Reduction of 4,5,?,?-Bis-tetramethylene-17-keto[2.2]paracyclophane to Mixture of XV and XVI.—A mixture of 1.21 g. of the above ketones was reduced by the Wolff–Kishner–Huang-Minlon procedure to give 1.14 g. of a tan solid. This material was chromatographed on 67 g. of alumina packed in benzene to give 0.968 g. (84%) of a white solid, m.p. 120–130°.

Anal. Calcd. for $C_{24}H_{28}$: C, 91.08; H, 8.92. Found: C, 91.26; H, 8.96.

Extensive attempts to separate XV and XVI at this stage through chromatography on silica gel failed to yield discrete compounds, although the mixture of XV and XVI were freed of minor amounts of impurities. Use of thin layer chromatography indicated that silica gel (Merck silica gel C) deactivated with 6% water packed in cyclohexane–isoöctane (1:1) was the best system. The same solvent was used for elution purposes, 50-ml. fractions being collected. The first 105 fractions contained traces of a yellow oil. Fractions 109 to 119 were combined, as were 120 to 152, and 153 to 185. Fractions 109–119 consisted of 0.174 g. of material whose n.m.r. indicated it to be 96% of XVI (n.m.r. aromatic band at 3.58 τ) and 4% of a non-paracyclophane but aromatic impurity (n.m.r. band at 3.05 τ). Fractions 120–152 (0.430 g.) consisted of 87% XVI and 13% XV, the latter being identified by its n.m.r. band at 3.75 τ. Fractions 153 to 185 consisted of 65% XVI and 35% XV, wt. 0.123 g. Fractions 109–119 were used for n.m.r. data for XVI and fractions 153–185 for XV (Table I).

4,5,7,8-Dibenzo[2.2]paracyclophane (XVII).—Combined fractions 109–119 (0.174 g., see above) were dissolved in 10 ml. of *p*-xylene and treated with 0.564 g. of pure chloranil. The mixture was refluxed under helium for 21 hr., cooled and chromatographed on 25 g. of alumina packed in benzene. A yellow solid, 0.144 g. (85%), m.p. 130–170°, was eluted with benzene. Recrystallization of this material resulted in the substance becoming much more yellow. The substance was chromatographed on 152 g. of silica gel packed in 2.5% chloroform in carbon tetrachloride. Various mixtures of chloroform and carbon tetrachloride eluted oils. Dichloromethane eluted 0.026 g. of a yellow solid, m.p. 205–210° (sublimed). Recrystallization of this material from ether gave pale yellow needles, m.p. 284–286° (in a capillary tube), undepressed by admixture with an authentic sample of anthraquinone. The infrared spectrum of the substance was identical with that of anthraquinone.

Anal. Calcd. for $C_{14}H_8O_2$: C, 80.73; H, 3.87. Found: C, 80.72; H, 4.35.

anti-**[2.2]Paracyclonaphthane** (*anti*-**II**).—Combined fractions 120–152 (0.430 g.) were treated with chloranil by the same procedure to give 0.358 g. of a yellow solid, m.p. 137–175°. Attempted recrystallization of this material from chloroform solution resulted in extensive decomposition. The total combined material was chromatographed on silica gel to give 0.017 g. of anthraquinone and 0.019 of *anti*-II, m.p. 294–296°.

Combined fractions 153–185 (0.123 g.) were aromatized by the same procedure to give 0.088 g. of a yellow solid, m.p. 139–159°. Again attempted crystallization of the material from chloroform resulted in extensive decomposition. The material was chromatographed over 106 g. of silica gel packed in 5% chloroform in carbon tetrachloride. Compound *anti*-II was eluted from the column with 5% chloroform in carbon tetrachloride; wt. 0.030 g., m.p. 298–300°, mixture melting point with *anti*-II prepared from I, 298–300°. The ultraviolet infrared and n.m.r. spectra of the two samples are identical (see spectra section of paper).

A sample of an isomeric mixture of compounds XV and XVI which had not been fractionated was aromatized. The n.m.r. spectrum of the product indicated the presence of 84% of XVII and 16% of *anti*-II. This material was used for the n.m.r. data of Table I for XVII.

