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Formation of 3-Amino-1,2,4-triazines by Thermolysis of Condensed *N*-Amino-α-Azidoimidazoles

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1-Amino-2-azidobenzimidazole **7**, 7-amino-8-azido- **9** and 9-amino-8-azido-theophillines **12**, on heating in chlorobenzene solution, lose a molecule of nitrogen and finally give 3-amino-derivatives of benzo-1,2,4-triazine **3**, 5,7-dimethylpyrimido[4,5-*e*]-1,2,4-triazine-6,8-dione **10** (isofervenulin) and 6,8-dimethylpyrimido[5,4-*e*]-1,2,4-triazine-5,7-dione **13** (fervenulin) in good yields; the reaction is thought to proceed through the recyclization of an intermediate *C*-nitrene of type **4**.

It is well known that oxidation of 1,2-diaminobenzimidazole **1** with lead tetraacetate[1] or manganese dioxide[2] leads to the formation of 3-aminobenzo-1,2,4-triazine **3** in high yield (Scheme 1). the reaction was originally thought to proceed *via* *N*-nitrene **2**, which then underwent ring expansion.[2] However, recently we made a suggestion[3] that various experimental data could be better explained on the basis of an alternative mechanism involving the generation of *C*-nitrene **4** and its subsequent recyclization to amine **3**, probably through the diazene intermediate **5**. The fact that benzotriazines can be obtained only from those *N*-aminobenzimidazoles which contain a 2-substituent with an acidic hydrogen (NH_2, NHPh,

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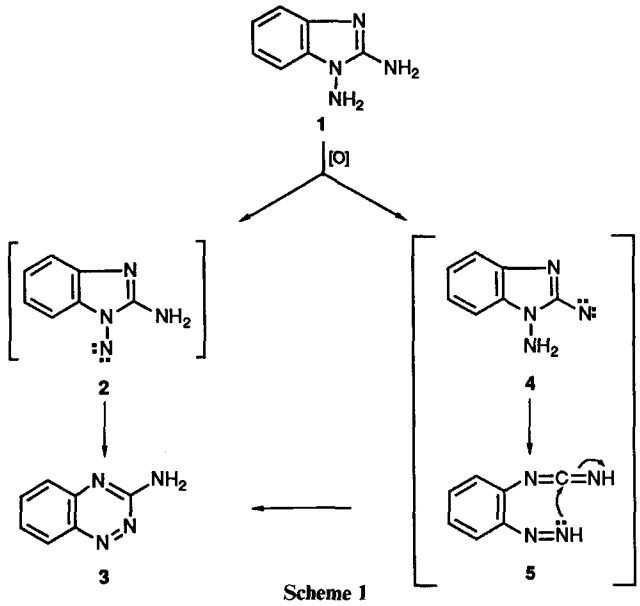
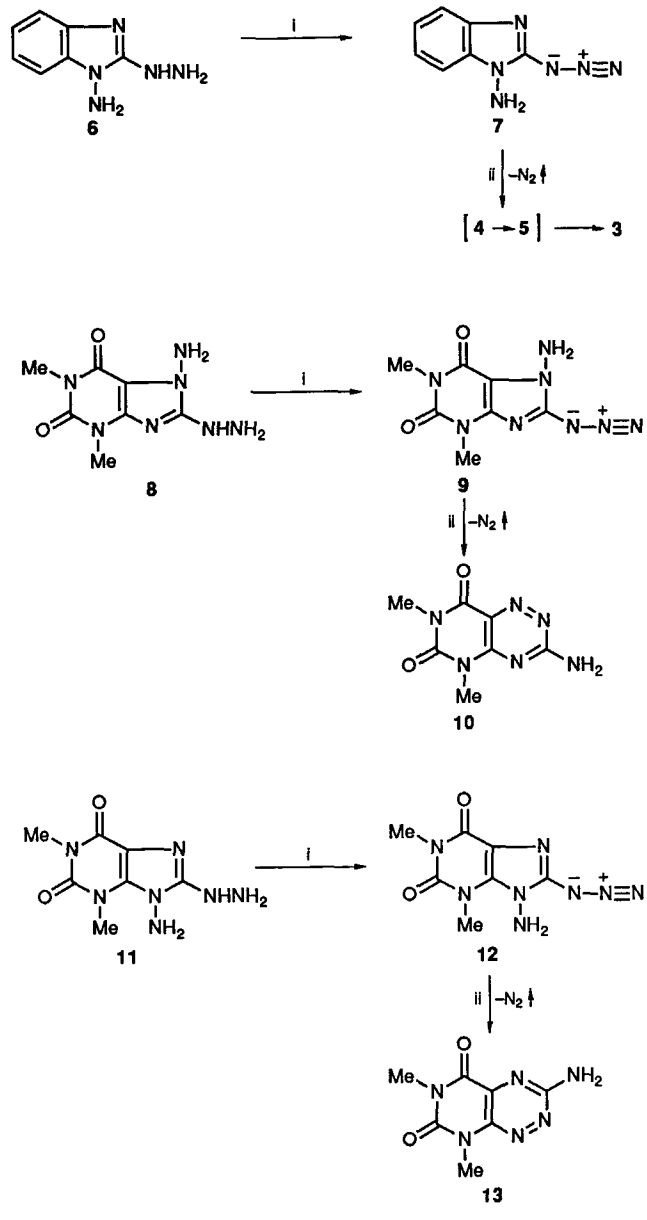


