Chiral Solvent-induced Asymmetric Synthesis; Photosynthesis of Optically Enriched Hexahelicene

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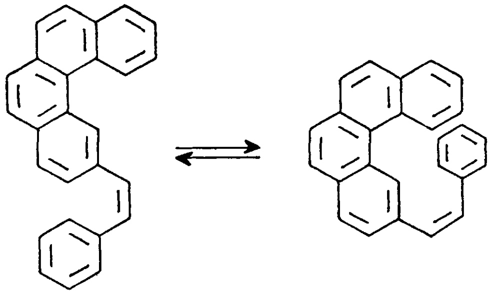
Summary Irradiation of 2-styrylbenzo[*c*]phenanthrene (**1**) in chiral solvents affords the optically active hexahelicene with optical yields between 0·2 and 2%; the sign of the optical rotation of the product is not directly related to the absolute configuration of the solvents used, but seems to depend on the position of the largest apolar group at the chiral centre.

Recently, it was found[1,2] that *cis*-1,2-diarylethylenes containing at least one relatively large aryl residue, *e.g.* *cis*-2-styrylbenzo[*c*]phenanthrene (**1**) have some preference for the prehelical *cis-syn* conformation (**1a**) rather than the *cis–anti* conformation (**1b**). This conformational preference does not depend only on the nature of the aryl residues, but also, as expected on the temperature and the solvent. In achiral solvents both the *P* and *M* conformations[3] of the prehelical form must be present in equal amounts. In chiral solvents, however, one of them might be expected to be present in excess. Photocyclization should then lead to an optically active helicene, derived from the form (either *P* or *M*) which was predominant in the prehelical state.



cis – anti (1b) *cis – syn* (1a)

In the Table the optical rotations and optical yields are given for samples of hexahelicene, obtained by irradiation of (**1**) in several chiral solvents. It appears that these solvents have a substantial effect on the formation of optically active hexahelicenes; the optical yield of samples obtained by irradiation of (**1**) with circularly polarized light is only 0·06%.[4]

Table

Optical rotations, $[\alpha]_D$, and optical yields of hexahelicene[a] obtained by irradiation of (**1**) in chiral solvents.

	Solvent	$[\alpha]_D$	Optical yield[a]/%
a,	(+)-α-Pinene	− 7°	0·21
b,	(*S*)(−)-Ethyl lactate (20 °C) ..	+15°	0·42
c,	(*S*)-(−)-Ethyl lactate (100 °C) ..	+ 6°	0·18
d,	(*S*)-(+)-Ethyl *O*-benzoyl-lactate ..	−30°	0·84
e,	(*R*,*R*)-(+)-Diethyl tartrate	−40°	1·1
f,	(*S*)-(+)-Ethyl mandelate	+71°	2·1
g,	(*S*)-(+)-Ethyl *O*-benzoylmandelate ..	+ 2°	0·04
h,	*rac.*-Ethyl mandelate	0°	0

[a] Hexahelicene $[\alpha]_D$ = 3570.

These results show that even in a series of structurally related solvents (b, d, or f) no direct correlation is found between the absolute configuration of the product and that of the solvent. The differences in the rotation of the sample obtained in (b) and (f) and their benzoylated derivatives (d and g) suggest that the position of the largest apolar residue at the chiral centre determines which enantiomer will predominate in the product. The influence of the temperature is the expected one (see b and c).

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[1] R. H. Martin, M. Defay, H. P. Figeys, K. Lè Van, J. J. Ruelle, and J. J. Schurter, *Helv. Chim. Acta*, 1972, **55**, 2241.
[2] M. H. de Jong and W. H. Laarhoven, *Rec. Trav. Chim.*, 1973, **92**, 673.
[3] R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem. Internat. Edn.*, 1960, **5**, 385.
[4] W. J. Bernstein, M. Calvin, and O. Buchardt, *J. Amer. Chem. Soc.*, 1973, **95**, 527.