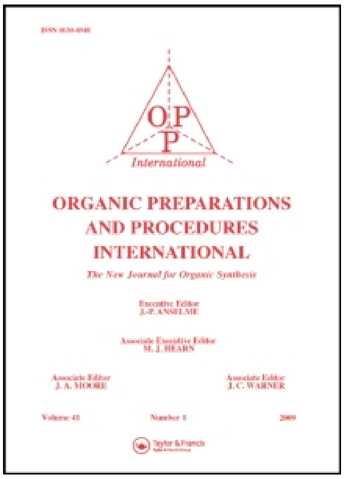

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FERROCENYLPHOSPHINES BY A REVISED PROCEDURE

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OPPI BRIEFS

FERROCENYLPHOSPHINES BY A REVISED PROCEDURE

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12/16/77
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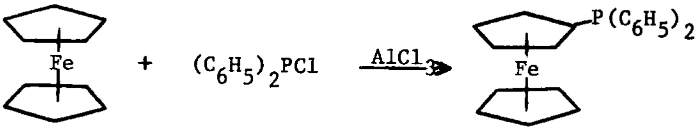
The synthesis of ferrocenyl-substituted tertiary phosphines by the Friedel-Crafts reaction[1] usually resulted in low yields or no yields of desired products. A modification of this procedure[2] though more reliable, than the first reported method, also gave low yields of products in our laboratory. This problem to some extent, appeared to be the oxidation of ferrocene, upon its admixture with aluminum chloride in the initial step. A revised procedure which minimizes this oxidation, for the preparation of ferrocenyldiphenylphosphine, which could probably be utilized in the synthesis of diferrocenylphenylphosphine, is described.



EXPERIMENTAL

To 100 ml of dry heptane in a 500 ml three-neck round-bottom flask fitted with ground-glass stirrer, condenser and equilibrating funnel was added 13.4 g (0.1 mole) of anhydrous aluminum chloride with stirring. Chlorodiphenylphosphine (22.4 g, 0.1 mole) in 25 ml of dry heptane was added to the flask from the funnel under nitrogen. A mildly exothermic reaction resulted. The mixture was stirred under nitrogen for 2 hrs. and changed to a colorless liquid. A solution of ferrocene (18.6 g, 0.1 mole) in heptane (100 ml) and

30 ml of methylene chloride was added to the chlorodiphenylphosphine-aluminum chloride complex from the equilibrating funnel with continued stirring. The mixture was refluxed under nitrogen for 22 hrs., then allowed to cool. The solvent was decanted and the residue was washed with hot heptane (until the heptane was colorless) to remove unreacted ferrocene. The washings were combined with the reaction solvent and distilled *in vacuo* to give a trace of ferrocene. The residue in the reaction flask was washed with hot water until the washings were colorless. Ascorbic acid was added to the blue washings, the solution became colorless and a yellow precipitate of ferrocene formed. The precipitate after filtering and drying, was recrystallized from 95% ethanol to give 0.6 g.

The reaction solids were extracted with hot benzene until the benzene extract was no longer dark orange (∿ 400 ml). The benzene extract was dried over anhydrous magnesium sulfate, then concentrated by vacuum distillation. The concentrate was chromatographed on neutral alumina and eluted with petroleum ether to remove a small amount of ferrocene. The phosphine was eluted with benzene and obtained in crystalline form upon removal of the eluting solvent by vacuum distillation. A yellow band of phosphine oxide, presumably from oxidation of the phosphine, remained on the column. The yield of orange-yellow crystalline ferrocenyldiphenylphosphine was 18.5 g (50%), mp. 117-121°. Recrystallization from 95% ethanol gave orange needles, mp. 121-123°, lit.[1] mp. 122-124°.

REFERENCES

1. G. P. Sollott, H. E. Mertwoy, S. Portnoy and J. L. Snead, J. Org. Chem., 28, 1090 (1963).
2. C. E. Sullivan and W. E. McEwen, Org. Prep. Proced., 2, 157 (1970).