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THE PREPARATION AND DETERMINATION OF OPTICAL PURITY OF METHYLPHENYL-1-NAPHTHYL-(−)-MENTHOXYSILANES

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SUMMARY

The reaction of (±)-methylphenyl-1-naphthylsilane with (−)-menthol using a palladium catalyst is a much more convenient method of preparing (±)-methylphenyl-1-naphthyl-(−)-menthoxysilane than the previously published methods. The separation of the diastereoisomers of the latter compound can be followed by NMR spectroscopy.

The preparation and fractional crystallisation of (±)-methylphenyl-1-naphthyl-(−)-menthoxysilane (I) has been described by Sommer *et al.*[1]. The preparation is by alkoxy exchange between (±)-methylphenyl-1-naphthylmethoxysilane and (−)-menthol with potassium hydroxide as catalyst. In the course of several attempts to repeat this preparation we have found that yields are low and variable, even after prolonged heating, and that considerable quantities of disiloxane are formed.

The reaction of (±)-methylphenyl-1-naphthylsilane with (−)-menthol in methylene chloride using catalytic quantities of 10% palladium on charcoal[2,3] was found to be a much more convenient method of preparing (I). The reaction was complete in 3 h at room temperature to give (I) in 75% yield. The product was contaminated with a little silanol but this was easily removed by chromatography on silica gel using a 1/4 mixture of benzene/light petroleum (60–80°) as eluent. This reaction also gave good yields of the alkoxysilane from 1-phenylethanol, and a moderately good yield of that from (−)-borneol. The highly hindered (+)-α-fenchyl alcohol scarcely reacted even when the solution was boiled under reflux for several hours.

Crystallisation of (I) from n-pentane at low temperatures[1] readily gives (−)-methylphenyl-1-naphthyl-(−)-menthoxysilane (Ia) in a high state of purity, but the more soluble (+)-methylphenyl-1-naphthyl-(−)-menthoxysilane (Ib) requires many recrystallisations from ethanol to render it completely pure. In the course of performing this resolution we noted that the NMR spectra of the separated diastereoisomers and the mixture (I) featured resonances which are extremely useful in determining the optical purity of the diastereoisomers during the resolution.

There are many instances of the magnetic nonequivalence of protons in diastereoisomers, and recently Raban and Mislow have demonstrated the applicability of NMR spectroscopy to the analysis of diastereoisomers as a means of determining optical purity[3]. There are, also, a number of reported instances where NMR spectroscopy has been applied in the analysis of diastereoisomeric organosilicon compounds[4]. The method is particularly useful in following the purification of the lower melting (Ib) where melting point and optical rotation are not very sensitive to purity.

The 60 Mc NMR spectrum in carbon tetrachloride of the mixed diastereoisomers features a complex aromatic multiplet at τ 1.8 to 2.8, a broad band centred at τ 6.50, and resonances from τ 7.4 to 9.3 ppm associated with the aliphatic protons in the menthoxy moiety and the methyl on silicon. In addition there are four sharp resonances with an intensity of three protons centred at τ 9.50. The spectrum of (Ia) showed two major differences from the above (Fig. 1). Firstly in the region τ 9.0 to 9.2 the peaks at τ 9.05 and 9.17, present in the mixture, were absent in the spectrum of the pure (Ia) and in addition there was a considerable intensification of the peak at τ 9.14. Secondly, the only resonance at high field were a doublet centred at τ 9.55 ($J = 7.1$ Hz). The spectrum of the lower melting (Ib) recrystallised from ethanol showed resonances at τ 9.05 and 9.17. The high field resonances consisted of a doublet at τ 9.51 ($J = 7.3$ Hz) together with a minor doublet due to (Ia) which was only completely removed with great difficulty. The high field doublets are due to the methyl on C(5) of the menthoxy moiety brought to high field by the shielding effect of the aromatic groups.

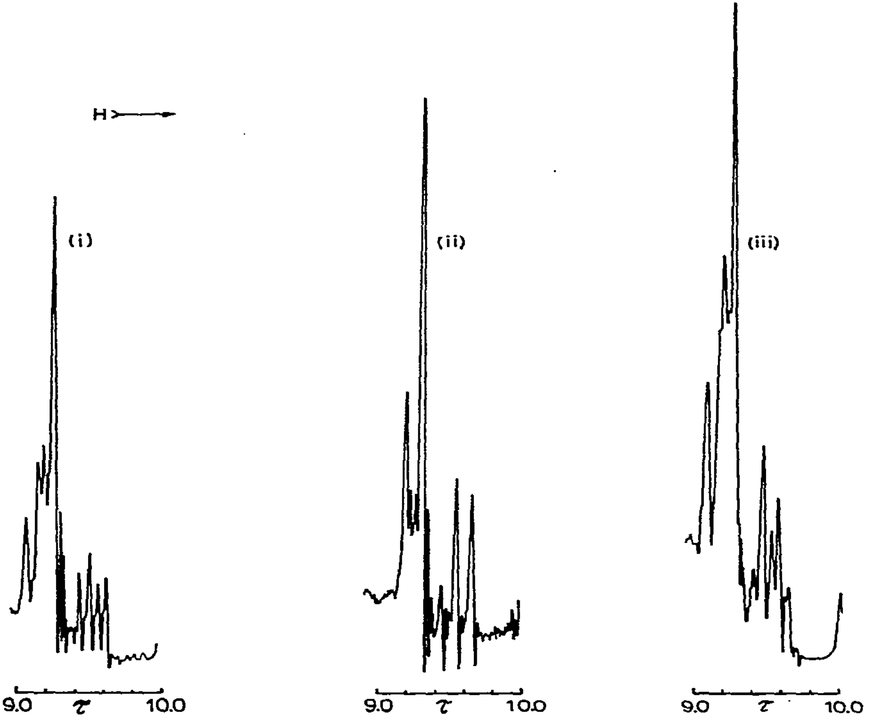

Fig. 1. 60 Mc NMR spectra of: (i) mixture of diastereoisomers (I) from reaction of (±)-MePhNpSiOMe with (−)-menthol; (ii) (−)MePhNpSiOMen(−) (Ia), m.p. 78–81°; (iii) (+)MePhNpSiOMen(−) (Ib), m.p. 49–51° (containing a little Ia) Np = 1-naphthyl; Men = menthyl.

The resonances of the diastereoisomers in the region τ 9.5 are useful in quantitatively assessing optical purity. Differences in the resonances in the region τ 9.0 to 9.2, due to the isopropyl group, provide additional indications of purity but are too close to the $SiCH_3$ resonances to be of great value on their own.

Spectra taken at 100 Mc confirm the above indications but give no additional information beyond that obtained from the 60 Mc spectra.

EXPERIMENTAL

The proton resonance spectra were obtained in carbon tetrachloride solution on a Perkin–Elmer R10 spectrometer at 35° with tetramethylsilane as internal standard.

The menthoxysilane (I) was prepared by dissolving 1.5 g (±)-methylphenyl-1-naphthylsilane and 1.88 g (−)-menthol in 12 ml methylene chloride (dried over a 5A molecular sieve), and adding 0.1 g of 10% palladium on charcoal. The mixture was allowed to stand at room temperature until evolution of hydrogen ceased (time from 30 min to 3 h, according to activity of catalyst). After removal of the catalyst and solvent the product was separated from silanol and excess menthol by a silica gel column using a 1/4 mixture of benzene and light petroleum (b.p. 60–80°).

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