Induced Asymmetric Polymerisation of Optically Active Vinyl Sulphoxide

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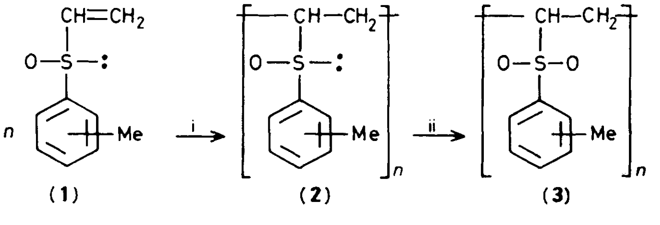
Induced asymmetric polymerisation of optically active *m*-tolyl vinyl sulphoxide was achieved by Bu^{n}Li or Bu^{n}MgBr at −78 °C.

In spite of a great deal of effort, all attempts at polymerisation and induced asymmetric polymerisation of optically active vinyl sulphoxide have failed.[1,2] Only a copolymerisation of vinyl sulphoxide and styrene in low yield has been reported.[1] We now report the first example of an induced asymmetric polymerisation of optically active *m*-tolyl vinyl sulphoxide (**1a**).†

Optically active (**1a**) was prepared according to the resolution method by complexation with optically active 2,2′-dihydroxy-1,1′-binaphthol (**5**).[3] For example, when a solution of racemic 2-chloroethyl *m*-tolyl sulphoxide (**4**) (10.1 g, 50 mmol) and (*R*)-(+)-(**5**) (7.15 g, 25 mmol) in benzene (60 ml) was kept at room temperature for 1 h, a 1:1 complex of (+)-(**4**) and (*R*)-(+)-(**5**) was obtained as colourless prisms (10.98 g, 90%, $[\alpha]_D$ +72.5°‡). Two recrystallisations of the complex from benzene gave the complex of optically pure (+)-(**4**) (8.78 g, 72%, $[\alpha]_D$ +79.4°, m.p. 143—144 °C). Treatment of the complex with 10% NaOH gave optically pure (+)-(**1a**) by HCl elimination as a colourless liquid (2.78 g, 67%, $[\alpha]_D$ +486 °), the optical purity of which was determined to be 100% by h.p.l.c. using a column containing an optically active solid phase, Chiralcel.§ Similar treatment with (*S*)-(−)-(**5**) of the filtrate left after the separation of the complex of (+)-(**4a**) and (*R*)-(+)-(**5**) finally gave optically pure (−)-(**1a**) (2.70 g, 65%, $[\alpha]_D$ −486°). A quick treatment of the complex of the optically pure (**4**) with 3% NaOH within 10 min gave optically pure (**4**) ($[\alpha]_D$ 252.8°) in about 65% yield, which upon further treatment with 10% NaOH gave optically pure (**1a**) by HCl elimination, quantitatively.

Rapid polymerisation of the optically active (**1a**) proceeds by treatment with Bu^{n}Li or Bu^{n}MgBr at −78 °C. For example, when a solution of Bu^{n}Li (19.2 mg, 0.3 mmol) in hexane (0.2 ml) was added to a solution of (+)-(**1a**) (1.0 g, 6 mmol) and (−)-sparteine (70 mg, 0.3 mmol) in toluene (10 ml) at −78 °C under N_2, polymerisation occurred immediately. The reaction mixture was kept for a further 30 min under the same conditions, and the precipitate formed was filtered, washed with MeOH, and dried to give the optically active polymer (**2a**) as a colourless powder (0.9 g, 90%, m.p. 105—107 °C, $[\alpha]_D$ +310°, $\bar{M}_n$ 3 500, $\bar{M}_w$ 4 250). Polymerisation using Bu^{n}MgBr in diethyl ether gave almost the same result as that with Bu^{n}Li. Although the $[\alpha]_D$ value of (**2a**) changed little on increasing the amount of (−)-sparteine, it decreased slightly when the polymerisation was carried out in the absence of the (−)-sparteine (Table 1). However, when (**1a**) contained a trace of water, polymerisation did not occur. The failure of all the attempted polymerisations of optically active *p*-tolyl vinyl sulphoxide (**1b**) by Bu^{n}Li[1] and Bu^{n}MgBr[2] is probably due to water contaminant.

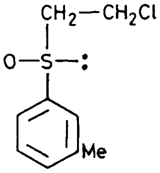


a; *meta*
b; *para*

Reagents: i, Bu^{n}Li or Bu^{n}MgBr; ii, H_2O_2.

The $[\alpha]_D$ value of the optically active polysulphone (**3a**) (m.p. 180—189 °C) obtained by oxidation of the optically active (**2a**) with H_2O_2 is shown in Table 1. The $[\alpha]_D$ value is attributed to the induced asymmetric polysulphone (**3a**) since the $[\alpha]_D$ value did not change on further oxidation, and since the polysulphone did not show any sulphoxide absorption peak in i.r. spectrum.

In c.d. spectra (EtOH), (+)-(**2a**) and (+)-(**3a**) showed positive bands at 248 and 258 nm, respectively, and negative bands at 222 nm in both cases. These c.d. spectra correspond


(**4**)

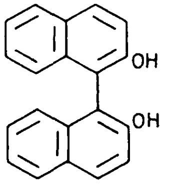

(**5**)

Table 1. The $[\alpha]_D$ (tetrahydrofuran, *c* 0.5) values of (**2a**) obtained by polymerisation of optically pure (+)-(**1a**) and (−)-(**1a**) by Bu^{n}Li at −78 °C under N_2 in the absence and presence of (−)-sparteine, and the $[\alpha]_D$ values of (**3a**) prepared by H_2O_2 oxidation of the (**2a**).

Molar ratio of	$[\alpha]_D$ (°)	
Bu^{n}Li: (−)-sparteine	(**2a**)	(**3a**)
1:0	+274 (−272)	+19 (−16)
1:1	+310 (−307)	+42 (−40)
1:10	+311 (−310)	+42 (−41)

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† Satisfactory elemental analyses were obtained for all new compounds and polymers.

‡ All the $[\alpha]_D$ values were measured in tetrahydrofuran (*c*, 0.5) at 25 °C.

§ Available from Daicel Chemical Industries, Ltd, Himeji, Japan.

to those of the u.v. aborption of (+)-(**2a**) (224 and 248 nm) and (+)-(**3a**) (222 and 270 nm).

It is not clear whether the large $[\alpha]_D$ value of the optically active (**3a**) is attributed to its asymmetric carbons or its helicity, even though the $[\alpha]_D$ value of induced asymmetric polymethacrylate has been attributed to helicity.[4,5]

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