

KINETIC RESOLUTION OF AN ORGANOSILANE

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It has been reported that optically active alcohols can be formed by an asymmetric synthesis involving the reduction of ketones by optically active alkoxy lithium aluminium hydrides (1). We wish to report that by the use of a similar reagent for the reduction of ( $\pm$ )-methyl-1-naphthylphenylmethoxysilane (I) we have obtained methyl-1-naphthylphenylsilane (II) which was optically active. The unreacted methoxysilane was also optically active. It is apparent that the two enantiomers of the methoxysilane (I) are reacting at different rates resulting in a kinetic resolution. A closely related reaction, the asymmetric synthesis of an optically active silane, based on differences in stability between diastereomeric-2-silaoxazolidones, has recently (2) been reported.

The methyl-1-naphthylphenylsilane system was used in the present work since this system has been thoroughly studied (3) and the rotatory powers and the absolute configurations of the compound concerned have been unambiguously established

The reduction was carried out in diethyl ether with a (+)-quinidine-lithium aluminium hydride complex (1:1 molar) and the reaction was stopped when approximately one third of the methoxysilane had been reduced. Chromatography of the reaction mixture gave silane (II), which was dextro-rotatory, and methoxysilane (I), which was laevorotatory, corresponding to an excess of the antipodes with the *R* and *S* configurations respectively. The optical purity of each of these fractions was approximately 6%, and each of them was worked up to give a product with a high degree of optical purity.

The complex hydride was prepared in situ by the addition of (+)-quinidine (3.56g, 11 m.mole) to lithium aluminium hydride (0.42g, 11 m.mole) in ether (100ml, previously distilled from lithium aluminium hydride). The mixture was refluxed for 30 min and a solution of ( $\pm$ )-methoxysilane (I) (10g, 34.8 m.mole) in ether (20ml) was added. After refluxing for a further 4 hours the excess hydride was decomposed

with dilute sulphuric acid, the ether layer was washed several times with dilute sulphuric acid and then with water, dried over anhydrous sodium sulphate, and the ether removed to give 9.07g of product. This reaction mixture (8.8g) was chromatographed on silica gel, using as eluant a mixture (1:9) of benzene and light petroleum (b.p. 60-80°) to give 2.93g of silane (II),  $[\alpha]_D^{20} = +1.96^\circ$  (c 13.91 in ethanol), and 4.31g of methoxysilane (I),  $[\alpha]_D^{20} = -0.93^\circ$  (c 14.34 in ethanol). The n.m.r. and i.r. spectra of these products were identical with those of authentic racemic samples. The silane was fractionally crystallised from hexane to give the pure dextro enantiomer, m.p. 63°,  $[\alpha]_D^{20} = +35.5^\circ$  (c 0.12 in hexane). Fractional crystallisation of the methoxysilane failed to increase its optical purity so it was completely reduced with lithium aluminium hydride in ether. Fractional crystallisation of the product gave the laevo enantiomer of the silane (II), m.p. 59°,  $[\alpha]_D^{20} = -29^\circ$  (c 0.34 in hexane). The optical rotatory dispersion curves of these silanes corresponded with those reported in the literature (3, 4).

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