methanol, filtered to remove insoluble suspended material, and recovered by evaporation of the methanol under reduced pressure. Three probes with **3** (1.5 mmol, [α]D −22.2°) and $LiAlH_4$ (0.8 mmol) in the following solvents (25 ml) were performed as indicated: THF (5 hr, room temperature), THF (3 hr, reflux), and di-*n*-butyl ether (0.5 hr, 80°). Recovery of **3** was 80, 50, and 85%, respectively, and [α]D's were −22.4, −25.4, and −21.0°. A fourth sample of **3** (2.2 mmol, [α]D −24.4°) was refluxed with $LiAlH_4$ (4.4 mmol) in 25 ml of THF-benzene (3:2) for 5 hr. Recovery of **3** ([α]D −25.4°) was 62%.

Nonstereomutated, optically active **4** could be recovered from its reaction mixtures by dissolving the originally isolated products (no distillation) in benzene, extracting the *N*-methylaniline and organophosphorus cleavage products from the solutions with 0.1 *M* aqueous HCl, and, after drying, evaporating the solvent under reduced pressure. Attempts to distil the reaction mixtures were accompanied by disproportionation of methylphenylphosphine oxide, and complicated efforts to recover unreacted starting material. Three probes gave the following results: (1) **4** (1.8 mmol, [α]D −40.8°) and $LiAlH_4$ (0.9 mmol), 10 min in THF-benzene (3:2, 20 ml) at room temperature with 72% recovery of starting material ([α]D −42.2°); (2) **4** (2.5 mmol, [α]D +12.0°) and $LiAlH_4$ (1.25 mmol), 15 min in THF (20 ml) with 40% recovery ([α]D +12.1°); and (3) **4** (2.4 mmol, [α]D −40.8°) and $LiAlH_4$ (0.5 mmol), 4 hr in THF-benzene (25 ml) with 98% recovery (no reaction observed) of starting material ([α]D −40.7°).

Methylphenylphosphine was prepared in 35% yield from methyl methylphenylphosphinate:[12] bp 67–69° (9 mm); ir (neat) 2280 cm^{-1} (P–H); nmr δ 1.3 (d, 3, J = 3 Hz, PCH_3), 4.3 (s, 1, PH), 6.5–8.0 (broad, 5, aromatic) [lit.[12] bp 62–63° (11 mm)].

Methylphenylphosphine oxide was prepared by the oxidation of methylphenylphosphine:[13] ir (neat) 2320 (P–H), 1190 cm^{-1} (P=O); nmr δ 1.7 (dd, 3, J = 14, 3 Hz), 7.7 (doublet of quartets, 1, J = 462 Hz), 6.2–7.9 (m, 5, aromatic).

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Registry No.—(−)-**3**, 50682-94-5; (±)-**3**, 51703-89-0; (−)-**4**, 51593-48-7; (±)-**4**, 51593-49-8; aniline, 62-53-3; menthyl methylphenylphosphinate, 39837-64-4; methylphenylphosphinyl chloride, 5761-97-7; *N*-methylaniline, 100-61-8; methylphenylphosphine, 6372-48-1; methylphenylphosphine oxide, 19315-13-0.

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Sterochemistry of the Reduction of Diastereomeric α-Bromo-α-methylbenzyl α-Methylbenzyl Sulfones[1]

