

Partial Asymmetric Synthesis of Substituted *trans*-2,3-Diaryloxirans using Optically Active Arsonium Ylides

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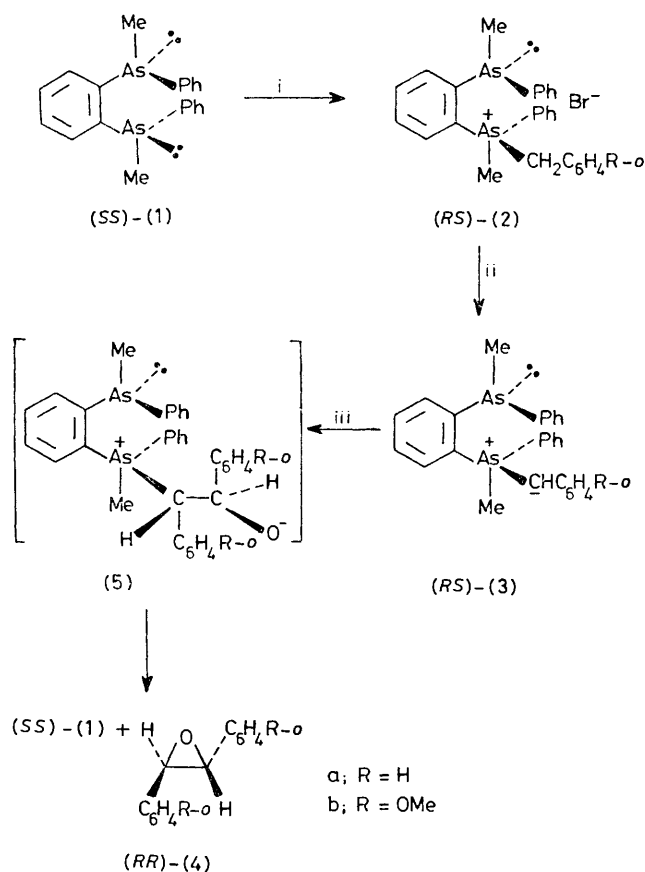
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Summary Ylides derived from optically active arsonium salts react with aromatic aldehydes to give *trans*-2,3-diaryl-oxirans in high chemical yields and with optical purities of between 4.7 and 38%.

ARSONIUM ylides react with aromatic aldehydes to yield either epoxides or olefins,¹ or a mixture of both,² depending upon the nature and electronic character of the substituent groups on the ylide and on the substrate molecule, and also upon the reaction conditions.³

We have found that high chemical yields of the dissymmetric *trans*-2,3-diaryloxirans result from the reaction between semi-stabilised ylides derived from the benzyl salts of the enantiomers of racemic *o*-phenylenebis(methyl phenylarsine)⁴ and of methyl- α -naphthyl-*p*-tolylarsine upon reaction with prochiral aromatic aldehydes. Furthermore, optical yields of between 4.7 and 38% are obtained using optically active arsonium salts.

Quaternisation of optically pure (SS)-(-)-(1),[†] $[\alpha]_D -95.2^\circ$ (CH₂Cl₂, *c* 8.0 g l⁻¹), with benzyl bromide proceeds with complete retention of configuration to afford (-)-*threo*-(*R*)-benzyl(methyl)[{(S)-2-methylphenylarsino}phenyl]-phenylarsonium bromide (2a)[‡], $[\alpha]_D -107.4^\circ$ (CH₂Cl₂, *c* 4.48 g l⁻¹). Treatment of (2a) with NaOEt in ethanol produced a pale yellow solution of the ylide (3a) to which an equimolar quantity of benzaldehyde was added. The reaction mixture was stirred for 18 h at 25 °C and then diluted with water. The products were extracted into dichloromethane and separated and purified by column chromatography on basic alumina. Optically pure (SS)-(-)-(1) was recovered first from the column by eluting with light petroleum (b.p. 48–65 °C) and was followed by the epoxide (RR)-(+)-2,3-diphenyloxiran (4a), m.p. 68–69 °C, $[\alpha]_D +55^\circ$ (Me₂CO, *c* 6.11 g l⁻¹), using chloroform-light petroleum (10:1) as eluent. The enantiomeric excess (e.e.) of (4a) was calculated using the value of $[\alpha]_D -291^\circ$ (Me₂CO, *c* 5.65 g l⁻¹) reported for (SS)-(-)-(4a) obtained from optically pure (2S,3S)-(+)-PhCH(NH₂)-CH(OH)Ph.⁵ When *o*-methoxybenzyl bromide was used to quaternise (SS)-(-)-(1), however, the *threo* salt (2b) was obtained which, after deprotonation and treatment with *o*-anisaldehyde, yielded under similar reaction conditions the oxiran (4b), m.p. 134–135 °C, $[\alpha]_D +8.8^\circ$ (CH₂Cl₂,



