Triferrocenylphosphine and diferrocenylphosphinous chloride. Novel preparation, and characterization

Recently, Nesmeyanov *et al.*[1] reported that triferrocenylphosphine oxide (I), first prepared by Sollott and Howard in 11 % yield from ferrocene and excess phosphorus trichloride under Friedel–Crafts conditions[2], can be obtained in 78 % yield by performing the reaction in methylene chloride. Several attempts to duplicate results with methylene chloride in this laboratory, however, have failed to produce any of (I), or any other product except a trace of diferrocenylphosphinic acid[2]. No detailed experimental procedure is given in ref. 1. In the present work, phosphorus trichloride in methylene chloride (dried over phosphorus pentoxide) was added dropwise to ferrocene and anhydrous aluminum chloride in the same solvent. As per ref. 1, the reactant ratio was 1:4:1 (ferrocene: PCl_3:$AlCl_3$), and the reflux time, 3 h. In another attempted procedure, ferrocene was added to the phosphorus trichloride and aluminum chloride. Attempts to prepare the triferrocenylphosphine oxide–benzene complex reported in ref. 1 were likewise unsuccessful.

We wish to report the preliminary results of our own work which has produced triferrocenylphosphine (II) and its oxide (I) in a combined yield of 70 % from ferrocene, N,N-diethylphosphoramidous dichloride [$(C_2H_5)_2NPCl_2$], and anhydrous aluminum chloride in *n*-heptane. The reaction is of particular interest in that triferrocenylphosphine, which earlier had eluded isolation attempts[*], can be obtained in at least 47 % yield *per se* from the mixture, and is potentially as useful as triphenylphosphine as ligand in the formation of novel coordination compounds, and as starting material for the preparation of novel phosphorane derivatives.

Compounds (I) and (II) were obtained as follows. A solution of the phosphoramidous dichloride (0.05 mole) in *n*-heptane (100 ml) was added dropwise over 30 minutes to ferrocene (0.15 mole) and anhydrous aluminum chloride (0.15 mole) in the same solvent (250 ml) with stirring under nitrogen. The mixture was refluxed 20 h with stirring, after which the reddish heptane-insoluble taffy was hydrolyzed in 500 ml of water, stirring until all solids became light yellow. The solids were extracted with 1 l of boiling benzene in portions, and the combined extracts were dried over anhydrous sodium sulfate, reduced to one-half the volume, then chromatographed on a 100-cm column of activated alumina (80–200 mesh). The phosphine (II) was eluted with benzene, then the phosphine oxide (I), with chloroform. Triferrocenylphosphine (II) has now been characterized for the first time; fine yellow needles from *n*-heptane or 95 % ethanol, m.p.[**] 271–273° (closed capillary). The compound is infusible and decomposes under normal melting procedure. The melting point was observed by immersion of the sample in the heating bath at 270°.

Compound (II), when isolated *via* chromatography, is stable to air oxidation despite the strong electron-donor character of the ferrocenyl group[3], and can be purified by crystallization. Concentration of benzene or *n*-heptane solutions of the phosphine (II) by boiling in an air stream caused partial conversion to the oxide. No oxidation occurred when solutions of (II) were evaporated in an air stream at room temperature, or when (II) was heated 1 h at 175°.

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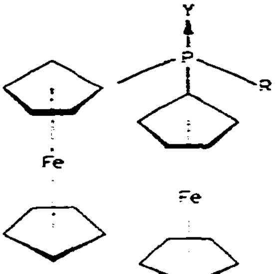
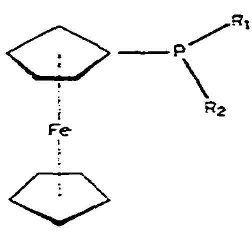
[*] The phosphine was previously isolated as the oxide and quaternary methiodide[2].

[**] Melting points are uncorrected. All new compounds prepared in the study gave satisfactory elemental analyses.