An infrared spectrum of *anti*-II in KBr pellet exhibited bands (μ) at: 6.33(m); 6.35(sh); 6.41(sh); 6.63(m); 6.88(sh); 6.91(m); 7.07(w); 7.22(m); 7.32(m); 7.67(w); 7.90)(w); 8.07, 8.20, 8.48, 8.59(w); 8.70(m); 8.85(sh); 9.24, 9.70, 10.12, 10.26, 10.80, 11.25(w); 11.58(m).

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

Electrophilic Substitution at Saturated Carbon. XVI. Stereochemistry of Carbanions Stabilized by Phosphine Oxide Group[1,2]

BY DONALD J. CRAM AND RICHARD D. PARTOS[3]

RECEIVED OCTOBER 9, 1962

Relative base-catalyzed racemization and hydrogen–deuterium exchange rates of diphenyl-2-octylphosphine oxide in various solvents were studied. Exchange occurred with moderate retention of configuration in *tert*-butyl alcohol, very slight retention in ethylene glycol, and racemization in methanol and in dimethyl sulfoxide–methanol. The observed stereospecificity is attributed to asymmetric solvation of the intermediate carbanion, and not to intrinsic asymmetry of the carbanion itself. These results indicate that carbanion–d-orbital interactions *per se* are insufficient to confer asymmetric properties on carbanions.

Six different classes of substituent effects on carbanion stability and on stereochemical capability in open-chain systems are visualized: (1) Groups such as alkyl or hydrogen do not stabilize carbanions, and anions with only these substituents are probably rapidly inverting, sp^3 hybrids.[4] (2) Groups such as carbonyl, ester, amide, cyano or nitro attached to carbanions produce sp^2 hybrids which are ambident in character, and capable of reacting at either carbon or oxygen (nitrogen). Reactions at the more electronegative center produce substances incapable of asymmetry.[5] (3) Aryl groups produce sp^2 hybrids essentially non-ambident, but capable of giving optically active products through asymmetric solvation.[6] (4) Substituents which contain elements such as silicon, phosphorus or sulfur possess d-orbitals capable of stabilizing attached carbanions, the configuration of which in open-chain systems is unclear. With the sulfone group, the carbanions have been demonstrated to be asymmetric.[7] (5) Groups, such as quaternary ammonium, attached to carbanions stabilize the anion through inductive and electrostatic effects (ylide formation); the hybridization at carbon in ylides is not known.[4] (6) Groups such as trifluoromethyl stabilize carbanions through both inductive and "negative hyperconjugative" effects, and the geometry of such carbanions is unknown.[4] Carbanions confined in small rings must accommodate their geometry to the ring system, and have been demonstrated to be special cases.[8]

The present study is addressed to the question of whether the asymmetry-conferring properties of the sulfone group on carbanions also applies to the phosphine oxide group. The system selected for study (I) bears the greatest possible resemblance to the sulfone

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[1] This work was supported by a grant from the National Science Foundation.

[2] Some of the results in 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] National Science Foundation Predoctoral Fellow, 1958–1959.

[4] Stereochemical capabilities of such carbanions are under active study.

[5] (a) D. J. Cram, B. Rickborn, C. A. Kingsbury and P. Haberfield, *J. Am. Chem. Soc.*, **83**, 3678 (1961); (b) D. J. Cram and P. Haberfield, *ibid.*, **83**, 2354 (1961), and references.

[6] (a) D. J. Cram, J. Allinger and A. Langemann, *Chem. Ind.* (London), 919 (1955); (b) D. J. Cram, C. A. Kingsbury and B. Rickborn, *J. Am. Chem. Soc.*, **81**, 5835 (1959); (c) **83**, 3688 (1961); (d) D. J. Cram and B. Rickborn, *ibid.*, **83**, 2178 (1961), and previous papers of this series.

[7] (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) D. J. Cram and A. S. Wingrove, *ibid.*, **84**, 1496 (1962); (d) E. J. Corey and E. T. Kaiser, *ibid.*, **83**, 490 (1961); (e) H. L. Goering, P. T. Towns and B. Dittmar, *J. Org. Chem.*, **27**, 736 (1962).

[8] H. M. Walborsky, A. A. Youssef and J. M. Motes, *J. Am. Chem. Soc.* **84**, 2465 (1962).