SCHEME. i, PhCH₂Br; ii, NaOEt in EtOH; iii, *o*-RC₆H₄CHO, *c* 4.23 g l⁻¹, in significantly higher optical yield (38% e.e.). The optical purity of (4b) was readily determined from its ¹H n.m.r. spectrum in the presence of the optically active shift reagent tris[trifluoroacetyl-(+)-camphorato]europium-(III).

We have also carried out some reactions using the ylide derived from the salts (6a) and (6b) and the results of both series of experiments are summarised in the Table.

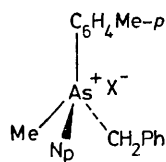
TABLE. Reagents and Yields of Products.

Salt	Base (solvent)	Substrate	Product	Yield/%	E.e./%
(RS)-(2a)	NaOEt (EtOH)	PhCHO	(RR)-(4a)	88	17
(RS)-(2a)	LiN(Pri) ₂ (Et ₂ O)	PhCHO	(RR)-(4a)	25	8
(RS)-(2b)	NaOEt (EtOH)	<i>o</i> -MeOC ₆ H ₄ CHO	(RR)-(4b)	86	38
(R)-(6a)	NaOEt (EtOH)	PhCHO	(RR)-(4a)	86	8.3
(R)-(6b)	LiOEt (dimethylformamide)	PhCHO	(RR)-(4a)	62	4.7
(R)-(6b)	LiOEt (diglyme)	PhCHO	(RR)-(4a)	26	5.0

[†] Absolute configuration known from X-ray crystal structure determination (B. W. Skelton and A. H. White, personal communication) of an internally diastereoisomeric palladium complex containing (*R*)-(+)-dimethyl(1-phenylethyl)amine.

[‡] The apparent inversion of configuration of the tertiary arsine species upon quaternisation is consistent with the rules of Cahn *et al.* for the assignment of absolute configurations (R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew Chem. Internat. Edn.*, 1966, 5, 385).

The chemical yields appear to be dependent on the counterion associated with the arsonium species and the base and solvent in which the ylide was generated as well as on electronic factors operating within the molecule. The



(R)-(6)

a; X = Br

b; X = PF₆

Np = α -Naphthyl

optical yields of the products, however, were improved significantly by introducing methoxy groups *ortho* to the reacting centres. This may reflect an increased chirality of the ylide by way of a chelating interaction between the methoxybenzyl group and the arsonium centre.

The absolute configuration and stereochemistry of the products may be rationalised in terms of the structures of the intermediate betaines (5) which are consistent with the following points: (i) the charged centres are situated *anti* with respect to one another consistent with epoxide rather than olefin formation⁶ and (ii) the absolute configurations of the carbon atoms derived from the benzaldehyde and the ylide have the same configuration in agreement with the observed *trans* geometry of the products. The degree of asymmetric induction therefore appears to ultimately depend upon the relative conformational stabilities of the betaines (5a) and (5b) and their diastereoisomers with opposite configurations of the two carbon centres. We are presently examining substituent effects on the optical yields of *trans*-diaryloxirans prepared by this method.

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