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Ring Expansion Reaction of Heterocyclic Cation Compounds by Incorporating One Nitrogen Atom Using I_2-NH_3 System

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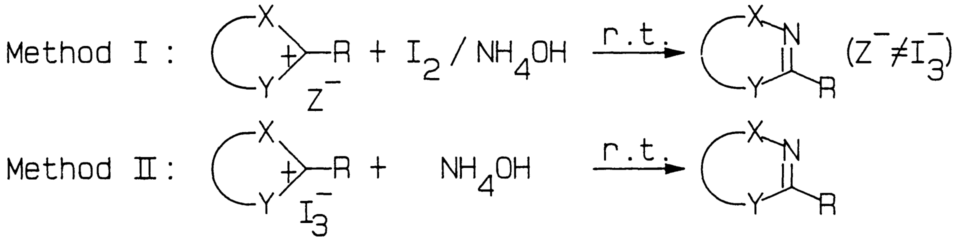
The reaction of various heterocyclic cation compounds with I_2/NH_4OH resulted in ring expansion on nitrogen atom. The similar ring expansion reaction occurred on the corresponding triiodides with NH_4OH. The reaction mechanism based on initial nucleophilic attack of NH_3 on cations, subsequent oxidative iodination, and liberation of I^- is proposed.

It is well known that the reaction of heterocyclic cation compounds with azides results in ring expansion on nitrogen atom.1) We recently reported the first example of application of N-unsubstituted sulfenamides for ring expansion.2) We now report an alternative and potentially general method for ring expansion on nitrogen atom using I_2-NH_3 system.

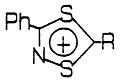
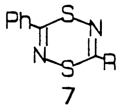
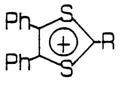
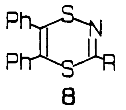
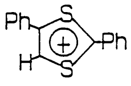
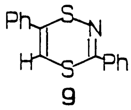
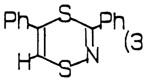
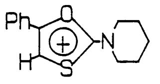
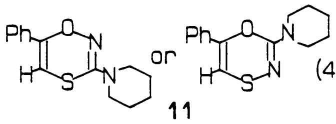
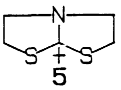
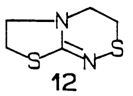
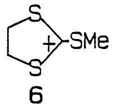
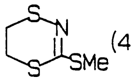
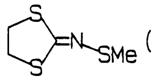


In a typical experiment, a large excess of aqueous ammonia (28%)(0.6 ml) was added to a stirred acetonitrile solution (6 ml) of heterocyclic cation compounds (1 mmol) and iodine (1 mmol) (Method I). In the case where the counter anion $Z^-=I_3^-$, there was no need for extra iodine (Method II). The reaction mixture was stirred at room temperature. The crude product was extracted with dichloromethane after addition of water, and purified by column chromatography and/or recrystallization.

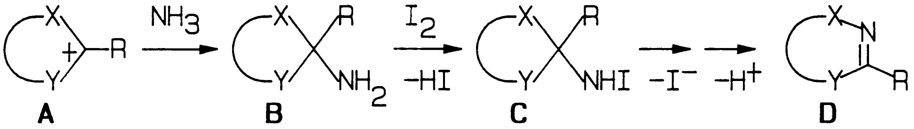
The reaction of various heterocyclic cation compounds **1-4** (aromatic) and **5,6** (aliphatic) with aqueous ammonia using Method I or II mentioned above were carried out to afford a number of "N-expansion" products **7-14**3) in favorable yields; the results are presented in Table 1. Some of these products are not accessible by known reactions of the corresponding cation compounds with NaN_3, because of low reactivity of the cations and decomposition of the products: the reaction is often carried out under forceful conditions such as irradiation and high temperature.

The reaction path is speculated that the initially-formed adduct **B** by reaction of cation **A** with NH_3 reacts with I_2 (oxidative iodination) to form intermediate **C**, which then undergoes ring expansion with a liberation of I^- followed by deprotonation to afford **D**. This mechanism is similar to that of the reaction of 9-substituted 9-fluorylamine with potassium hypochlorite leading to chloramine derivative which undergoes ring expansion via nitrene.[4] On treatment with NaN_3 instead of I_2-NH_3 system, **1b** afforded 3,5-diphenyl-1,4,2,6-dithiadiazine, isomeric ring system of **7**, in 50% yield. This significant difference in reactivity seems to be attributable to contribution of a different type of intermediates, i.e., nitrene for NaN_3 and nitrenium ion[5] for I_2-NH_3 system.

Table 1. Ring Expansion Reaction of Heterocyclic Cations

Cation	Z^-	Condition a)	Products (Yield / %) b)
 **1**	ClO_4^-	Method I	 **7** a: R=NEt_2 (54) b: R=Ph (33)
 **2**	I_3^-	Method II	 **8** a: R=NMe_2 (88) b: R=Ph (77)
 **3**	I_3^-	Method II	 **9** (23)  **10** (33)
 **4**	BF_4^-	Method I	 **11** (40)
 **5**	I_3^-	Method II	 **12** (25)
 **6**	I^-	Method I	 **13** (41)  **14** (7)

a) At r.t. in MeCN for 30 min-2 h. b) Isolated yield.



In summary, this new method offers the following advantages: wide application; easy availability of reagents, i.e., iodine and aqueous ammonia; simple experimental procedures; mild reaction conditions; favorable yields in short reaction times. Thus, we believe that it belongs to an important class of ring expansion reaction.

References
1) J. Nakayama, A. Sakai, A. Tokiyama, and M. Hoshino, Tetrahedron Lett., 24, 3729 (1983); E. Fanghänel, K. H. Kühnemund, and A. M. Richter, Synthesis, 1983, 50.
2) K. Yonemoto, I. Shibuya, and K. Honda, Bull. Chem. Soc. Jpn., 61, 2232 (1988).
3) Products **7-10** are known. **11**: yellow oil; ^{1}H-NMR($CDCl_3$,δ) 1.5-1.7(6H,m), 3.4-3.6(4H,m), 6.49(1H,s), 7.3-7.6(5H,m); ^{13}C-NMR($CDCl_3$,δ) 24.25(t), 25.28(t), 46.30(t), 105.68(d), 123.61(d), 128.11(d), 128.54(d), 132.66(s), 144.60(s), 154.57(s). **12**: mp 73.5-74.0 °C; ^{1}H-NMR($CDCl_3$,δ) 3.16(4H,br.t), 3.65(4H,br.t); ^{13}C-NMR($CDCl_3$,δ) 25.58(t), 26.47(t), 46.03(t), 55.32(t), 155.19(s). **13**: colorless oil; ^{1}H-NMR($CDCl_3$,δ) 2.38(3H,s), 3.1-3.5(4H,m); ^{13}C-NMR($CDCl_3$,δ) 13.94(q), 26.91(t), 28.64(t), 149.29(s). **14**: colorless oil; ^{1}H-NMR($CDCl_3$,δ) 2.78(3H,s), 3.4-3.8(4H,m): the methylene peaks coalesced at about 100°C in DMSO-d_6 to turn out singlet; ^{13}C-NMR($CDCl_3$,δ) 23.66(q), 36.53(t), 39.69(t), 161.78(s).
4) L. A. Pinck and G. E. Hilbert, J. Am. Chem. Soc., 59, 8 (1937).
5) P. Kovacic, M. K. Lowery, and K. W. Field, Chem. Rev., 70, 539 (1970).

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