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A Novel Route to Menthyldiphenylphosphine

Masato TANAKA and Ikuei OGATA

National Chemical Laboratory for Industry (Tokyo Kogyo Shikensyo), Hon-machi, Shibuya-ku, Tokyo 151

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Synopsis. As evidence of a novel, configurationally-stable Grignard reagent, menthyldiphenylphosphine (MDPP) has been obtained by the reaction of diphenylphosphinous chloride with the Grignard reagent derived from menthyl chloride.

During the past several years, a variety of optically active phosphines have been used in asymmetric syntheses by homogeneous phosphine–transition metal complex catalysts. Neomenthyldiphenylphosphine (NMDPP) and menthyldiphenylphosphine (MDPP) have also been examined as chiral ligands in asymmetric hydrogenation,[1] hydroformylation,[2] and hydrosilylation.[3]

Since it has been believed that the preparation of a Grignard reagent from an optically active halide where halogen is attached to the asymmetric carbon results in significant racemization,[4] MDPP has been prepared according to the same procedure as was used in the case of NMDPP by

$$\mathrm{NaP(C_6H_5)_2} + \text{Neomenthyl chloride} \longrightarrow \mathrm{(Menthyl)P(C_6H_5)_2}$$

the reaction of sodium diphenylphosphide with neomenthyl chloride, whose preparation is fairly difficult.[5] The present authors, however, have found, as a rare example, that MDPP can be easily prepared by the reaction of diphenylphosphinous chloride with a Grignard reagent derived from menthyl chloride:

$$\text{Menthyl chloride} + \mathrm{Mg} \longrightarrow \xrightarrow{\mathrm{P(C_6H_5)_2Cl}} \mathrm{(Menthyl)P(C_6H_5)_2}$$

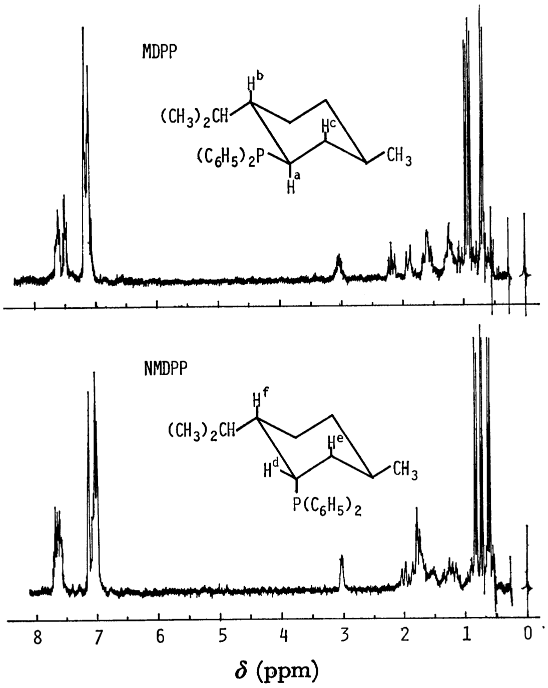

Fig. 1. The PMR spectra of MDPP and NMDPP at 220 MHz (benzene-d_6 solution).

The PMR spectra of the MDPP thus prepared is distinctly different from that of NMDPP, as is shown in Fig. 1; this indicates that MDPP is not contaminated by NMDPP. MDPP has an axial α-hydrogen (H^a) and two axial β-hydrogens (H^b and H^c) in the most stable conformation, and therefore MDPP exhibits an α-hydrogen multiplet with relatively large coupling constants. On the other hand, NMDPP has an α-hydrogen in the equatorial position, coupling and so the constant between H^d and H^e, and that between H^d and H^f, are much smaller.

The new route also offers a convenient way to prepare dimenthylphosphines and possibly even trimenthylphosphine.

Experimental

Neomenthyldiphenylphosphine was prepared by the method outlined in the literature.[1] The PMR spectra were recorded on a Varian HR-220 NMR spectrometer.

Menthyldiphenylphosphine. Menthyl chloride was prepared according to the method reported by Smith and Wright,[6] $[\alpha]_D$ −45.0° (neat). Magnesium (3.4 g, 0.14 mol) and 35 ml of dry tetrahydrofuran were placed in a 200 ml flask, and the mixture was treated with ethyl bromide (0.5 ml). Then, a solution of 20 ml of menthyl chloride (0.11 mol) in 40 ml of tetrahydrofuran was added, portion by portion, over a period of 4 hr at 50 °C, followed by reflux for 30 min. To the filtrate of the mixture, a 20 g portion of diphenylphosphinous chloride (0.091 mol) was added at 0 °C over a 10 min period. The resultant mixture was refluxed for 20 min, hydrolyzed by the cautious addition of 50 ml of water, and then extracted with hexane–ether. The organic layer was washed with water, dried over calcium sulfate, and concentrated. Through an agitated pot-still molecular distillation under 4—5×10^{-4} mmHg, a fraction boiling at 110—120 °C (bath temperature) was collected, yield; 15 g (51%). A viscous oily substance solidified in several days and was then recrystallized from methanol to give large colorless needles; mp 52.9—54.0 °C (under nitrogen, corrected), $[\alpha]_D$ −93.5° (c 1.56, CH_2Cl_2).

Found: C, 81.60; H, 8.75%. Calcd for $C_{22}H_{29}P$: C, 81.44; H, 9.01%.

References

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