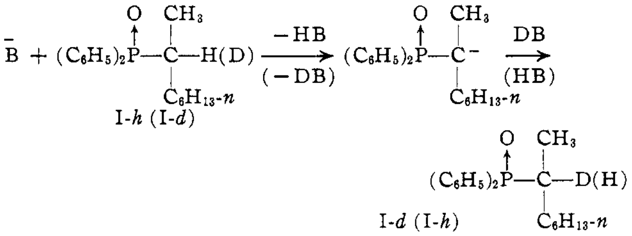
TABLE I

STERIC COURSE OF BASE-CATALYZED HYDROGEN ISOTOPE EXCHANGE REACTIONS OF DIPHENYL-2-OCTYLPHOSPHINE OXIDE (I)

		Base		Substrate										
Run No.	Solvent	Nature	Concn., *M*	Nature	Concn., *M*	*T*, °C.	Time, hr.	Yield, %	M.p., °C.	Rac., %	Exch., %	$k_\alpha \times 10^5$, sec.$^{-1}$	$k_e \times 10^5$, sec.$^{-1}$	k_e/k_α
1	$(CH_3)_3COD$	$(CH_3)_3C\overset{-}{O}\overset{+}{K}$	0.34	I-*h*	0.20	100	11.5	87	84–92	32	71	0.92	3.0	3.3
2	$(CH_3)_3COH$	$(CH_3)_3C\overset{-}{O}\overset{+}{K}$	.34	I-*d*	.20	100	11.75	84	86–94	18	47	.47	1.6	3.4
3	$DOCH_2CH_2OD$	$DOCH_2CH_2OK$	.29	I-*h*	.21	175	96.3	83	85–92	30	34	.10	0.12	1.2
4	$HOCH_2CH_2OH$	$HOCH_2CH_2OK$	.28	I-*d*	.20	175	96	77	85–94	31	43	.11	.16	1.4
5	CH_3OH	CH_3OK	.30	I-*d*	.21	175	90	68	87–95	63	66	.30	.33	1.1
6	CH_3OH	HOK	.33	I-*d*	.20	175	96	66	85–94	56	63	.24	.29	1.2
7	96% DMSO–4% CH_3OH[a]	CH_3OK	.20	I-*d*	.20	75	0.83	78	87–93	16	16	5.9	5.9	1.0
8	96% DMSO–4% CH_3OH[a]	CH_3OK	.21	I-*d*	.21	75	2.75	61	85–92	44	42	5.9	5.5	0.93

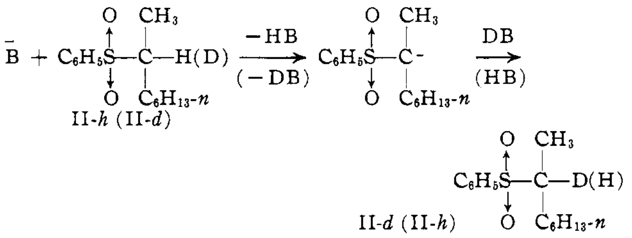
[a] Wt. %. DMSO = dimethyl sulfoxide.

system II.[7] The leaving group (H or D), electrophile (B–D or B–H), media and other substituents are the same.



$$\overset{-}{B} + (C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}-\overset{CH_3}{\underset{C_6H_{13}\text{-}n}{C}}-H(D) \xrightarrow[(-DB)]{-HB} (C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}-\overset{CH_3}{\underset{C_6H_{13}\text{-}n}{C}}^{-} \xrightarrow[(HB)]{DB} (C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}-\overset{CH_3}{\underset{C_6H_{13}\text{-}n}{C}}-D(H)$$

I-*h* (I-*d*) I-*d* (I-*h*)



$$\overset{-}{B} + C_6H_5\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-\overset{CH_3}{\underset{C_6H_{13}\text{-}n}{C}}-H(D) \xrightarrow[(-DB)]{-HB} C_6H_5\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-\overset{CH_3}{\underset{C_6H_{13}\text{-}n}{C}}^{-} \xrightarrow[(HB)]{DB} C_6H_5\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-\overset{CH_3}{\underset{C_6H_{13}\text{-}n}{C}}-D(H)$$

