Synthesis of Optically Active 'Dewar' Benzenes;[1] Asymmetric Induction

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Summary The optically active 'Dewar' benzene (**4**) has been prepared from the menthyl, bornyl, or s-octyl acetylenic esters (**1**) and the cyclobutane (**2**) followed by hydrolysis; the product with the highest optical purity was obtained from the menthyl ester.

WE report the preparation of the optically active 'Dewar' benzene (**4**) by asymmetric induction. When a solution of (**2**)[2] in CH_2Cl_2 was treated at 0—5 °C† with Me_2SO in the presence of a slight excess of the menthyl ester (**1a**), m.p. 59—62 °C, the ester (**3a**) was obtained in 60% yield.[3] The crude menthyl ester‡ was hydrolysed and optically active (**4**) was obtained in 75% yield (Scheme). The bornyl and s-octyl esters, (**1b**), m.p. 77·5—78·5 °C, and (**1c**), b.p. 130 °C at 0·6 mmHg, respectively, also gave (**4**), but in lower optical yield (Table).§

One important result of this experiment is that the enantiomer produced in excess is of opposite sign to that produced in the resolution of (**4**) *via* its dehydroabietylamine salt.[1]

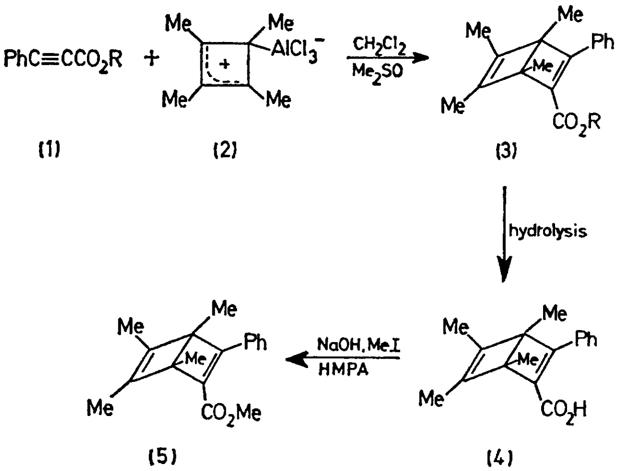
The optical purity of (**4**) was determined using a sample of $[\alpha]_{578}^{20}$ −74·0° (*c* 0·35, EtOH), the sodium salt of which was transformed quantitatively into optically active (**5**),¶ $[\alpha]_{578}^{20}$ −62·2° (*c* 1·2, EtOH), by treatment with MeI in hexamethylphosphoramide.[1] Addition of the shift reagent Eu(tfc)$_3$[4] to a solution of (**5**) in $CDCl_3$ gave rise to two separate singlets for the ester methyl group, with an integrated intensity ratio of 1:2, which corresponds to an optical purity of 33%.

TABLE. Optical data.[a]

Starting compound	Product[b]	Values for (**4**) after hydrolysis	Optical purity
(**1a**) [α] − 57·90°, *c* 0·27	(**3a**) [α] − 24·2°, *c* 0·60	[α] + 48·3°, *c* 0·3	21%
(**1b**) [α] − 38·30°, *c* 0·47	(**3b**) [α] − 50·0°, *c* 0·28	[α] − 14·3°, *c* 0·42	6·5%
(**1c**) [α] − 55·88°, *c* 0·68	(**3c**) [α] + 1·94°, *c* 0·52	[α] + 14·8°, *c* 0·44	6·9%

[a] All rotations are given at 578 nm, ethanolic solutions were used. [b] See footnote ‡.

From these data we can now assign $[\alpha]_{max}$ values for the chiral 'Dewar' benzenes (**4**) and (**5**), namely (**4**): $[\alpha]_{578}^{20}$ −224°, $[\alpha]_{546}^{20}$ − 272°, $[\alpha]_{436}^{20}$ − 485°, and $[\alpha]_{405}^{20}$ 520°; (**5**): $[\alpha]_{578}^{20}$ − 186°, $[\alpha]_{546}^{20}$ − 228°, $[\alpha]_{436}^{20}$ − 405°, and $[\alpha]_{405}^{20}$ − 432°.



a; R = menthyl
b; R = bornyl
c; R = $Me[CH_2]_5CHMe$–

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† CH_2Cl_2 gave better results than $CHCl_3$ and cyclohexane which were also tried; 0—5 °C was the optimal temperature range.

‡ Analytically pure (**3a**—**c**) were not obtained. The rotations in the Table are given for the crude mixtures.

§ For the preparation of (**1a**—**c**) the following alcohols were used: l-menthol $[\alpha]_{578}^{20}$ − 53·5°, l-borneol $[\alpha]_{578}^{20}$ − 32·5°, octan-2-ol $[\alpha]_{578}^{20}$ − 7·95° (rotations were measured in EtOH, *c* 0·5).

¶ In an additional experiment it was proven that during the esterification of (**4**) loss of optical activity does not occur.

[1] For previous paper in this series, see: J. H. Dopper, B. Greijdanus, and H. Wynberg, *J. Amer. Chem. Soc.*, 1975, **97**, 216.

[2] J. B. Koster, G. J. Timmermans, and H. v. Bekkum, *Synthesis*, 1971, 139.

[3] Other products were hexamethylbenzene and the *syn*-tetramer of but-2-yne. (H. Hogeveen, J. Jorritsma, P. A. Wade, F. v. Rantwijk, J. B. Koster, J. J. Prooi, A. Sinnema, and H. v. Bekkum, *Tetrahedron Letters*, 1974, 3915). The starting ester (**1a**) was also partly recovered.

[4] V. Schurig, *Tetrahedron Letters*, 1972, 3297.