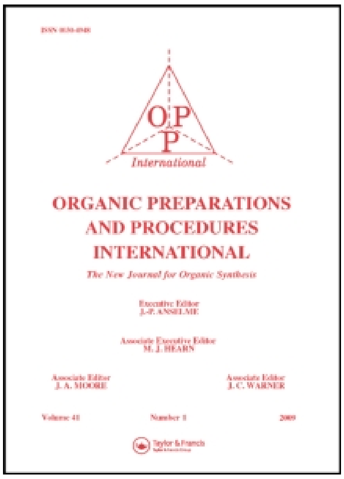

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DIFERROCENYLPHENYLPHOSPHINE AND DIPHENYLFERROCENYLPHOSPHINE

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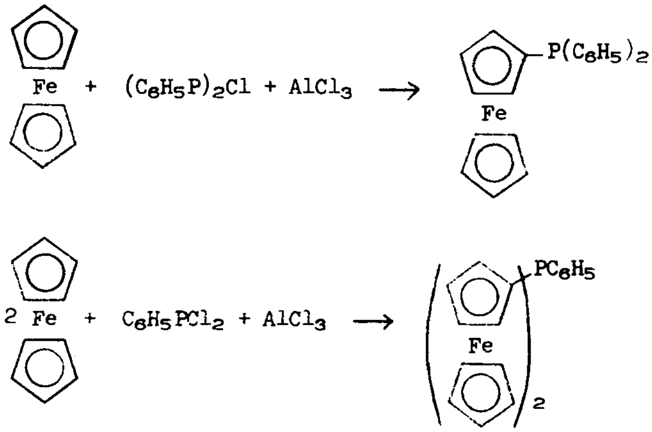

The preparations of diferrocenylphenylphosphine and diphenylferrocenylphosphine have been reported by Sollott and co-workers.[1] However, in our hands yields were quite erratic. In the case of diferrocenylphenylphosphine, frequently no product was obtained; when a product was obtained, purification by the described methods was not efficient and led to large losses of material. We have found that these phosphines can be converted readily to stable ylids, which give yields of trans-olefins in reactions with aldehydes comparable to or better than those obtained by use of semi-stable ylids.[2,6] We thus would like to report a modified procedure which gives consistent yields of pure phosphines.[3]

Experimental

Ferrocenyldiphenylphosphine. To 500 ml. of anhydrous heptane contained in 1 ℓ., 3-necked round bottomed flask fitted with a stirrer, condenser, and dropping funnel, was added, in a nitrogen atmosphere, 37.2 g. (0.2 mole) of ferrocene and 26.8 g. (0.2 mole) of $AlCl_3$. Diphenylchlorophosphine (44.2 g., 0.2 mole) was then added dropwise over a period of 15 min. The mixture was stirred and refluxed for 20 hrs. The warm heptane solution was decanted, the black, tarry residue extracted with two additional 200 ml. portions of boiling heptane and the extracts discarded. A second extraction with 350 ml. portions of boiling water (until the extracts were no longer blue-green in color) gave a brown-orange residue which was extracted with 300 ml. portions of boiling benzene (until the extracts were no longer colored). The dried, combined benzene extract was chromatographed on a 30 x 1 in. column of neutral alumina, activity I. A small yellow band consisting of unreacted ferrocene passed through very quickly. The product was eluted with benzene and ferrocenyldiphenylphosphine oxide remained on the column. The benzene eluate was evaporated under vacuum to give 35.7 g. of a yellow-orange solid. One recrystallization from 95% ethanol gave 33 g. (45%) of orange needles, mp. 122-124°, lit.[1] mp. 122-124°.

Diferrocenylphenylphosphine. This compound was prepared in the same manner as ferrocenyldiphenylphosphine from 13.4 g. (0.1 mole) of aluminum chloride, 37.2 g. (0.2 mole) of ferrocene and 17.9 g. (0.1 mole) phenyldichlorophosphine. One recrystallization of the crude product (21.1 g.) from 40:60 benzene-heptane gave 18.7 g. (40%) of yellow platelets, mp. 191-194° (dec.), lit.[1,4], mp. 191-193°.

References

1. G. P. Sollott, H. E. Mertwoy, S. Portnoy and J. L. Snead, J. Org. Chem., 28, 1090 (1963).

2. For example, carbethoxymethylenetri-n-butylphosphorane and carbethoxymethylenetri-p-anisylphosphorane, which are not isolable, react with benzaldehyde to give olefinic product that is 95% and 85% trans-isomer, respectively.[5] The corresponding ylids derived from the ferrocenyl substituted phosphines described here react with

benzaldehyde to give ester that is 96% trans-isomer.[6] These ylids are isolable and, if kept protected from light, can be stored for prolonged periods of time.

3. The chromatographic procedure used in the purification is quite efficient in removing phosphine oxide impurities.

4. In our hands, diferrocenylphenylphosphine was not sufficiently soluble to be recrystallized from 95% ethanol.[1]

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