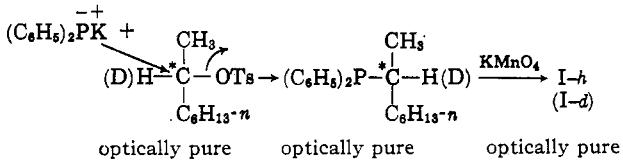
II-*h* (II-*d*) II-*d* (II-*h*)

The ratio of rate constants for hydrogen-isotopic exchange and for racemization (k_e/k_α) were determined in I for purposes of comparison with II. The results and general conclusions are set forth in this paper, but a detailed discussion of mechanism is reserved for paper XVIII of this series.[9]

Results

Preparation of optically pure diphenyl-2-octylphosphine oxide (I-*h*) is formulated. Deuterated material (I-*d*) was similarly prepared from essentially optically pure 2-octyl-2-*d* *p*-toluenesulfonate (97% deuterated in the position indicated). The base-catalyzed deuterium–hydrogen exchange experiments were carried out in *tert*-butyl alcohol, methanol, ethylene glycol and 96% dimethyl sulfoxide–4% methanol, whereas the hydrogen–deuterium exchange runs were made in deuterated *tert*-butyl alcohol or ethylene glycol. In each experiment the reaction was carried part of the way, the phosphine oxide was isolated, subjected to polarimetric analysis to determine the % racemization, and to infrared analysis to determine the % exchange. From the resulting data, single point-pseudo-first-order rate constants were calculated to give values for k_e (rate constant for exchange) and k_α (rate constant for racemization). The ratios for k_e/k_α provide a convenient means of expressing the stereochemistry for the exchange reaction. Thus as $k_e/k_\alpha \rightarrow \infty$, the reaction approaches 100% retention of configuration; as $k_e/k_\alpha \rightarrow 1$, the reaction approaches 100% racemization; as $k_e/k_\alpha \rightarrow 0.5$, the reaction approaches 100% inversion of configuration. Table I lists the results.

$$K + (C_6H_5)_2PCl \longrightarrow (C_6H_5)_2\overset{-}{P}\overset{+}{K}$$



$$(C_6H_5)_2\overset{-}{P}\overset{+}{K} + (D)H-\overset{CH_3}{\underset{C_6H_{13}\text{-}n}{\overset{*}{C}}}-OTs \rightarrow (C_6H_5)_2P-\overset{CH_3}{\underset{C_6H_{13}\text{-}n}{\overset{*}{C}}}-H(D) \xrightarrow{KMnO_4} I\text{-}h\ (I\text{-}d)$$

optically pure optically pure optically pure

Discussion

Configurational and Conformational Requirements for d-Orbital Stabilization of Carbanions.—Experimental evidence has accumulated that d-orbital stabilization of carbanions has little configurational or conformational requirements.[10] Crystal structure determination of $(CH_3)_2NSO_2N(CH_3)_2$ revealed that hybridization at sulfur was $sp^{2.23}$.[11] Molecular orbital calculations[11] carried out on the same compound gave $p^{2.23}$–d overlap of 0.31 as compared to p^2–d overlap of 0.32. This neutral tetramethylsulfonamide in the crystalline state was then considered as a model for the charged 2-octyl phenyl sulfone anion in solution. The conclusion was reached that inversion of the carbanion would be too rapid to explain the stereochemistry of the reaction, which was attributed to restriction of rotation of a planar or near planar carbanion. This latter explanation was attributed to Corey, *et al.*,[7d] although in actual fact we first discussed this possibility.[7a]

We consider that tetramethylsulfonamide in a crystal lattice is a poor model for the sulfonyl carbanion in solution,[11] both on structural and environmental grounds. The only structural features that the two species have in common is that both contain an SO_2 group. Two amino groups bear little resemblance to a phenyl and a 2-octyl anion group. Solvation energies of a carbanion in media which contain hydroxyl groups amount to many kilocalories per mole, since at least one and possibly more hydrogen bonds are involved.[12] Since the activation energy for racemization of an asymmetric carbanion also involves only a few kilocalories per mole, carbanion solvation undoubtedly is very important in both determining its configuration and fate.[9]

