SHORT PAPER

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Facile and effective preparation of substituted phenylferrocene under phase transfer catalysis[†]

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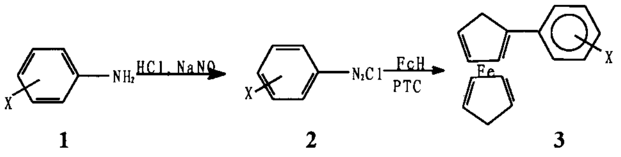
A series of phenylferrocene were synthesized *via* diazo-salts under PTC in excellent yield.

Procedures have been reported for the synthesis of phenylferrocene *via* diazo-salt reactions,[1] but the methods were tedious and the yields were usually low. Phase transfer catalysis (PTC) is one of the most attractive techniques in organic synthesis and the use of it for nucleophillic substitution reactions is well documented.[2] We know phase-transferring agents can activate oxidation[3] and other reaction such as synthesis of chiral complexes,[4] and of coordination compounds[5] *etc*. However, to the best of our knowledge, the application of phase-transfer catalyst as a preparative method in the reaction of synthesis of substituted phenylferrocene is little described so far.[6] We are interested in developing new methods of simplicity, convenience and efficency to synthesize a variety of substituted phenylferrocene compounds using diazonium-salts of aromatic amines under PTC[$C_{16}H_{33}N(CH_3)_3Br$] for our further work.[7] The procedure of synthesis is shown in Scheme 1.



Scheme 1

We have synthesized a series of phenylferrocene derivatives under PTC and obtained product easily and efficiently. The yields of these reactions are high, usually more than 80%, although the aromatic amine has a big *o*-substituted function such as $-NO_2$, $-OCH_3$ *etc*. Furthermore, we hardly observed the bi-substituted product of two cyclopentadienyl rings and this make the separation of product easy. At the same time, unreacted ferrocene is rare. The experiment results were summarized in Table 1.

Table 1 The results of preparation of arylferrocenes **3a–3m** under PTC

Product	X	Time[a]/h	Yield (%)	m.p[b]/°C (lit.)
3a	H	1.0	98.7	107–108.5(109–110)
3b	2-CH_3	2.5	94.5	51–52 (51–52)
3c	3-Cl	1.2	88.5	78–80(77–78)
3d	4-Cl	1.0	88.5	121–123 (122–123)
3e	4-OCH_3	1.5	85.3	112–114 (112–114)
3f	4-OH	1.5	93.2	163–165 (163–164)
3g	4-NO_2	1.0	97.5	161.5–163 (163–165)
3h	4-CHO	1.0	85.5	134–135 (134–135)
3i	2-CH_3, 4-NO_2	2.5	94.0	126–127 (127–129)
3j	3-NO_2, 5-NO_2	8.0	Trace	_
3k	2-CO_2H	2.0	97.3	127–129 (128–129)
3l	2-NO_2	2.0	79.0	110–112 (112–114)
3m	2-OCH_3	2.5	83.2	43–45 (42–44)

[a]monitored by TLC. [b] uncorrected.

General procedures for the synthesis of substituted phenyl ferrocene: To a three-necked flask with stirring equipment and thermometer, aromatic amine (0.1 mol), H_2O (30 ml) and concentrated HCl aqueous (30 ml) were added. The solution was heated to dissolve the aromatic amine, then cooled to 0–5°C. While maintaining the temperature of the solution below 5°C, $NaNO_2$ aqueous (7 g $NaNO_2$ in 20 ml H_2O) was added dropwise. After the addition, the mixture was stirred for 1–1.5 h at the same temperature. Adequate urea was added to decompose the surplus HNO_2· $C_{16}H_{33}N(CH_3)_3Br$ (0.5g) was used as catalyst. Then, keeping the temperature below 5°C, the solution of ferrocene (0.01 mol ferrocene in 20ml ether) and 0.5 g $C_{16}H_{33}N(CH_3)_3Br$ was added dropwise over 0.5–1h under stirring. The solution was stirred for 0.5–2.5 h at room temperature. The reaction was monitored by TLC. After the completion of the reaction, the ether was evaporated under reduced pressure. The precipitated solid product was collected by filtration and washed with water.

The unreacted ferrocene was removed from product by vapour distillation, the residue was crude product. The pure product was recrystallized from a suitable solvent as reported.[1]

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*