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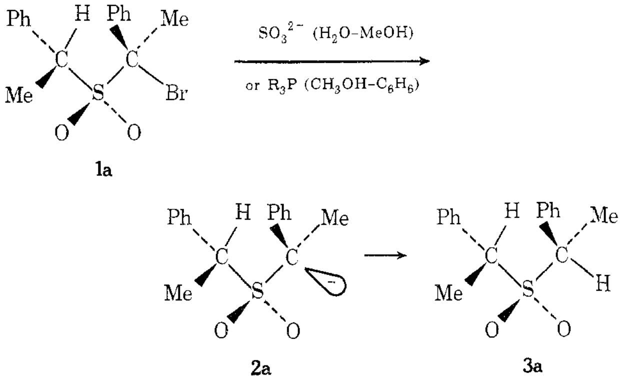
There are numerous reports in the literature of the reduction of α-halo sulfones by removal of a "positive" halogen atom in the presence of a proton donor. Electron donors such as alkoxide ions,[2-4] phenylmagnesium bromide,[3] mercaptide ions,[3] thiophenoxide ion,[4] piperidine,[4] sulfite ion,[1] and triphenylphosphine,[1,5] have been used. The mechanism of these reductions has been assumed in recent years to involve slow generation of an α-sulfonyl carbanion intermediate and rapid subsequent protonation.[4] A recent detailed study of the mechanism of the reduction of $ArCHXSO_2PH$ sulfones with triphenylphosphine in aqueous DMF provides strong evidence for the formation of an α-sulfonyl carbanion intermediate.[6]

Generation of asymmetric α-sulfonyl carbanions has been accomplished by deprotonation (or dedeuteration), decarboxylation, or a reverse aldol reaction.[7] A high degree of stereospecificity has been observed for the overall generation and protonation of the 2-octylphenylsulfonyl carbanion $[PhSO_2C(Me)(C_6H_{11})]^-$, by each of these methods. Base-catalyzed deprotonation and deuteration occurs with retention of configuration, and the same stereochemistry has been assumed for the other two reactions.[7,8] Generation of an asymmetric α-sulfonyl carbanion by a reverse aldol in such a manner as to produce a carbanion in which the orbital containing the electron pair is anti to the sulfonyl oxygen atoms results in overall inversion of configuration.[11] Inversion also appears to be the usual result when the carbanion, generated either by deprotonation[12] or dehalogenation,[5] reacts with an electrophilic site within the molecule to effect a 1,3-elimination reaction. The present paper is concerned with the stereochemistry of the reduction of an α-bromo sulfone (**1**) by generation of the corresponding α-sulfonyl carbanion (**2**) in the presence of a proton donor.[1]

Results and Discussion

The *dl*-erythro structure for the higher melting isomer (**1a**) of the diastereomeric α-bromo-α-methylbenzyl α-methylbenzyl sulfones $C_6H_5C(Br)(Me)SO_2CH(Me)C_6H_5$ (**1a** and **1b**) has been assigned by X-ray crystallographic analysis.[1] Structure assignments to the reduction products of **1a** and **1b**, *dl*- and *meso*-bis(α-methylbenzyl) sulfones (**3a** and **3b**), have been made by nmr spectroscopy.[13]



Most of the reduction experiments were carried out with the more readily isolable erythro isomer **1a**. Reduction of

Table I
Reduction of *erythro*- and *threo*-α-Bromo-α-methylbenzyl α-Methylbenzyl Sulfones (1a and 1b)

Reactant	Reducing agent	Solvent	Reaction time, hr	Yield of α-methylbenzyl sulfones,[a] %	
				Meso	*dl*
1a	Na_2SO_3[b]	H_2O–CH_3OH (1:3)	14	90 (89)[c]	~10
1a	$P[N(C_2H_5)_2]_3$[d]	CH_3OH–C_6H_6 (1:1)	24	>90 (60)[c]	<10
1a	$P(n\text{-}C_4H_9)_3$[d]	CH_3OH–C_6H_6 (1:1)	24	(64)[c]	
1a	$P(C_6H_5)_3$[d]	CH_3OH–C_6H_6 (1:1)	72	>90 (73)[c]	<10
1a	Zn	CH_3OH	6	~80 (50)[c]	~20
1a	C_6H_5SK[e]	CH_3OH	48	~70	~30
1b	Na_2SO_3[b,f]	H_2O–CH_3OH (1:3)	4	~10	~90

[a] Nmr analysis of the crude product (after solvent removal) indicated this composition of reduction product. The signal for the methine proton was examined.[14] [b] A portion of the sodium sulfite remained suspended. [c] Isolated yield from dichloromethane–hexane. [d] Phosphorus derivatives and products were separated by column chromatography on acidic alumina. [e] 80% of the product was the 1,3-elimination reaction product; the remaining 20% was sulfones in the indicated ratio. [f] 20% of the reactant remained and 10% 1,3 elimination occurred.