Although the sulfonyl group stabilizes carbanions more than the phosphinoxy group, the presence of multiple bonding between sulfur and carbon in the sulfonyl carbanion would imply similar multiple bond-

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(9) D. J. Cram and A. S. Wingrove, *J. Am. Chem. Soc.*, **85**, 1100 (1963)

(10) (a) W. E. Doering and L. K. Levy, *ibid.*, **77**, 511 (1955); (b) H. E. Zimmerman and B. S. Thyagarajan, *ibid.*, **82**, 2505 (1960); (c) R. Breslow and E. Mohacsi, *ibid.*, **83**, 4100 (1961); (d) S. Oae, W. Tagaki and A. Ohno, *ibid.*, **83**, 5037 (1961).

(11) T. Jordan, W. Smith and W. N. Lipscomb, *Tetrahedron Letters*, **2**, 37 (1962).

(12) The fact that negative carbon forms strong hydrogen bonds with hydroxylic solvents is now well established [L. L. Ferstandig, *J. Am. Chem. Soc.*, **84**, 1323 (1962)].

ing in the anion of the phosphine oxide. The difference in behavior of the two systems suggests that factors other than multiple bonding control the stereochemistry. The balance of evidence points to no strict conformational or configurational requirements for p–d-overlap for carbanions attached to second row elements.

Intrinsic Asymmetry *vs.* Asymmetric Solvation of Carbanions.—Table II compares the k_e/k_α values for phosphine oxide I, sulfone II[7b] and 2-phenylbutane.[6c] Although I and II are both systems which provide d-orbitals for stabilization of the carbanion intermediates, the k_e/k_α values of the exchange reactions for the two systems are different over the whole range of solvents. Sulfone II in *tert*-butyl alcohol exhibits values of k_e/k_α of 73 to 1980 (I gives 3.3), in methanol and dimethyl sulfoxide values of 10 (I gives 1), in ethylene glycol values of 15 to 32 (I gives 1.3). On the other hand, the values of k_e/k_α for phosphine oxide I and 2-phenylbutane are of the same order of magnitude in *tert*-butyl alcohol, and are identical in dimethyl sulfoxide. Although k_e/k_α for 2-phenylbutane was not determined in ethylene glycol, values of 0.7–0.9 (small net inversion) were observed in diethylene glycol, whose dielectric constant and polarity closely resemble that of ethylene glycol. In ethylene glycol, phosphine oxide I exchanges with very low net retention (k_e/k_α = 1.3).

TABLE II

VARIATION OF k_e/k_α WITH SOLVENT AND WITH CARBANION STABILIZING SUBSTITUENT

Substituent	T, °C.	Solvent	k_e/k_α
$SO_2C_6H_5$[a]	25	$(CH_3)_3COH$	73–1980
$PO(C_6H_5)_2$	100	$(CH_3)_3COH$	3.3
C_6H_5[b]	~215	$(CH_3)_3COH$	2.3–13
$SO_2C_6H_5$[a]	100	$HOCH_2CH_2OH$	15–32
$PO(C_6H_5)_2$	175	$HOCH_2CH_2OH$	1.3
C_6H_5[b]	~260	$(HOCH_2CH_2)_2O$	0.7–0.9[c]
$SO_2C_6H_5$[a]	100	CH_3OH	10
$PO(C_6H_5)_2$	175	CH_3OH	1.1
$SO_2C_6H_5$[a]	25	$(CH_3)_2SO$[d]	10
$PO(C_6H_5)_2$	75	$(CH_3)_2SO$[e]	~1
C_6H_5[b]	84	$(CH_3)_2SO$[f]	~1

[a] Data taken from ref. 7b. [b] Data taken from ref. 6c. [c] Values are crude. [d] 8% by wt. in methanol. [e] 4% by wt. in methanol. [f] 1.35 M in *tert*-butyl alcohol.

