table I records the results.

TABLE I

EPIMERIC EQUILIBRATION OF 0.17 M SOLUTIONS OF OPTICALLY PURE DIASTEREOMERS OF 2-OCTYL PHENYL SULFOXIDE AT 60° IN DIMETHYL SULFOXIDE

Run	Substrate	M KOC(CH$_3$)$_3$	Time, hr.	I $[\alpha]^{25}_{546}{}^a$	Sulfone % opt. pur.	% R-R or S-S at equil.
1	$(-)$-R-R-III-h	0.025	4.0	$+3.3°$	23^b	62
2	$(+)$-S-S-III-h	.001	4.0	-3.7	25^c	63
3	$(+)$-R-S-III-d	.3	1.0	-3.4	23^d	62

^{a} c 6.5, chloroform. ^{b} Based on $[\alpha]^{25}_{546}$ $+14.5°$ (c 6.5, chloroform) for sulfone produced by direct oxidation of $(-)$-R-R-III-h. ^{c} Based on $[\alpha]^{25}_{546}$ $-14.5°$ (c 6.5, chloroform) for sulfone produced by direct oxidation of sulfoxide $(+)$-S-S-III-h. ^{d} Based on $[\alpha]^{25}_{546}$ $+15.1°$ (c 6.5, chloroform) for sulfone produced directly by oxidation of $(+)$-R-S-III-d.

Diastereomer S-S-III (or R-R-III) dominated in the equilibrated mixture by a factor of 1.6. This fact lends strong support to the configurational assignment

$(+)$-R-S-III-h
I

KOC(CH$_3$)$_3$
(CH$_3$)$_2$SO
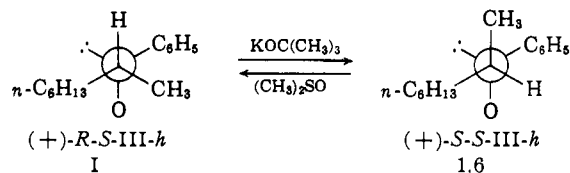
$(+)$-S-S-III-h
1.6

made above based on asymmetric induction. The most stable rotomers of diastereomer $(+)$-R-S-III-h and of diastereomer $(+)$-S-S-III-h are formulated. The latter is expected to be more stable than the former, since the H $>$—$<$ O and CH$_3$ $>$—$<$: steric repulsions of the latter should be less than the CH$_3$ $>$—$<$ O and H $>$—$<$: repulsions of the former. Other steric interactions are common to both A and B. The principles involved in this conformational analysis have been used elsewhere.[13]

Kinetics.—The kinetics of isotopic exchange and epimerization of the diastereomers of III were studied

(12) In unpublished work (D. J. Cram and S. H. Pine), attempts to racemize optically active benzyl O-carboxy phenyl sulfoxide with strong base, strong acid or heat have failed.

(13) F. A. Abd Elhafez and D. J. Cram. *J. Am. Chem. Soc.*, **75**, 339 (1953).

in *tert*-butyl alcohol with potassium *tert*-butoxide as base, and in dimethyl sulfoxide, 1.2 M in methanol with potassium methoxide as base. Both reactions were followed through use of the following device. Optically pure sulfoxide was used in all runs. For each kinetic point, sulfoxide was isolated and oxidized to sulfone I, which was examined for its optical purity and deuterium content through use of techniques used previously.[3b] First-order rate constants were calculated for each point and averaged to give k_α (epimerization) and k_e (isotopic exchange). No trends were observed in the rate constants. In calculations of k_α, the rotation of sulfone obtained from epimerically equilibrated sulfoxide was used as the rotation that would have been obtained at infinite time. The equilibrium constant for the two epimers was assumed to be the same for *tert*-butyl alcohol as for dimethyl sulfoxide, and the diastereomer ratio at equilibrium was taken from Table I. The results are recorded in Table II.