1a with sodium sulfite in aqueous methanol, or with various phosphines in methanolic benzene, gave the meso product (**3a**) to the extent of at least 90% (Table I). This corresponds to overall retention of configuration with a high degree of stereoselectivity. Comparable stereochemistry and stereoselectivity were observed in a reduction of the threo isomer (**1b**) with sulfite ion. Reduction of **1a** with zinc in methanol or with potassium thiophenoxide in methanol occurred with overall retention of configuration, but with a much lower degree of stereoselectivity (Table I).

The course of the reaction is represented as involving loss of ("positive") bromine from **1a** in such a way as to give a carbanion in which the electron pair is in an orbital flanked by the two oxygen atoms of the sulfonyl group (**2a**). There is some experimental evidence to indicate that this asymmetric carbanion is formed preferentially in the loss of H^+ or Br^+,[1,5,11,14] and there is evidence from *ab initio* calculations that this structure represents an energy minimum for the carbanion.[15] Protonation of carbanion **2a** then presumably occurs preferentially from the side cis to the sulfone oxygen atoms[11] (overall retention of configuration). Inversion of **2a** followed by protonation would give *dl*-bis(α-methyl)benzyl sulfone (**3b**). This could account for formation of **3b** as a minor product in reductions of **1a** (retention–inversion). Another mechanism for formation of **3b** from **1a** would be abstraction of Br^+ from a conformation wherein the bromine is anti to the sulfonyl oxygen atoms, followed by inversion of the carbanion and protonation.

The high degree of stereoselectivity of the reductions involving phosphine reducing agents may be a consequence of formation of an intermediate ion pair.[5] Interestingly enough, however, the stereoselectivity is almost as high with sulfite ion, where ion pair formation does not occur.

These results contrast with those recently reported for reduction of (*R*)- or (*S*)-2-bromo-2-octyl *p*-tolyl sulfone with sodium sulfite, where highly stereoselective inversion was observed.[16] Inversion appears to have been observed also in the reduction of optically active 2-bromo-2-octyl 2-octyl sulfone with either sulfite ion or zinc. It would appear that a different or modified mechanism is involved here. Cram has shown that the generation and protonation of carbanions can lead to retention, inversion, racemization, or isoracemization, depending on the structure of the substrate and the nature of the base–solvent system.[7] The basicity of the benzyl carbanion **2a** differs from that derived from 2-bromo-2-octyl *p*-tolyl sulfone by *ca.* five powers of ten, judging from the p*K*'s of the corresponding sulfones as measured in dimethyl sulfoxide solution.[17] It is perhaps not surprising, then, that the reductions of 1 and 2-bromo-2-octyl *p*-tolyl sulfone occur by different mechanisms.

Experimental Section[18]

Reduction Reactions of α-Bromo-α-methylbenzyl α-Methylbenzyl Sulfones (1a and 1b). Samples of **1a** (or **1b**) ranging from 0.200 to 0.100 g (*ca.* 0.5 mmol) were treated with at least 4 molar equiv (*ca.* 2 mmol) of reducing agent in *ca.* 20 ml of solvent and heated at reflux temperature for the indicated periods. The conditions of the experiments and results are summarized in Table I. See previous reports of α-halo sulfone reductions with sodium sulfite in protic media and with phosphine derivatives in benzene-methanol mixtures for details.[5a,19]

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Registry No.—**1a**, 51380-66-6; **1b**, 51380-67-7.

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