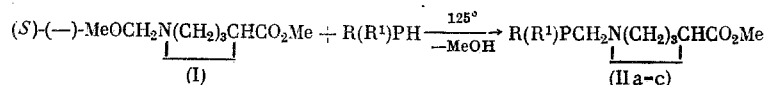


OPTICALLY ACTIVE AMINOMETHYLPHOSPHINES

R. G. Kostyanovskii, Yu. I. El'natanov,
and Sh. M. Shikhaliev

UDC 541.65:547.233:547.1'118

Optically active aminomethylphosphines IIa-IIc, which are of interest as ligands for catalysts of asymmetric reactions [2], have been synthesized for the first time after [1] according to the reaction scheme



R = R¹ = i-Pr (IIa); R = i-Pr, R¹ = PhCH₂ (IIb); R = Me₃C, R¹ = Ph (IIc). Compound I was synthesized according to [3].

Compound IIa, 94% yield, bp 100–104°C (2 mm), m/e 245 (M⁺), [α]₅₄₆²⁰ –76.8° (c 8.5, MeOH). PMR spectrum (60 MHz, CDCl₃ relative to HMDS), δ, ppm (J, Hz): 1.2 (Me_A, J_{HH} = 6, J_{HP} = 11.25), 1.1 (Me_B, J_{HH} = 6, J_{HP} = 9.75), 1.72 (HCP), 1.91 and 3.3 (m, ring CH₂), 2.92 (CH₂P, Δν = 28 Hz, J_{HA}P = 2.5, J_{HB}P = 4.5, J_{HAHB} = 12.5), 3.75 (MeO).

Compound IIb, 63% yield, bp 150–152°C (1 mm), [α]₅₄₆²⁰ –22.3° (c 0.5 MeOH). PMR spectrum (80 MHz, C₆F₆, 1:1 mixture of diastereomers): 1.06 (Me_A, J_{HH} = 6, J_{HP} = 14), 0.98 (Me_B, J_{HH} = 6, J_{HP} = 12.6), 1.81 (HCP), 1.79 and 2.69 (m, ring CH₂), 3.56 (MeO¹), 3.66 (MeO²), 7.15 (Ph).

Compound IIc, 78% yield, bp 149–150° (1.5 mm), [α]₅₄₆²⁰ –57.0° (c, 1.9, MeOH). PMR spectrum (C₂Cl₄, 1:1.2 mixture of diastereomers): 0.88 (Me₃C¹, J_{HP} = 12), 0.91 (Me₃C², J_{HP} = 12), 3.44 (MeO¹), 3.52 (MeO²), 3.21 (CH₂¹, AB, Δν = 66 Hz, J_{HA}P = 3.5, J_{HB}P = 2.5, J_{HAHB} = 13), 3.18 (CH₂², AB, Δν = 72 Hz, J_{HA}P = 3.5, J_{HB}P = 2.5, J_{HAHB} = 13), 1.66 and 2.82 (m, ring CH₂), 7.0 (Ph).

The reaction of Me₃C(Ph)PCH₂NMe₂ (III) with 1/2 mole of (S)(–)-TsN(CH₂)₃CHCOCl [4] (in ether, 0.5 h,

–50°C) yielded enantiomer-enriched (–)-III. Compound III was synthesized according to [1] in a 65% yield with bp 130°C (10 mm) and m/e 233 (M⁺). PMR spectrum (C₆F₆): 0.87 (Me₃C, J_{HP} = 12), 2.2 (MeN), 2.81 (CH₂P, AB, Δν = 22 Hz, J_{HA}P = 5.5, J_{HB}P = 3.75, J_{HAHB} = 13.8), 7.25 (Ph). ³¹P NMR spectrum (Ph₂O): 11.5 ppm. (–)-III: [α]₅₄₆²⁰ –8.2°, [α]₄₀₄²⁰ –28.1° (c 1.0, C₆H₆), identical to III according to its constants. N-Bromobenzylated (–)-III: [α]₅₄₆²⁰ –3.4°, [α]₄₀₄²⁰ –5.5° (c 0.6, MeOH). PMR spectrum (60 MHz, CD₃OD): 1.05 (Me₃C, J_{HP} = 13.5), 2.98 (d, MeN, Δν = 9 Hz), 4.2 (CH₂P, AB, Δν = 36 Hz, J_{HA}P = 5.0, J_{HB}P = 1.5, J_{HAHB} = 15), 4.65 (CH₂Ph), 7.5 (Ph).

LITERATURE CITED

1. R. G. Kostyanovskii, Yu. I. El'natanov, and Sh. M. Shikhaliev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 249 (1977).
2. R. H. Grubbs and R. A. Devries, *Tetrahedron Lett.*, 1879 (1977).
3. R. G. Kostyanovskii, A. E. Polyakov, M. D. Isobaev, G. K. Kadorkina, and V. I. Markov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1444 (1974).
4. A. F. Beecham, *J. Am. Chem. Soc.*, **79**, 3257 (1957).

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 4, pp. 972–973, April, 1978. Original article submitted January 6, 1978.