A control run made under the conditions of run 11 without added base led to sulfone identical in deuterium content and rotation with that produced from the same 2-octyl-2-d phenyl sulfoxide used to prepare 2-octyl-2-d phenyl sulfone directly.

Discussion

The values of k_e/k_α provide a convenient means of expressing the stereochemical results of the exchange reactions. As this ratio approaches infinity, the reaction approaches a steric course of complete retention of configuration. Complete racemization is expressed by a ratio equal to unity, whereas complete inversion requires a value for the ratio of 0.5. Table III records values for k_e/k_α for sulfone I; phosphine oxide II and sulfoxides III. The three systems exhibit wide differences in their stereochemical behavior. The mechanisms for the exchange reactions are discussed in detail in paper XVIII of this series.[4b] A number of specific points are considered below.

Comparison of Stereochemistry of Exchange Reactions of d-Orbital Containing Systems.—The values of k_e/k_α for sulfone I in *tert*-butyl alcohol range from 73 to 1980, whereas the values are reduced to 1.2–3.6 for phosphine oxide II and sulfoxide III. In dimethyl sulfoxide, sulfone I gave k_e/k_α of 10, and oxides II and III gave values of 0.58 to 1.4. Thus the stereochemical effects of the sulfone and sulfoxide groups on carbanions are markedly different from one another. Two possible causes of this difference will be evaluated here.

The first possibility is that the sulfonyl group stabilizes charge on the anion largely through p–d overlap, whereas the phosphinoxy and sulfinyl groups act only by an inductive effect. If this were true, the relatively high configurational stability of the sulfonyl carbanion could be correlated with overlap effects.

The Hammett σ-constants calculated from the acidity constants of *m*- and *p*-methylsulfinylbenzoic acid,[14a] *m*- and *p*-methylsulfonylbenzoic acid,[14b] *m*- and *p*-methylsulfinylphenol[14a] and *m*- and *p*-methylsulfonylphenol[14b] have been reported. Comparison of the differences between the σ_p constants for the phenol and benzoic acid can be employed as a measure of the conjugative ability of the methylsulfonyl and methylsulfinyl groups, and has been found to be 0.26 and 0.25 σ-unit for the two groups, respectively.[14] The near identity of these values is strong evidence that the two groups are not far from one another in their ability to stabilize negative charge through overlap effects.[14] Application of the Taft method[15] for

(14) (a) F. G. Bordwell and P. J. Boutan, *ibid.*, **79**, 717 (1957); (b) F. G. Bordwell and G. D. Cooper, *ibid.*, **74**, 1058 (1952).

(15) R. W. Taft and I. C. Lewis, *ibid.*, **80**, 2436 (1958).

TABLE II

ISOTOPIC EXCHANGE AND EPIMERIZATION RATES OF 0.17 M SOLUTIONS OF DIASTEREOMERS OF 2-OCTYL PHENYL SULFOXIDE AT 60.0 ± 0.3°

Run	Isomer	Solvent	Base Type	Base Concn., M	No. pts.	React., %	k_e, sec.$^{-1}$ × 10⁵	$k_α$, sec.$^{-1}$ × 10⁵
4	(−)-R-R-III-h	(CH₃)₃COD[a]	(CH₃)₃COK	0.78	7	88	2.7 ± 0.2	2.3 ± 0.2
5	(−)-R-R-III-h	(CH₃)₃COH	(CH₃)₃COK	.78	3	40	......	1.4 ± .2
6	(−)-R-R-III-d	(CH₃)₃COH	(CH₃)₃COK	.78	7	65	1.4 ± 0.1	1.2 ± .2
7	(−)-R-R-III-d	(CH₃)₃COD[a]	(CH₃)₃COK	.78	3	75	......	1.8 ± .4
8	(+)-R-S-III-d	(CH₃)₃COH	(CH₃)₃COK	.78	6	62	3.6 ± 0.3	1.0 ± .2
9	(+)-R-S-III-d	(CH₃)₃COD[a]	(CH₃)₃COK	.78	1	50	......	1.3 ± .3
10	(−)-R-R-III-d	DMSO[b]	CH₃OK	.20	5	73	19 ± 1	33 ± 3
11	(+)-R-S-III-d	DMSO[b]	CH₃OK	.18	1	70	32 ± 2	23 ± 6

[a] >99% OD. [b] Dimethyl sulfoxide 1.2 M in CH₃OH.