These data indicate that the carbanion stabilized by the phosphinoxy group resembles the phenyl carbanion, whose stereochemical behavior was largely governed by asymmetric solvation effects of an otherwise symmetric species. The similarity suggests that the phosphinoxy carbanion likewise provides stereospecific results because of asymmetric solvation, and not because of intrinsic asymmetry. A detailed discussion of reaction mechanism is given in paper XVIII of this series.[9]

Experimental

(—)-Diphenyl-2-octylphosphine Oxide ((—)-I-*h*).—The *p*-toluenesulfonate of optically pure (−)-2-octanol, $[\alpha]^{25}_{546}$ −11.8° (neat), was prepared as before.[13] Potassium, 25 g., was added (with stirring) to a solution of 30 g. of diphenylchlorophosphine in 400 ml. of dry, pure dioxane under an atmosphere of dry helium. The mixture was heated at reflux for 2 hr. during which time the solution changed from orange to an intense green. The solution was then transferred with helium pressure to a second helium flushed flask, care being taken to leave the excess potassium behind. To the stirred mixture held at 40°, 39 g. of *p*-toluenesulfonate ester was added slowly in small portions. The color of the solution was completely discharged. Moist ether followed by wet dioxane were added cautiously, and the mixture was shaken with a 1:1 mixture of ether and water. The aqueous layer was washed with ether, and the combined ether layers were washed with water, dried and evaporated. The residue was distilled at 1.5 mm., and diphenyl-2-octylphosphine was collected at 180–200° pot temperature. This material was dissolved in 300 ml. of acetone and "titrated" with a saturated solution of potassium permanganate in acetone until a red color persisted. A trace of aqueous hydrogen peroxide was added to destroy the slight excess of potassium permanganate. The mixture was filtered and the solvent was evaporated. The residual oil crystallized to give 21 g. of the phosphine oxide ((−)-I-*h*). Two recrystallizations of this material from high boiling ligroin followed by molecular distillation gave 11 g. (25%) of (−)-I-*h*, m.p. 94–96°, $[\alpha]^{25}_{546}$ −14.5° (*c* 7, carbon tetrachloride). A small amount of this material was chromatographed on silica gel with 25% ether in benzene as developer to give (−)-I, m.p. 93–95.5°, $[\alpha]^{25}_{546}$ −14.7° (*c* 6.4, carbon tetrachloride). The infrared spectrum of this material was identical with that of unchromatographed compound.

Anal. Calcd. for $C_{20}H_{27}PO$: C, 76.43; H, 8.60; P, 9.87. Found: C, 76.52; H, 8.78; P, 9.95.

(+)-**Diphenyl-2-deuterio-2-octylphosphine Oxide** ((+)-I-d).—Essentially optically pure 2-octanol-2-*d*, $[\alpha]^{25}_{546}$ +11.5° (neat), was prepared as before,[7b] converted to its *p*-toluenesulfonate, and this ester was submitted to the above procedure. The product, (+)-I-*d*, was obtained in about 10% yield, m.p. 96–98°, $[\alpha]^{26}_{546}$ +15.2° (*c* 5.1, carbon tetrachloride). Combustion and analysis of the water by the falling drop method demonstrated the compound to have 97.3% of one atom of deuterium per molecule.

Isotopic Exchange Experiments.—All solvents were dried over Molecular Sieves. Deuterated *tert*-butyl alcohol (99.5% OD by combustion analysis and falling drop method) was prepared as before,[6c] as was deuterated ethylene glycol[6c] (99.5% $(OD)_2$ by combustion analysis and falling drop method). All basic solutions were prepared by dissolving the approximate amount of potassium in solvent under an atmosphere of dry purified nitrogen. Aliquots of the solutions obtained were titrated to obtain the exact base concentrations. The dissolution of potassium in methanol and ethylene glycol was carried out at 0°. The solution of potassium methoxide–methanol–dimethyl sulfoxide was prepared by mixing a 4 N solution of potassium methoxide in methanol with dry pure dimethyl sulfoxide. All runs were made in sealed ampoules, and product was isolated in the same way in each case. The procedure is illustrated with run 2.

A sample of (+)-I-*d* prepared above, 0.127 g., was placed in a test-tube with a constricted neck which had been flushed with nitrogen; 2 ml. of a solution of 0.34 N potassium *tert*-butoxide in *tert*-butyl alcohol was added, the tube was sealed and placed in a 100° bath for 11.75 hr. The ampoule was cooled, opened, and its contents shaken with 30 ml. of water and ether. The water layer was extracted with 30 ml. of ether, the combined ether layers were washed with four 15-ml. portions of water, dried and evaporated under vacuum on a rotatory evaporator. The total residue was transferred to a sublimation apparatus with a few ml. of chloroform, the chloroform was evaporated and the residue was sublimed (total sample) at 150° (1 mm.) to give 0.107 g. of material, which was homogenized and submitted to polarimetric and deuterium analysis (see below).

