1,2-Radical Rearrangements of Aryl, Furanyl and Thiophenyl Groups from Carbon to Nitrogen

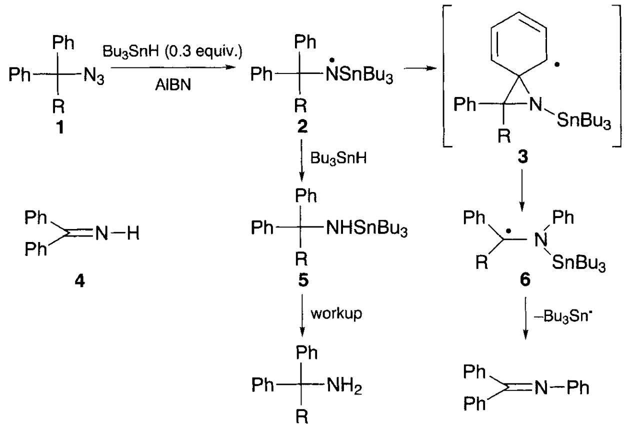
Sunggak Kim* and Jung Yun Do

Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea

1,2-Radical rearrangements of aryl, furanyl and thiophenyl groups from carbon to nitrogen using azido groups as radical precursors are observed for the first time; the 1,2-aryl rearrangement is applied to the synthesis of phenanthridine derivatives from 6-fluorenyl azides.

The 1,2-radical rearrangement of aryl groups[1] has been well studied and have been shown to occur from carbon to carbon[2] and from carbon to oxygen.[3] However, there are relatively few examples of 1,2-radical rearrangements between carbon and heteroatoms[4] or between heteroatoms.[5] Although 1,2-aryl rearrangements from carbon to nitrogen, *via* intermediate alkyl nitrenes, has been observed in the thermolysis of tertiary alkyl azides,[6] as far as we are aware, a 1,2-aryl radical rearrangement from carbon to nitrogen has not yet been reported. In connection with our research interest in the synthetic utility of the radical reactions of alkyl azides,[7] we have studied the possibility of 1,2-aryl radical rearrangements from carbon to nitrogen using alkyl azides as radical precursors.

The radical reaction of azide **1a** with $\mathrm{Bu^n_3SnH}$ (0.3 equiv.) and AIBN (0.1 equiv.) in refluxing benzene for 5 h under high dilution, afforded imine **4** as the major product with amine **7a** and imine **8a** as minor products, Scheme 1. It is evident that **7a** was produced from the direct reduction of **2a** by $\mathrm{Bu^n_3SnH}$ and subsequent workup of **5a**. Although the mechanism for the conversion of azides to the corresponding imines was previously reported,[8] an exact mechanism for the formation of **4** requires further studies because the reaction of **1a** with AIBN or benzoyl peroxide without $\mathrm{Bu^n_3SnH}$ gave **4** only in very low yields (9, 13%, respectively). We thought that **8a** might result from the previously unknown 1,2-aryl rearrangement from carbon to nitrogen.

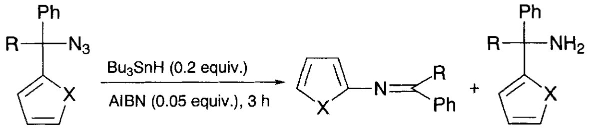


	4	7	8
a R = H	50%	11%	17%
b R = Me	—	15%	83%
c R = *sec*-Bu	—	2%	92%
d R = Ph	—	—	95%

Scheme 1

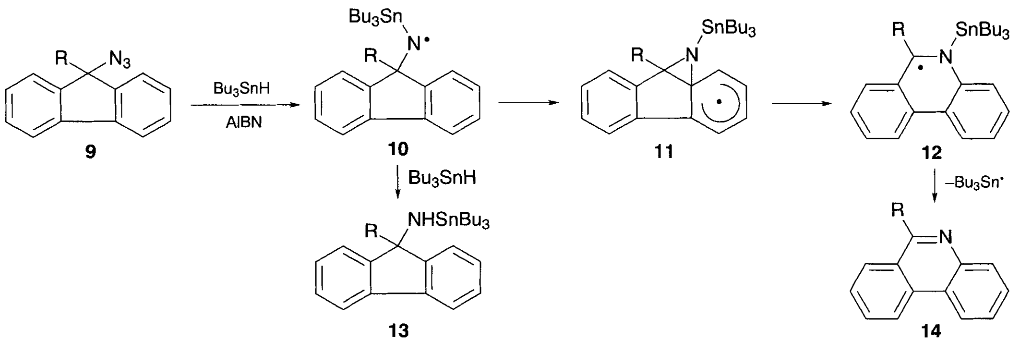
It is expected that the 1,2-aryl rearrangement should proceed *via* an intermediate spiro cyclohexadienyl radical **3**, and should be largely affected by the stability of the intermediate radical **6**. Thus, the more stable the intermediate radical **6** is, the more efficient 1,2-aryl rearrangement should be. In order to prevent the formation of imine **4**, and to generate the more stable intermediate radical, the radical reaction was carried out with tertiary azide **1b** under the same conditions. As we expected, the 1,2-aryl rearranged product was isolated as the major product **9b** (83%) with the direct reduction product **8b** (15%). Much better results were obtained with **1c** and **1d**. In the case of **1d**, only the 1,2-aryl rearrangement took place.

To demonstrate the synthetic utility of 1,2-aryl radical rearrangements, we briefly studied the conversion of 9-azidofluorenes into phenanthridine derivatives as shown in Scheme 2. Treatment of **9a** in refluxing benzene with $\mathrm{Bu^n_3SnH}$–AIBN under high dilution, afforded the reduction



	16	17
a X = O, R = Me	97%	1%
b X = O, R = Ph	72%	—
c X = S, R = Me	95%	3%
d X = S, R = Ph	91%	—

Scheme 3



	13	14
a R = Me	78%	12%
b R = *sec*-Bu	42%	30%
c R = Ph	14%	83%

Scheme 2

product **13a** in 78% yield with the 1,2-rearranged product **14a** in only 12% yield. Changing the R substituent from a methyl group to a *sec*-butyl or a phenyl group greatly improved the yield of the 1,2-rearranged product **14**, indicating that the success of the rearrangement depends on the stability of the intermediate radical **12**. Furthermore, it is noteworthy that the 1,2-rearrangement of the phenyl group in **10c** did not occur.

We next focused our attention on the 1,2-furanyl and 1,2-thiophenyl rearrangement. Furans and thiophenes are expected to have strong migratory aptitude owing to their low resonance energy which would be lost during the rearrangement. 2-Furanyl azides **15a** and **15b** underwent 1,2-rearrangement to yield **16a** and **16b**, indicating preferential rearrangement of a furanyl group over a phenyl group. Similar results were obtained with 2-thiophenyl azides **15c** and **15d**, demonstrating the efficiency of the 1,2-radical rearrangement from carbon to nitrogen, although aminyl radicals have relatively low reactivity.

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