TABLE III

COMPARISON OF $k_e/k_α$ VALUES FOR SULFONE I, PHOSPHINE OXIDE II AND SULFOXIDES III

Compound	Solvent	Temp., °C.	$k_e/k_α$
Sulfone I	(CH₃)₃COH(D)	25	73–1980[a]
Phosphine oxide II	(CH₃)₃COH	100	3.3[b]
(−)-R-R-III-h	(CH₃)₃COD	60	1.2
(−)-R-R-III-d	(CH₃)₃COH	60	1.2
(+)-R-S-III-d	(CH₃)₃COH	60	3.6
Sulfone I	DMSO[c]	25	10[a]
Phosphine oxide II	DMSO[d]	75	1[b]
(−)-R-R-III-d	DMSO[e]	60	0.58
(+)-R-S-III-d	DMSO[e]	60	1.4

[a] Taken from ref. 3b. [b] Taken from ref. 4a. [c] 8% by weight in methanol. [d] 4% by weight in methanol. [e] 1.2 M in methanol.

calculation of $σ_I$ (inductive contribution to $σ$) to Bordwell's[14] $σ_m$ and $σ_p$ values based on dissociation of the substituted phenols gives $σ_I^{SO_2} = 0.56$ and $σ_I^{SO} = 0.44$. If $σ_R = σ − σ_I$ ($σ_R$ is the resonance contribution to $σ$), then for ionization of the p-substituted phenols, $σ_R^{SO_2} = 0.42$ and $σ_R^{SO} = 0.29$. These latter values compose 43% of $σ_p^{SO_2}$ and 40% of $σ_p^{SO}$ for the p-substituted phenols. Thus the % contribution of the resonance component to the total stabilization of charge for the methylsulfonyl and methylsulfinyl groups are close together. This conclusion rules out any explanation of the difference in stereochemical capabilities of the sulfonyl and sulfinyl carbanions in terms of differences in the relative importance of inductive and resonance (or overlap) effects for the two groups.

Another possible difference in the sulfone I and the two oxides II and III which might be associated with the difference in stereochemistry of exchange is the fact that the sulfone is only weakly hydrogen bonding, and the oxides possess very strong hydrogen-bonding properties.[16] Protonation on oxygen of II and III would lead to optically inactive tautomers. No experimental evidence is available on this possibility.

The differences in the stereochemical behavior of the sulfonyl carbanion on the one hand and the sulfinyl and phosphinoxy carbanions on the other are best explained on the basis of the intrinsic symmetry properties of the ions themselves. The results point to an asymmetric sulfonyl carbanion which is consumed faster than it racemizes, and to either symmetric sulfinyl and phosphinoxy carbanions or equilibrating asymmetric but enantiomeric species.[4b] Superimposed on each type of ion are asymmetric solvation effects.

Comparison of the Stereochemistry of Exchange Reactions of Phosphine Oxide II and Sulfoxides III.— In *tert*-butyl alcohol, phosphine oxide II gave $k_e/k_α$ of 3.3, whereas sulfoxide III gave values that ranged be-

(16) For example, D. J. Cram, M. R. V. Sahyun and G. R. Knox, *J. Am. Chem. Soc.* **84**, 1734 (1962).

tween 1.2 and 3.6, depending on which diastereomer was involved. In dimethyl sulfoxide, $k_e/k_α = 1$ for the phosphine oxide, but the two diastereomers of the sulfoxide gave values of 1.4 (net retention) and 0.58 (net inversion). In both solvents, the less thermodynamically stable diastereomer, (+)-R-S-III-d gave the higher value for $k_e/k_α$ (higher retention).

