

Photostimulated $S_{RN}1$ Reactions of Benzyl Chloride with Carbazolyl Nitrogen Anion

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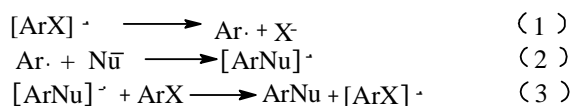
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Abstract: The photostimulated reactions of benzyl chloride with carbazolyl nitrogen anion in dimethyl sulfoxide gave 9-benzylcarbazole and 3-benzylcarbazole. The reactions are suggested in term of $S_{RN}1$ mechanism of nucleophilic substitution.

Keywords: $S_{RN}1$ reaction, carbazole, nucleophilic substitution.

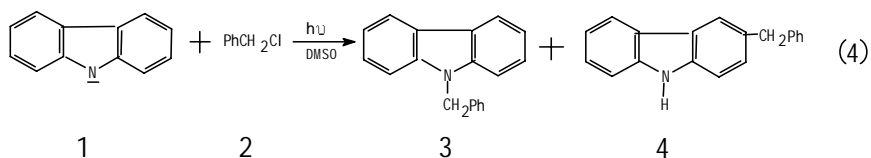
In recent years, the studies of the radical chain nucleophilic substitution reaction ($S_{RN}1$) have been active area in both mechanism and organic synthesis¹⁻³. The main steps of this mechanism are sketched in **scheme 1**.

Scheme 1



As nucleophile, various anions have been used in $S_{RN}1$ reaction. However, the studies of the reactions of organic nitrogen anions are not so much reported⁴. We have reported that photostimulated reactions of carbazolyl nitrogen anion with aryl halides in dimethyl sulfoxide by $S_{RN}1$ mechanism formed the corresponding N-arylated products⁵. In this paper, the photostimulated reactions of benzyl chloride with carbazolyl anion were studied and N- and C-substituted products were obtained in the reactions (**Scheme 2**). The results of the reactions

Scheme 2



are listed in **Table 1**. The photostimulated reaction of **1** and **2** occurs in a 12% yield of 3-benzylcarbazole **4**⁶ and 75% yield of 9-benzylcarbazole **3**⁷ (**Table 1**, entry 1). In the reaction carried out in the absence of light (**Table 1**, entry 2), the product **3** was formed in

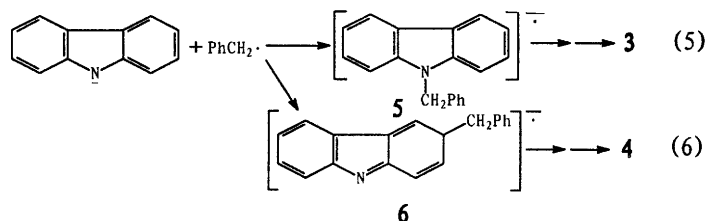
85.05% yield and the product **4** was not observed. This result shows that the formation of product **3** is according to S_N2 mechanism. In addition, the formation of product **4** was inhibited by *m*-dinitrobenzene (**Table 1** , entry 3) , a well known inhibitor of $S_{RN}1$ reaction, and the yield of

Table 1. Photostiumlated reactions of benzyl chloride with carbazolyl nitrogen anion in DMSO (under N_2)^a

No.	1(mole)	2(mole)	reaction time (h)	yields (%)	
				3	4 ^b
1	0.02	0.03	2	75.1	12.0
2 ^c	0.02	0.03	2	85.0	...
3 ^d	0.02	0.03	4	76.7	7.2
4 ^e	0.02	0.03	2	71.3	9.1

a. Carbazolyl nitrogen anion was obtained by reaction of carbazole with KOH in DMSO (70-80⁰c); Irradiation was performed with a 250w high pressure mercury arc lamp. b. Yields were determined by TLC-Densitometry.c. Dark reaction .d. *m*-Dinitrobenzene was added. e. The reaction was carried out under air .

4 was reduced in absence of inert atmospheric protection (Table 1,entry 4). All these results let us to propose a $S_{RN}1$ mechanism in play for the above reactions. Formation of the C- and N-substitution products could be ascribed to following equation (eq. 5, 6):



Acknowledgment

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References and notes

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6. 3-benzylcarbazole IR (KBr) cm^{-1} : 3473, 3049, 2929, 2853, 1600, 1486, 1453, 1398, 1324, 1303, 1238, 1152, 1129, 749, 724; 1H NMR δ_{ppm} : 6.9-8.5 (m,13H,Ar-H,N-H), 3.2 (s,2H).
7. 9-benzylcarbazole IR (KBr) cm^{-1} : 3049, 2900, 2853, 1600, 1460, 1450, 1398, 1324, 1300, 1235,1150, 745, 715; 1H NMR δ_{ppm} : 7.0-8.5 (m,13H), 5.5 (s,2H); Anal cald. for $C_{19}H_{15}N$: C, 88.68; H, 5.88; N, 5.44. Found: C, 88.65; H, 5.92; N, 5.25.

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