

CHROM 4030

Resolution of some secondary aliphatic alcohols by thin-layer chromatography of their N-(1-phenylethyl)urethanes

During investigations into naturally occurring alcohols the determination of the optical configuration proved difficult in cases where only a few milligrams of material were available. If very dilute solutions are used for polarimetry, errors can be caused by the dependence on concentration of the specific rotation¹. We have now found that diastereomeric N-(1-phenylethyl)urethanes of some aliphatic secondary alcohols can be separated by thin-layer chromatography.

The N-(1-phenylethyl)urethanes were prepared by reacting the alcohols with a small excess of (+)- or (-)-1-phenylethyl isocyanate at 110° for 7 h; the excess of isocyanate was removed at 50° and 1 mm Hg. The N-(1-phenylethyl)urethanes were made of racemic 1-octen-3-ol, 2-octanol, 2-heptanol, 3-octanol and 2-pentanol. In addition to these racemic alcohols the two optical isomers of 1-octen-3-ol, obtained by fractional crystallisation of the strychnine salt of mono-1-octen-3-yl phthalate², were converted into their N-(1-phenylethyl)urethanes. The urethane from (+)-1-octen-3-ol and the (+)-isocyanate as well as the enantiomeric derivative from (-)-1-octen-3-ol and (-)-isocyanate both melted at 49–51.5° after recrystallisation from heptane. The (+)-(-)- and (-)-(+)-urethanes could not be obtained in a crystalline form.

Glass plates of 20 × 30 cm were coated with a 0.25 mm layer of a Kieselgel G slurry, using a Desaga applicator, and dried at 110° for 1 h and 30 min. Conventional 20 × 20 cm thin-layer plates did not give a satisfactory resolution.

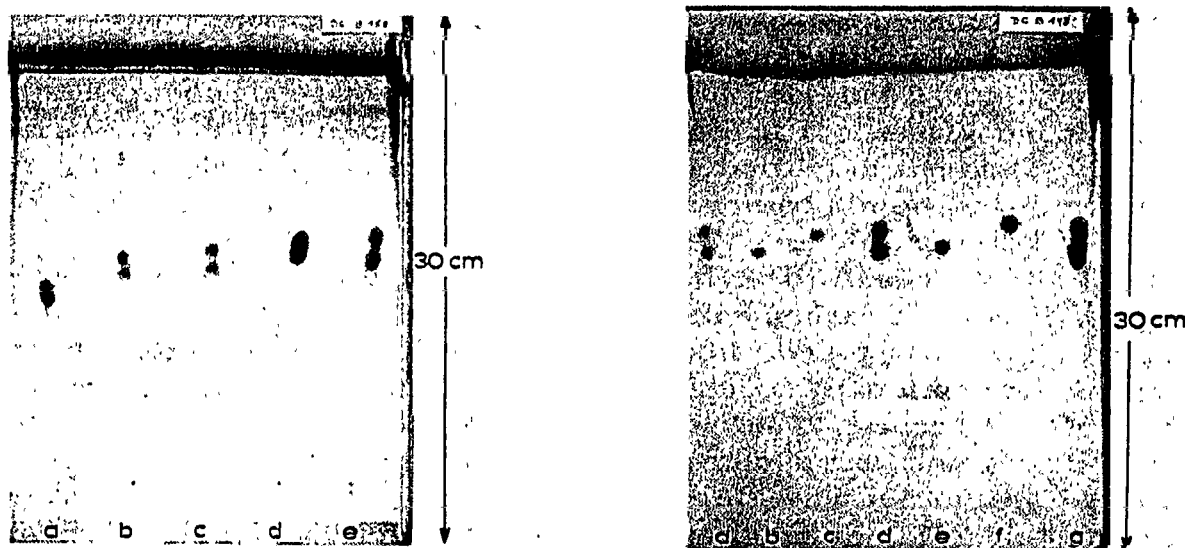


Fig. 1. Thin-layer chromatogram of N-(1-phenylethyl)urethanes (20 μ g each), prepared from: (a) 2-pentanol, (b) 2-heptanol, (c) 2-octanol, (d) 3-octanol, (e) 1-octen-3-ol and (+)-1-phenylethyl isocyanate. Solvent: benzene-ether (95:5, v/v).

Fig. 2. Thin-layer chromatogram of the N-(1-phenylethyl)urethanes. Made from (\pm)-, (-)- and (+)-1-octen-3-ol and (+)-1-phenylethyl isocyanate: (a) 10 μ g, (d) 20 μ g and (g) 30 μ g urethane of the (\pm)-alcohol; (b) 5 μ g and (e) 10 μ g urethane of the (-)-alcohol; (c) 5 μ g and (f) 10 μ g urethane of the (+)-alcohol. Solvent: benzene-ether (95:5, v/v).

The thin-layer chromatograms were developed with mixtures of benzene and a polar solvent such as acetone, ether, ethyl acetate or tetrahydrofuran in the ratio 95:5 (v/v); benzene-ether gave the best results. Spots were made visible by spraying with a 10% (w/v) solution of phosphomolybdic acid in ethanol and heating to 120°.

Chamber saturation was found to have a detrimental effect on the separations.

Fig. 1 shows a typical chromatogram of the N-(1-phenylethyl)urethanes prepared with (+)-1-phenylethyl isocyanate; the urethanes of racemic 1-octen-3-ol, 2-octanol and 2-heptanol are each separated into two distinct spots, whereas the diastereomeric urethanes of 3-octanol and 2-pentanol overlap somewhat.

The urethane from (+)-1-octen-3-ol and (+)-1-phenylethyl isocyanate and the enantiomeric (—)-(—)-urethane were found to run as upper spots, the (—)-(+) urethane and its (+)-(—)-enantiomer as lower spots. Fig. 2 shows a thin-layer chromatogram of different amounts of the urethanes made from (±)-, (+) and (—)-1-octen-3-ol and (+)-1-phenylethyl isocyanate.

It appears that thin-layer chromatography of the N-(1-phenylethyl)urethane derivatives is a useful means of determining the optical configuration of small amounts of secondary alcohols or to check their optical purity.

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