

Separation of asymmetric quadricovalent phosphonium bases into optically active components.

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The resolution of RR'R'R''PX into optically active forms is reported. For prepn. of the necessary asymmetric tertiary phosphines, the following quaternary salts were prepd.: Et₂Ph(~~XXXXXX~~)PCl, m. 194-5°; Et₂Bu(~~XXXXXX~~)PCl, m. 148-9°; Pr₂Ph(~~XXXXXX~~)PCl, m. 134-5°; Pr₂Bu(~~XXXXXX~~)PCl, m. 154.5-5.0°; Bu₂Ph(~~XXXXXX~~)PCl, m. 156-7°. Thermal decompn. of these in CO₂ atm. gave asymmetric phosphines: EtPh(~~XXXXXX~~)P, b₁₈ 165-8°, d₂₀ 1.0393, n_D²⁰ 1.5960; PrPh(~~XXXXXX~~)P, b₁₂ 172-5°, n_D²⁰ 1.5880; BuPh(~~XXXXXX~~)P, b₁₁ 184-90°, d₂₀ 1.0112, n_D²⁰ 1.5729; EtBu(~~XXXXXX~~)P, b₆ 135-9°, d₂₀ 0.9838, n_D²⁰ 1.5310; PrBu(~~XXXXXX~~)P, b₁₁ 113-15°, d₂₀ 0.99467, n_D²⁰ 1.5090. Their formation proceeded with evolution of olefins, HCl and PhCH₂Cl. Reaction of these phosphines with CH₂:CHCH₂Br and BuBr gave the following ~~XXXXXX~~ phosphonium salts: Et(PhCH₂(CH₂:CHCH₂)₂)PBr, m. 148-50°; EtBuPh(PhCH₂)PBr, m. 141-2°; EtBu(CH₂:CHCH₂)(PhCH₂)PBr, m. 87-9°; PrPh(PhCH₂)(CH₂:CHCH₂)PBr, m. 153-4°; (BuPh(CH₂:CHCH₂)(PhCH₂)PBr, m. 102-2.5°. When these salts were treated with Ag d-~~XXXXXX~~-bromocamphorsulfonate only 2 crystalline bromocamphorsulfonates were obtained: EtPh(~~XXXXXX~~)(CH₂:CHCH₂)₂P, (I) and BuPh(~~XXXXXX~~)(CH₂:CHCH₂)₂P; the others formed sirups. I ~~XXXXXX~~ was taken up in EtOAc and the solvent was partly evapd., yielding a crop of crystals of I, m. 148-50°. Further fractions were obtained by evapn. of the solvent, with [α]_D changing from 53.6° to 38.8° in the last fraction. When II, m. 141-2°, was similarly crystallized, no sepn. occurred and [α]_D remained at 44.1-45°. Attempts to convert I and II into crystalline bromides which could be resolved were fruitless.

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