Scheme 1

OH *etc.*) is especially remarkable. Evidently, only in these cases can an acyclic intermediate of type **5** be produced. At the same time *N*-aminobenzimidazole itself and its 2-R-derivatives without an acidic functional group at position 2 (R = Me, Ph, Cl, NMe_2, SO_2Me *etc.*) give only the corresponding 1,1'-azobenzimidazole on oxidation, as a result of the interaction of the *N*-nitrene with the initial *N*-amino-compound.[4]

In order to obtain more direct evidence supporting a *C*-nitrene pathway for the formation of amine **3** in the present work we decided to generate *C*-nitrene **4** by an independent method. With this aim, the previously unknown 1-amino-2-azidobenzimidazole **7** was chosen as a starting compound to generate such a *C*-nitrene. The analogous behaviour of 7-amino-8-azido- **9** and 9-amino-8-azido-theophillines **12** has also been studied. All three azides were obtained by treatment of hydrazines **6**, **8** and **11** with one equivalent of nitrous acid. the latter compounds were synthesized by hydrazinolysis of 1-amino-2-benzimidazolesulfonic acid,[5] 7-amino-8-bromo-[6] and 9-amino-8-bromo-theophillines,[7] respectively.

Furthermore, we have found that evolution of nitrogen takes place on heating aminoazides **7**, **9** and **12** for a short time in chlorobenzene solution. Aminotriazines **3**, **10**[8] and **13** are formed as single products in 65, 80 and 55% yields, respectively (Scheme 2).† The latter compound is the first 3-amino-derivative of the antibiotic fervenulin to be isolated; a previous attempt to synthesize these compounds by a different method was unsuccessful.[8]



Scheme 2 *Reagents and conditions*: i, $NaNO_2$ (1 mole) in 2 M HCl, 0–5 °C, 30 min; ii, reflux, chlorobenzene, 30 min

The only reasonable way to rationalize the course of the reaction is in terms of initial generation of the corresponding *N*-aminoimidazolyl-2-nitrene followed by recyclization through an open-chain intermediate. Thus, oxidation of 1,2-diaminobenzimidazole **1** is very likely to proceed in the same way.

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† All new compounds gave satisfactory analytical and spectroscopic data. For **6**: m.p. 216–218 °C (decomp., from water); IR ν_{max}/cm^{-1} (Nujol) 3315, 3280, 3210 (NH_2, $NHNH_2$), 1645 (C=N), 1610, 1560 (C—C_{ar}).

7: m.p. 137–138 °C (decomp., from ethanol); IR ν_{max}/cm^{-1} (Nujol) 3330, 3200 (NH_2), 2160, 2133 (N_3), 1640 (C=N), 1617, 1583 (C—C_{ar}); ^{1}H NMR δ (90 MHz,[$^2H_6$]Me_2SO, standard $SiMe_4$) 5.88 (m, 2H, NH_2), 7.07–7.28 (m, 2H, 4,7-H), 7.32–7.54 (m, 2H, 5,6-H).

8: m.p. 139–140 °C (decomp., from water); IR ν_{max}/cm^{-1} (Nujol) 3305 (NH_2), 1717, 1673 (C=O), 1640 (C=N).

9: m.p. 190–191 °C (decomp., from ethanol); IR ν_{max}-cm^{-1} (Nujol) 3350, 3250 (NH_2), 2183 (N_3), 1700, 1680 (C=O), 1656 (C=N); ^{1}H NMR δ (90 MHz, [$^2H_6$]Me_2SO, standard $SiMe_4$) 3.21 (s, 3H, N^1—Me), 3.37 (s, 3H, N^3—Me), 6.04 (m, 2H, NH_2).

11: m.p. 230–231 °C (decomp., from water); IR ν_{max}/cm^{-1} (Nujol) 3325, 3280, 3210, 3120 (NH_2, $NHNH_2$), 1685, 1660 (C=O), 1639 (C=N); ^{1}H NMR δ (90 MHz, [$^2H_6$]Me_2SO, standard $SiMe_4$) 3.25 (s, 3H, N^1—Me), 3.75 (s, 3H, N^3—Me), 5.78 (m, 2H, NH_2).

12: m.p. 160–161 °C (decomp., from ethanol); IR ν_{max}/cm^{-1} (Nujol) 3500, 3303 (NH_2), 2143, (N_3), 1706, 1660 (C=O), 1605 (C—C_{ar}); ^{1}H NMR δ (90 MHz, [$^2H_6$]Me_2SO, standard $SiMe_4$) 3.22 (s, 3H, N^1—Me), 3.72 (s, 3H, N^3—Me), 6.04 (m, 2H, NH_2).

13: m.p. 353–355 °C (decomp., from ethanol); IR ν_{max}/cm^{-1} (Nujol) 3375, 3256, 3163 (NH_2), 1720, 1680 (C=O), 1620 (CκN), 1598 (C—C_{ar}); ^{1}H NMR δ (90 MHz, [$^2H_6$]Me_2SO, standard $SiMe_4$) 3.29 (s, 3H, N^6—Me), 3.58 (s, 3H, N^8—Me), 7.40 (m, 2H, NH_2); *m/z* 208.

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