ENANTIOMERIC PAIRS OF IPSENOL AND IPSDIENOL USING ASYMMETRIC ISOPRENYLBORYLATION

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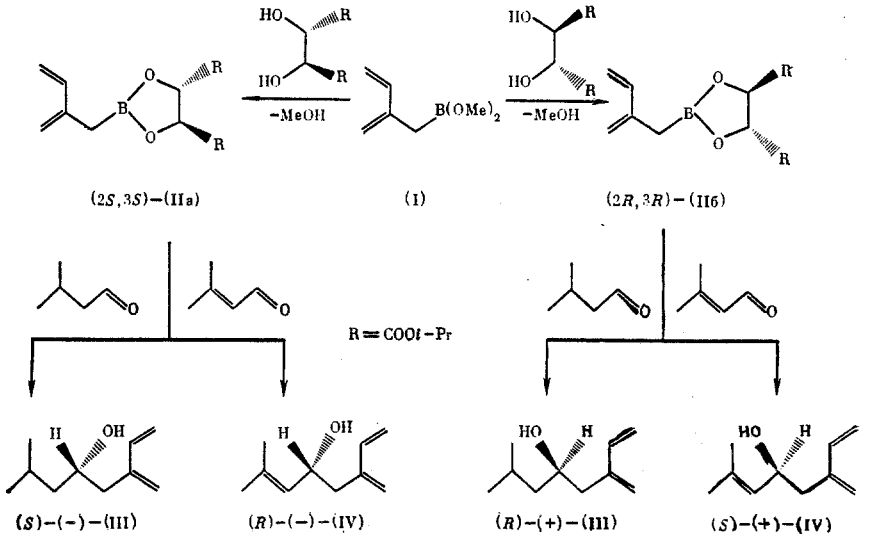
One of the methods for the preparation of (±)-ipsenol and (±)-ipsdienol is the isoprenylborylation of isovaleraldehyde and β,β-dimethylacrolein [1].

We have synthesized the enantiomer parts of ipsenol (III) and ipsdienol (IV) with 46-63% optical purity using chiral isoprenylborylating reagents, namely, (2S,3S)- and (2R, 3R)-diisopropyltartrates of isoprenylboric acid (IIa) and (IIb). The latter are readily obtained by the transesterification of dimethoxyisoprenylborane [I, bp 55-60°C (30 mm)] by (2S,3S)-(−)- ([α] from −16 to −17°) or (2R,3R)-(+)-diisopropyltartrate ([α] from +16 to +17°).



A solution of an equimolar amount of aldehyde (~1 g) in 10 ml abs. toluene was added to a solution of borane (IIa) or (IIb) (~1 g) in 10 ml abs. toluene at −75°C. The mixture was maintained for 1 h at −75°C and slowly warmed to 20°C. Toluene was removed in vacuum and the viscous residue consisting of a borate ester, was dissolved in ether and hydrolyzed at 0°C by a 1.5-fold excess of 3 N aq. NaOH. The ethereal layer was separated off and dried over Na_2SO_4. The solvent was removed. The residue of crude (III) or (IV) was purified by chromatography on silica gel using 9:1 and 4:1 pentane–ether as the eluent, respectively. (S)-(−)-(III) was obtained in 90% yield, n_D^{20} 1.4680, $[\alpha]_D$ −8.3° (25°C) (c 1, EtOH). The optical purity of this product was 48%. (R)-(+)-(III) was obtained in 86% yield, n_D^{20} 1.4680, $[\alpha]_D$ +8.08° (25°C) (c 1, EtOH). The optical purity of this product was 46%. (S)-(+)-(IV) was obtained in 85% yield, n_D^{20} 1.4900, $[\alpha]_D$ +6.3° (20°C) (c 1, MeOH). The optical purity of this product was 63%. (R)-(−)-(IV) was obtained in 84% yield, n_D^{20} 1.4900, $[\alpha]_D$ −5.8° (20°C) (c 1, MeOH). The optical purity of this product was 58% [2, 3].

The structures of (I)-(IV) were supported by spectral data.

LITERATURE CITED

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