When attempts were made to obtain (II) directly from the benzene extracts of the reaction solids without resorting to column chromatography, however, oxidation resulted. That the phosphine (II) was not characterized previously[2], is attributable to this yet unexplained sensitivity to oxidation. It is of interest that triphenylphosphine on standing in benzene is converted to its oxide by air[4]. It is significant that ferrocenylphosphines containing the benzene nucleus, such as diferrocenylphenylphosphine[5] and diferrocenyl(*p*-methoxyphenyl)phosphine*, can be isolated *sans* chromatography. Oxidation of (II), and the interesting question of whether (II) is stabilized by delocalization of the lone electron pair on phosphorus into the ferrocene ring system is under further investigation.

The phosphine (II) was converted, by treatment with sulfur and selenium in benzene, to the sulfide (III) and selenide (IV) in nearly quantitative yields; both yellow needles from benzene–heptane, m.p., respectively, 291–293° (dec.) and 297–299° (dec.). The former compound is infusible and decomposes under normal melting procedure. The melting point was observed by immersion of the sample in the heating bath at 290°. The conversion of triferrocenylphosphine oxide (I) to the sulfide (III) by reaction with phosphorus pentasulfide has been reported by Nesmeyanov *et al.*[1], but this also could not be duplicated in our laboratory. (The melting point of triferrocenylphosphine sulfide is not reported in ref. 1.)





(I), R = $C_5H_5FeC_5H_4$, Y = O
(III), R = $C_5H_5FeC_5H_4$, Y = S
(IV), R = $C_5H_5FeC_5H_4$, Y = Se
(VII), R = $N(C_2H_5)_2$, Y = O
(VIII), R = H, Y = O

(II), $R_1 = R_2 = C_5H_5FeC_5H_4$
(V), $R_1 = R_2 = Cl$
(VI), $R_1 = C_5H_5FeC_5H_4$, $R_2 = Cl$

The Friedel–Crafts reaction of ferrocene with *N,N*-diethylphosphoramidous dichloride is additionally useful in that, on modification of the reactant ratio, ferrocenylphosphonous dichloride (V), diferrocenylphosphinous chloride (VI), and diferrocenyl-*N,N*-diethylphosphinic amide (VII) also are isolable. Thus (V), (VI), and (VII) were obtained in 5%, 9%, and 13% yields, respectively, together with other products giving an over-all yield of 95% [including (I) (53%), and diferrocenylphosphinic acid[2] (15%)], when the reactants were employed in equimolar amounts. Compound (V) was reported previously[6]. Compounds (VI) and (VII) were characterized for the

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* Diferrocenyl-*p*-tolylphosphine and diferrocenyl(*p*-chlorophenyl)phosphine are others; unpublished results, this laboratory.

first time; the former, yellow crystals, sometimes orange needles from *n*-heptane, m.p. 183–184° (closed capillary); the latter, orange crystals from *n*-heptane, m.p. 134–136.5°. The phosphinous chloride (VI) was converted to diferrocenylphenylphosphine[5] by reaction with phenylmagnesium bromide. Trituration of (VI) with water caused quantitative hydrolysis to the previously unknown diferrocenylphosphine oxide (VIII)**; orange needles from benzene-heptane, m.p. 190–193° (dec.), slightly soluble in hot water. Melting at 194–195° without decomposition was observed when the sample was immersed in the heating bath at 193°. Boiling of the phosphinous chloride (VI) with aqueous alkali largely produced (VIII), but also caused some oxidative hydrolysis to diferrocenylphosphinic acid[2] which precipitated on acidification of the solution.

Investigation of the scope and mechanism of the reaction of phosphorus$^{\mathrm{III}}$ amides with ferrocene under Friedel–Crafts conditions is continuing.

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** For a recent discussion of the hydrolysis of phosphinous chlorides to secondary phosphine oxides, see ref. 7.