# A Simple Modification of Vilsmeier Method for the Preparation of Formylferrocene

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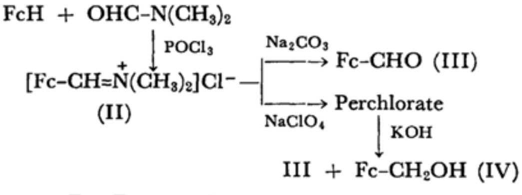
(Received July 25, 1967)

Various routes to obtain formylferrocene (III), which serves as an important starting material for the synthesis of many ferrocene derivatives, have been reported.[1-6] The Vilsmeier reaction of ferrocene with *N*-methylformanilide and phosphoryl chloride was most conveniently utilized for the preparation of the aldehyde.[1-5] Graham and his coworkers[3] reported that the aldehyde could be prepared also with dimethylformamide and phosphoryl chloride as formylating reagent, but their method gave only 23% yield. In the course of synthetic investigation of ferrocene derivatives, the present authors found a modified Vilsmeier method using dimethylformamide instead of *N*-methylformanilide, in which the yield of the aldehyde was much improved and the separation of the product from the reaction mixture was much easier than the original method,[3] a troublesome chromatographic separation being unnecessary. In this modification, phosphoryl chloride was introduced into a chloroform solution of the mixture of ferrocene and dimethylformamide to form a Vilsmeier complex (II), which on careful neutralization by sodium carbonate afforded the aldehyde (III). The addition of ferrocene to the mixture of dimethylformamide and phosphoryl chloride also gave no unfavorable effect on the reaction. However, direct addition of phosphoryl chloride to ferrocene at the primary stage of the reaction decreased the yield of the product. This is probably due to the decomposition of ferrocene which is expected to occur to a certain extent by the action of phosphoryl chloride.



Fc = Ferrocenyl

When an aqueous solution of sodium perchlorate was added to the initial reaction mixture, followed by decomposition by water at the end of the reaction, violet crystals separated from the solution. Their IR spectrum showed the existence of $-C{=}\overset{+}{N}-$ group by the characteristic absorption band at 1668 cm$^{-1}$. Therefore, this substance is considered to be a perchlorate of the Vilsmeier complex (II) corresponding to that previously suggested by Jutz.[7] The perchlorate gave formylferrocene and hydroxymethylferrocene by treatment with 10% aqueous potassium hydroxide solution. Neither the Vilsmeier complex itself nor formylferrocene gave hydroxymethylferrocene by the action of aqueous alkali.

## Experimental

A typical procedure for the modified Vilsmeier method was carried out as follows:

14.6 g (0.2 mol) of dimethylformamide was added to the solution of 18.6 g (0.1 mol) of ferrocene in 75 m*l* of dry chloroform and the resulting mixture was stirred in an ice-bath under nitrogen atmosphere for 10 min. Then, 30.6 g (0.2 mol) of phosphoryl chloride was added dropwise to the mixture over about half an hour. After the addition had been completed, the reaction mixture was kept stirring for 20 hr under heating at 55—60°C on a water-bath taking care that the temperature did not exceed 60°C. At the end of the reaction, chloroform was evaporated off under reduced pressure below 60°C,[*] and the residue was poured into the mixture of ice and water. Solid precipitates, most of which should be unreacted ferrocene, was filtered off. The filtrate, aqueous solution of the Vilsmeier complex, was neutralized carefully with sodium carbonate powder and then was extracted repeatedly with ether. All the extracts were combined together and dried over anhydrous magnesium sulfate after washing with water. The crude product obtained by evaporation of the solvent was pure enough for most synthetic purpose. Recrystallization from a mixed solvent (dichloromethane 3 : *n*-hexane 1) gave pure formylferrocene as reddish-brown crystals, mp 124.5°C. The yield was 15.2—15.7 g (71—74%).

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1) G. D. Broadhead, J. M. Osgerby and P. L. Pauson, *Chem. Ind. (London)*, **1957**, 209.

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3) P. J. Graham, R. V. Lindsey, G. W. Parshall, M. L. Peterson and G. M. Whitman, *J. Am. Chem. Soc.*, **79**, 3416 (1957).

4) M. Rosenblum, *Chem. Ind. (London)*, **1957**, 72.

5) K. Schlögl, *Monatsh. Chem.*, **88**, 601 (1957).

6) K. Schlögl and A. Mohar, *ibid.*, **92**, 219 (1961).

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[*] The evaporation of solvent above 60°C will be hazardous because of accidental explosion.