Infrared and Polarimetric Analysis.—Polarimetric analyses were made with 1-dm. tubes in carbon tetrachloride solutions, *c* 7, at λ 546 mμ with a Zeiss circular scale polarimeter. Observed rotations ranged from $\alpha = 0.40 \pm 0.02°$ to $\alpha = 0.98 \pm 0.02°$.

Infrared spectra (Beckman IR-5 spectrophotometer rock salt prism and cells 0.1-mm. thickness) of I-*h* and I-*d* in carbon tetrachloride were taken. Bands of medium intensity at 10.98 μ and strong intensity at 14.29 μ were observed in the spectrum of I-*d* which were absent in that of I-*h*. Five 18–21% solutions (by weight) of I-*h* and I-*d* (97.5% deuterated at the 2-octyl position) were prepared in benzene, the relative amounts of the I-*h* and I-*d* varying regularly from 19% I-*d*, 81% I-*h* to 97.5% I-*d*, 2.5% I-*h*. A plot of % I-*d* against (10^4 × absorbance)/(concentration of I-*d* + I-*h*) was made for λ 10.98 μ and was found to be linear. At total concentrations (I-*h* + I-*d*) below 18%, Beer's law was not followed. Solutions of the unknown (18–21%) were prepared, the absorbance determined and the % of I-*d* was read from the graph.

Analyses at λ 14.29 μ were conducted in carbon tetrachloride solution at 2.8–3.0% (by weight) concentrations. Twelve known mixtures of I-*h* and I-*d* ranging from 100% I-*h* to 97.5% I-*d* and 2.5% I-*h* were prepared and dissolved in carbon tetrachloride to give 2.8–3.0% solutions, and absorbance at 14.29 μ was determined. A plot of (10^2 × absorbance)/(concentration of I-*d* + I-*h*) *vs.* % I-*d* in sample was found to be linear. Solutions of unknowns (2.8–3.0%) were prepared, the absorbance determined, and the % I-*d* was read from the graph. Small deviations from Beer's law were found when solutions much greater or less than 2.8–3.0% were employed, particularly when the % of I-*d* exceeded 60. The averages of the values obtained at the two wave lengths for isotopic exchange are recorded in Table I. The actual values are recorded below. The product of run 2 was found by deuterium analysis by combustion and falling drop

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(13) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **78**, 5597 (1956).

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

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

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

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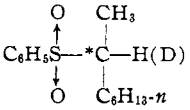
Two diastereometrically related isomers of 2-octyl phenyl sulfoxide were prepared in an optically pure state. The kinetics of base-catalyzed hydrogen–deuterium exchange and of epimeric equilibrium were studied in *tert*-butyl alcohol-OD. The same isomers deuterated in the 2-octyl position were also prepared, 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_α = 1.2 to 3.6). In dimethyl sulfoxide, one diastereomer gave small net retention and the other net inversion (k_e/k_α = 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.

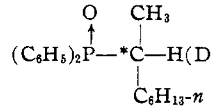
Previous investigations in this series[3] established that the carbanion derived from optically active 2-octyl phenyl sulfone (I) was asymmetric. However, the carbanion generated from optically active diphenyl-2-octylphosphine oxide (II) by proton abstraction did not itself exhibit any asymmetric properties.[4]

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.



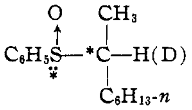
$$C_6H_5\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-{}^*\overset{\overset{CH_3}{|}}{\underset{\underset{C_6H_{13}\text{-}n}{|}}{C}}-H(D)$$

I



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

II



$$C_6H_5\overset{\overset{O}{\uparrow}}{\underset{\ddot{*}}{S}}-{}^*\overset{\overset{CH_3}{|}}{\underset{\underset{C_6H_{13}\text{-}n}{|}}{C}}-H(D)$$

III-*h*, III-*d*

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°, $[\alpha]^{25}\text{D}$ $+173°$ (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.

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[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).

[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.

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[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.