Optical Resolution of Phosphines by Asymmetric Platinum(II) Complexes

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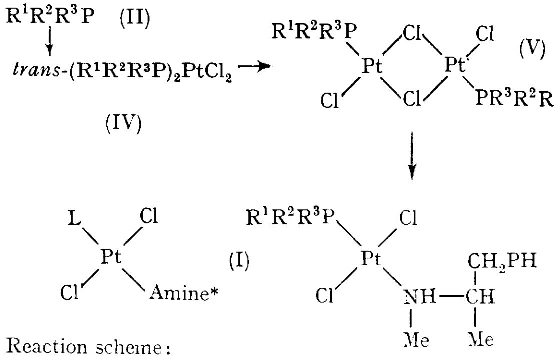
ASYMMETRIC platinum(II) complexes (I) have been used to resolve strained cyclo-olefins[1] and sulphoxides.[2] We report the extension of this method to the optical resolution of an asymmetric phosphine.

Methylphenyl-t-butylphosphine (II), prepared by the method of Hoffmann,[3] can be oxidized to its oxide (III). The phosphine (II) was treated with potassium chloroplatinite to give *trans*-dichlorobis(methylphenyl-t-butylphosphine)platinum(II) (IV), m.p. 196—198°. The assignment of the *trans*-configuration was based on n.m.r. which showed three triplets ($\delta = 1{\cdot}81$ p.p.m.) for the methyl protons and one triplet ($\delta = 1{\cdot}33$ p.p.m.) for the t-butyl protons. The appearance of the single triplet is due to the virtual coupling of the protons with the two phosphorus atoms.[4] Shaw had taken advantage of this phenomena to assign stereochemistry to a number of square-planar complexes of dimethylphenylphosphine.[5]

When compound (IV) was refluxed with platinum dichloride in a solution of xylene, orange crystals, m.p. 273—275°, were formed, which is the binuclear compound (V). It did not give a crystalline product on reaction with (+)-1-phenylethylamine. (+)-Deoxyephedrine,[6] however, reacted with (V) and the resultant product could be recrystallized to give two isomers: α-*trans*-dichloro(deoxyephedrine)(methylphenyl-t-butylphosphine)platinum(II) (VIa), m.p. 125—126°, $[\alpha]_{578} = +10^\circ$, and the β-isomer (VIb), m.p. 120—122°, $[\alpha]_{578} = +16^\circ$.

The same diastereomeric mixture could not be obtained from the reaction of (II) with *trans*-dichloroethylenedeoxyephedrineplatinum(II) which was prepared from potassium ethylenetrichloroplatinum(II) and deoxyephedrine and had m.p. 90—93°, $[\alpha]_{578} = -7{\cdot}4^\circ$. The product of the reaction was identified as the bis-phosphine complex (IV). Apparently, (II) displaced both ligands with great ease.



Reaction scheme:

R^1=Ph, R^2=Me, R^3=Bu^t (VI)

The phosphine (II) and deoxyephedrine could be liberated from (VIa) by stirring the complex in a suspension of methanolic potassium cyanide. The phosphine so generated was shown to be optically active in two ways. (II) was converted into its oxide (III) by passing a stream of oxygen through the solution containing both (II) and deoxyephedrine. (III) was separated from deoxyephedrine by acid extraction and was found to be optically active, $[\alpha]_{578} = +10°$. Alternatively, potassium chloroplatinite(II) was added to the phosphine and amine mixture. Optically active (IV) could be isolated, it had m.p. 190—192°, $[\alpha]_{578} = -11°$.

This sequence of reactions therefore constitutes the optical resolution of an asymmetric phosphine. Previously, optically active phosphines have been obtained by cathodic reduction of phosphonium salts[7] or by silane reduction of phosphine oxide.[8] Recently Wittig has resolved triarylphosphine by reaction with formaldehyde and (+)-camphorsulphonic acid.[9] These methods do not seem to be amenable to the optical resolution of other tervalent phosphorus compounds such as phosphites.

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