The small difference between the behavior of the phosphine oxide and the diastereomers of the sulfoxide is undoubtedly associated with the difference in symmetry properties. The presence of asymmetric sulfur in the anion of the sulfoxides is expected to provide a low order of asymmetric induction for proton capture by the sulfinylcarbanions. Thus the results reflect a blend of effects due to asymmetric solvation of the carbanion itself, and effects due to steric control of asymmetric induction by the adjacent asymmetric sulfur.

In dimethyl sulfoxide as solvent, if the diastereomeric carbanions equilibrate faster than they capture protons or deuterons *from the medium*,[17] $k_e/k_α = 1$ only if $F_{RSe}^{\ddagger} − F_{SSe}^{\ddagger} = F_{RS} − F_{SS}$, where $F_{RSe}^{\ddagger}$ and $F_{SSe}^{\ddagger}$ are the free energies of the diastereomeric transition states and F_{RS} and F_{SS} those of the respective ground states. The data indicate this condition does not apply, and that the more stable diastereomeric transition state leads to the less thermodynamically stable product.

Conformational analysis[13] applied to the transition states for proton capture (and proton abstraction) provides a clue as to the relative importance of steric and electrostatic effects. A simple electrostatic model for the transition states would place the two negatively charged oxygens *trans* to one another.[18] The two transition states differ only in two sets of steric repul-

Electrostatic model for transition states

sions: S-S-III has C_6H_5 >—< C_6H_{13}-n and CH₃ >—< : whereas R-S-III has C_6H_5 >—< CH₃ and C_6H_{13}-n >—< :. This model predicts that the transition state for R-S-III is more stable than that for S-S-III, which is consistent with the facts. A model for the transition states based only on steric repulsions conflicts with observation. That rotamer is selected for each transition state which places the deuterium–carbon bond in the least hindered position (between O and :). The two transition states differ only in these sets of repul-

(17) The results obtained on the phosphine oxide in the same medium (ref. 4a) suggest this condition applies.

(18) Here and elsewhere enantiomeric structures are sometimes drawn rather than the structures of the compounds actually used. This allows formulas to be compared in which the configuration at sulfur is kept constant. The principles involved remain the same.

sions: S-S-III has CH_3 >—< O and n-C_6H_{13} >—<:, whereas R-S-III has n-C_6H_{13} >—< O and CH_3 >—<:. This model predicts the transition state for S-S-III to be the more stable of the two, which is not in harmony with observation.

Steric model for transition states

In *tert*-butyl alcohol as solvent, asymmetric solvation is superimposed on asymmetric induction to produce net retention for the exchange. Clearly the two diastereomeric carbanions are not equilibrating faster than they react with proton donors of the medium, as was the case in dimethyl sulfoxide. The more stable diastereomer (R-R-III) gives the lower value (1.2) for k_e/k_α, and the less stable diastereomer (R-S-III) the higher value (3.6). As in dimethyl sulfoxide, asymmetric induction favors production of the less stable diastereomer. Asymmetric solvation favors exchange with retention. Thus for R-S-III, the effects combine to produce the higher value for k_e/k_α, but oppose one another to provide the lower value for S-S-III.

Isotope Effects.—As with sulfone I,[3b] the kinetic isotope effects for the exchange and epimerization reactions of (—)-R-R-III-h and (—)-R-R-III-d in *tert*-butyl alcohol are small (Table IV). The isotope effects for exchange and epimerization when solvent and substrate are of opposite isotopic type are both 1.9 (k^H/k^D). The isotope effect for epimerization when solvent and substrate are of the same isotopic type is 0.8. Interpretation of low and even negative isotope effects has been given in detail for sulfone I,[3b] and would seem to apply equally well to sulfoxide III. Only the central idea will be set forth here.

