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$(Et_4N)_2[Fe_4(SPh)_{10}]$ Stimulated $S_{RN}1$ Reactions of α-Bromonaphthalene with Pinacolone Carbanion

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Abstract: The $(Et_4N)_2[Fe_4(SPh)_{10}]$ stimulated reaction of α-bromonaphthalene with pinacolone carbanion in DMSO leads to the formation of 1-(α-naphthyl)pinacolone. The reaction is suggested in terms of $S_{RN}1$ mechanism of aromatic nucleophillic substitution and has potential value in synthesis to obtain α-substituted naphthalene derivaties.

Keywords: $S_{RN}1$ reaction, naphthalene derivative, pinacolone carbanion, nucleophilic substitution.

The studies of the radical chain nucleophilic substitution reaction ($S_{RN}1$) have been active field in both mechanism and organic synthesis research[1-4]. The mechanism is a well known process by which a nucleophilic substitution is produced on a non-actived adequated substituted substrate. It is a chain process which involves radicals and radical anions as intermediates. The main steps of this mechanism are sketched in **scheme 1**.

Scheme 1

$$\mathrm{ArX} + e \longrightarrow [\mathrm{ArX}]^{\overline{\bullet}} \qquad (1)$$

$$[\mathrm{ArX}]^{\overline{\bullet}} \longrightarrow \mathrm{Ar}^{\bullet} + \mathrm{X}^{-} \qquad (2)$$

$$\mathrm{Ar}^{\bullet} + \mathrm{Nu}^{-} \longrightarrow [\mathrm{ArNu}]^{\overline{\bullet}} \qquad (3)$$

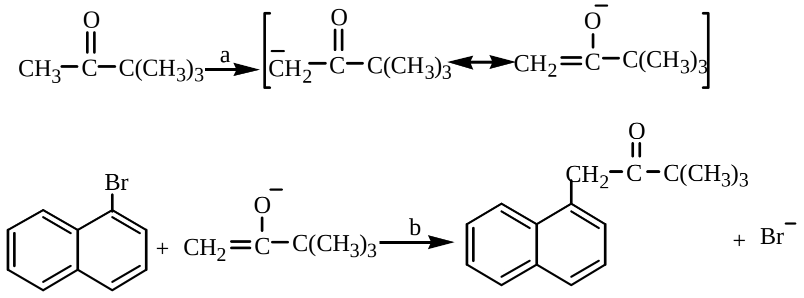
$$[\mathrm{ArNu}]^{\overline{\bullet}} + \mathrm{ArX} \longrightarrow \mathrm{ArNu} + [\mathrm{ArX}]^{\overline{\bullet}} \qquad (4)$$

As stimulated methods of initiation step, the photostimulated[5-7], solvated electrons such as sodium amalgam in liquid ammonia[8], or electrochemically induced[9] $S_{RN}1$ reactions have been studied in detail. We have reported the photostimulated reactions of aryl halides with some nitrogen anions by $S_{RN}1$ mechanism[10,11]. However, the studies on metal ion stimulated $S_{RN}1$ reaction are not so much reported. In this paper, the $(Et_4N)_2[Fe_4(SPh)_{10}]$, as an electronic doner, stimulated reaction of α-bromonaphthalene with pinacolone carbanion in DMSO by $S_{RN}1$ mechanism offered 1-(α-naphthyl) pinacolone **(Scheme 2)**.

During experiment, materials were prepared in advance. Potassium *tert*-butoxide was sublimed, pinacolone and DMSO distilled under vacuum and stored over molecular sieves. EFSP was synthesized according to the literature[12]. 1-(α-naphthyl)pinacolone was obtained by the following method. Potassium *tert*-butoxide and DMSO were added to a single-necked round-bottomed flask equipped with an argon inlet and magnetic stirrer, and degassed under argon, then pinacolone carbanion and EFSP were added. After potassium *tert*-butoxide and EFSP were fully dissolved in DMSO, α-bromonaphthalene was added. The reaction was carried out at stirring under argon for a peirod of time and then quenched by adding NH_4Cl and water. The reaction mixture was extracted with diethyl ether for three times of 20 mL. The diethyl ether extract was washed twice with water and the solvent was removed under reduced pressure. The residue, after column chromatography on silica gel (eluted with petroleum ether: 1,2-dichloroethane =7:3) gave the substitution product. The results of the reactions are listed in **Table 1.**

Scheme 2

1 **2** **3**



a: $(CH_3)_3COK$, DMSO **b:** $(Et_4N)_2[Fe_4(SPh)_{10}]$

The yield of the reaction **1** with **2** stimulated by EFSP was not influenced by the amount of EFSP (**Table 1**). To prolong the reaction time also could not increase the yield of reaction (**Table 1**), but the reaction temperature influenced the reaction yield significantly. The yield of **3** was increased with the rise of temperature (**Table 1**,entry 4,6,7). When temperature got over 80°C, the yield decreased due to the decomposition of the solvent (DMSO). The yield of **3** was only 35% when $FeCl_2{\cdot}4H_2O$ was used as stimulator (**Table 1**, entry 10).

m-Dinitrobenzene is a well known inhibitor of $S_{RN}1$ reactions, and it also inhibited the above reactions. In the absence of EFSP, the reactions did not occur at all **(Table 1)**. All these results let us to propose that the mechanism of the above reactions is $S_{RN}1$ reaction **(Scheme 1)**.

Table 1 EFSP stimulated reactions of α -bromonaphthalene with pinacolone carbanion in DMSO (under Ar)

No.	1 (mmol)	2 (mmol)	EFSP (mmol)	Reaction time (h)	Temperature (^0C)	Yields(%)^a **3**
1	2	20	0.1250	3	80	61.7
2	2	20	0.0625	1.5	80	51.2
3	2	20	0.0625	1.5	80	43.4
4	2	20	0.0625	3	80	60.2
5	2	20	0.0625	5	80	60.0
6	2	20	0.0625	3	20	17.8
7	2	20	0.0625	3	40	46.7
8^b	2	20	——	3	80	——
9^c	2	20	0.0625	3	80	4.1
10^d	2	20	0.64	3	80	35.0

a. Yields are comparative content of products and were determined by TLC-Densitiometry.
b. No EFSP was added.
c. *m*-Dinitrobenzene was added (0.1mole).
d. $FeCl_2{\cdot}4H_2O$ (0.64mmol) was employed in the reaction.

Acknowledgments

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References and notes

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