TABLE IV

ISOTOPE EFFECTS IN RACEMIZATION AND EXCHANGE REACTIONS

Run	Isomer	Solvent	$k_e^H/k_e^{D\,a}$	$k_\alpha^H/k_\alpha^{D\,a}$
4	(—)-R-R-III-h	$(CH_3)_3COD$		
6	(—)-R-R-III-d	$(CH_3)_3COH$	1.9	1.9
5	(—)-R-R-III-h	$(CH_3)_3COH$		
7	(—)-R-R-III-d	$(CH_3)_3COD$		0.8

[a] Isotope label applies to substrate rather than solvent.

In eq. 1, k_{-1}, k_2 and k_3 would be expected to vary with the relative acidity of substrate and the molecule made by proton abstraction from substrate. When the pK_a of the carbon acid is many units of ten greater than that of the oxygen acid, $k_{-1} \gg k_2 + k_3$.

Under these conditions, the rate-controlling transition states for epimerization and exchange only involve the breaking of hydrogen bonds to carbanions rather than covalent bonds. Consequently, the isotope effects reflect only the difference in zero point energies for solvation of the starting and rate-controlling transition states, which should be small and not necessarily positive.

$$k = k_1 \times \frac{k_2 + k_3}{k_{-1} + k_2 + k_3} \text{ and } k_\alpha = k_1 \times \frac{k_3}{k_{-1} + k_3} \quad (1)$$
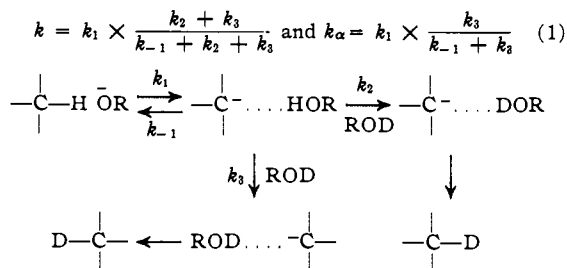
Attempted Exchange Reactions of 2-Octyl-2-d Phenyl Sulfide.—Attempts were made to carry out base-catalyzed exchange reactions with 2-octyl-2-d phenyl sulfide under conditions drastic enough to destroy partially the sulfide. No exchange was observed.

Experimental

Diastereomers of 2-Octyl Phenyl Sulfoxide.—Essentially optically pure (+)-2-octanol, $[\alpha]^{25}_{546} +11.5°$ (neat, l 1 dm.),[19] was converted through its tosylate to (—)-2-octyl phenyl sulfide,[5] $\alpha^{25}_{546} -12.38°$ (neat, l 1 dm.) in 86% yield. The sulfide was oxidized to the sulfoxides with *tert*-butyl hydroperoxide[6] as follows. A mixture of 400 ml. of dry methanol, 15 g. of trichloroacetic acid, 50 g. of *tert*-butyl hydroperoxide and 20 g. of (—)-2-octyl phenyl sulfide was heated at 40° for 85 hr. under a dry atmosphere. The resulting solution was poured into 200 ml. of 5% sodium hydroxide and extracted with 200 ml. of pentane 3 times. The pentane extracts were washed with 150 ml. of 5% sodium hydroxide, three times with water, were dried and evaporated to give 16 g. of crude oily product. This product (5 g.) was purified by chromatography on a 3 by 60 cm. column packed with Baker 80–200 mesh silica gel. Developer was 20% ether–80% pentane. Eluate was collected in 250-ml. fractions. Fractions 1–5 contained sulfide and sulfone, whereas sulfoxide started coming from the column with fraction 9 and was largely eluted with fraction 36. The first sulfoxide eluted had $[\alpha]^{25}_{546} -180°$ (c 2 ethanol, 95%), and the rotation gradually changed to an extreme of $[\alpha]^{25}_{546} +166°$ (c 2 ethanol, 95%) for the last fraction. A total weight of sulfoxide obtained after chromatography was 4.7 g. (71%). The (—)-rotating fractions were recrystallized 4 times from heptane at —30° to 0° to give material (1.5 g.) whose rotation and m.p. remained constant with more recrystallizations: $[\alpha]^{25}_{546} -192 \pm 3°$, $[\alpha]^{25}_D -155 \pm 3°$ (c 2 ethanol, 95%), m.p. 20.5–21.5° ((—)-R-R-III-h). This material exhibited a strong infrared absorption at 9.6 μ characteristic of sulfoxides.[20]

Anal. Calcd. for $C_{14}H_{22}SO$: C, 70.54; H, 9.30; S, 13.45. Found: C, 70.42; H, 9.47; S, 13.45.

The (+)-rotating fractions were combined and rechromatographed as above. The (+)-rotating fractions from this chromatograph were combined, crystallized and recrystallized 5 times from heptane at —50 to —20° to give material (1.0 g.) whose m.p. and rotation did not change with further recrystallizations: $[\alpha]^{27}_{546} +173 \pm 3°$, $[\alpha]^{27}_D +140 \pm 3°$ (c 2 ethanol, 95%), m.p. —3.7 to —2.2° ((+)-R-S-III-h). The deuterated counterpart of this substance was analyzed (see below).

From the total weight of sulfoxide obtained from the first chromatogram, and the weight and rotation of each fraction the % of each diastereomer present in the total was calculated: 62% of (—)-R-R-III-h and 38% of (+)-R-S-III-h.

Diastereomers of 2-Octyl-2-d Phenyl Sulfoxide.—From lithium aluminum deuteride and 2-octanone, 2-octanol-2-d was prepared[21] which was 98.5% deuterated (combustion and falling drop method). This material was resolved,[19] and the optically pure (+)-2-octanol-2-d was converted to 2-octyl-2-d phenyl sulfide, $\alpha^{25}_{546} -12.62°$ (l 1 dm., neat), and to the two diastereomeric sulfoxides by the same method utilized above. Compound (—)-R-R-III-d exhibited $[\alpha]^{25}_{546} -189 \pm 3°$, $[\alpha]^{25}_D -152 \pm 3°$ (c 2 ethanol, 95%), m.p. 20.0–21.8°.

Anal. Calcd. for $C_{14}H_{21}DSO$: C, 70.24; $H_2O + D_2O$, 0.83 mg./mg. of sample. Found: C, 70.21; $H_2O + D_2O$, 0.82 mg./mg. of sample.

Combustion and deuterium analysis by the falling drop method gave 98.5% of one gram atom of deuterium. Compound (+)-R-S-III-d gave $[\alpha]^{25}_{546} +173 \pm 3°$, $[\alpha]^{25}_D +140 \pm 3°$ (c 2 ethanol, 95%), m.p. —1.0 to +1.0°.

Anal. Calcd. for $C_{14}H_{21}DSO$: C, 70.24; $H_2O + D_2O$, 0.83 mg./mg. of sample; S, 13.39. Found: C, 70.13; $H_2O + D_2O$, 0.84 mg./mg. of sample; S, 13.82.

Oxidation of Sulfoxide to Sulfone.—To 0.15 to 0.20 g. of 2-octyl phenyl sulfoxide was added 2.0 ml. of glacial acetic acid and 1.0 ml. of 30% hydrogen peroxide. The solution was heated at 95° for 1 hr., and an additional 1.0 ml. of peroxide was added each hour for a 4-hr. period at 95°. The mixture was cooled and shaken with 4 ml. of water and 25 ml. of pentane. The pentane layer was washed twice with 10-ml. portions of water, dried, and the solvent was evaporated to give 2-octyl phenyl sulfone, which was submitted directly to polarimetric and deuterium analyses. From optically pure (—)-R-R-III-h was obtained (+)-R-I-h,[α] $^{25}_{546} +14.5 \pm 0.4°$ (c 6.5 chloroform), m.p. 45–46°. From optically pure (—)-R-R-III-d was obtained (+)-

(19) J. Kenyon, "Organic Synthesis," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 418.

(20) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 358.

(21) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **75**, 5014 (1953).

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

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

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.

[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

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_H/k_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.

(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).

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).

(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.