Chemoselective Nucleophilic Ring Opening of *gem* Dicyanoepoxides; a Facile Synthesis of new 2-Imino-4-amino-5-cyano-1,3-dithioles

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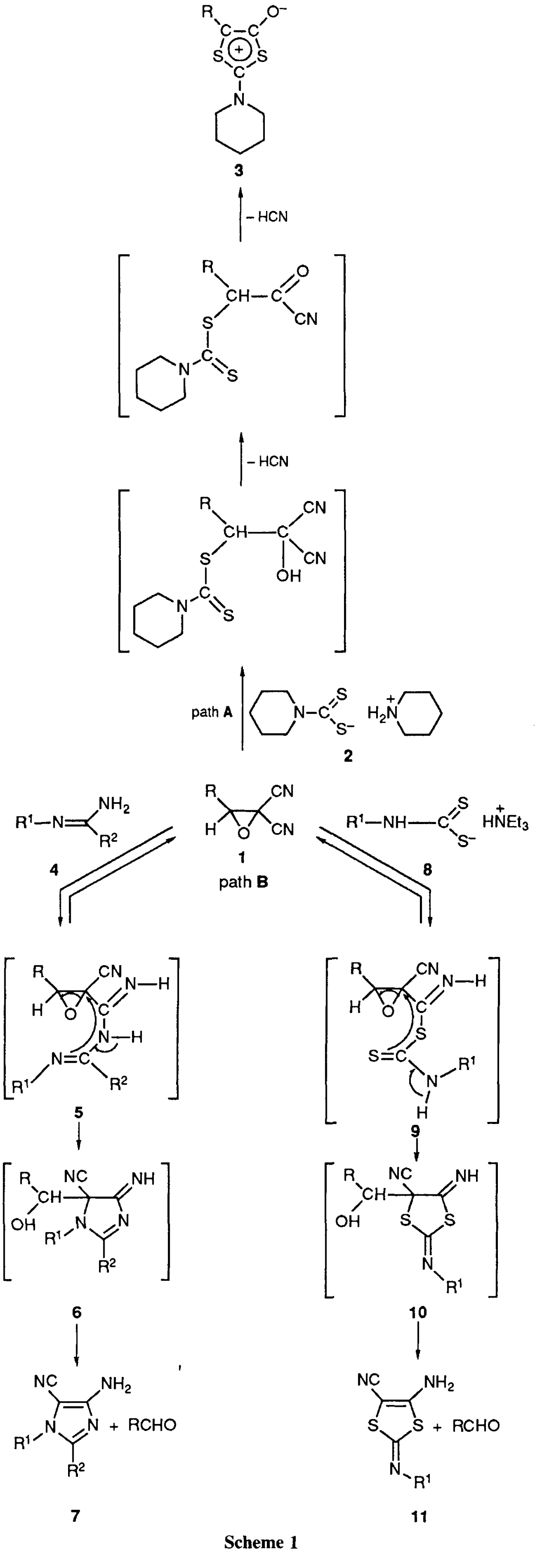
A chemoselective reaction of *gem* dicyanoepoxides with various triethylammonium dithiocarbamates salts leads to new 2-imino-4-amino-5-cyano-1,3-dithioles.

Nucleophilic reagents can react with α-functionalized epoxides to give either ring opened products or new functionalized epoxides.[1] In the case of *gem* dicyanoepoxides **1**, these two possibilities have already been observed. (i) Binucleophiles such as piperidinium dithiocarbamates open selectively the epoxide **1** and lead after the loss of two hydrogen cyanide molecules to *meso*-ionic dithioles **3**[2] (Scheme 1, path *A*). (ii) Some other binucleophilic reagents such as amidines **4** react with the epoxides **1** in a very different way. The reaction is a nucleophilic attack on a nitrile group, followed by the ring



Scheme 1

opening and by a fragmentation leading to a 4-amino-5-cyanoimidazole **7**[3] (Scheme 1, path *B*).

We propose that the course of the reactions can be accounted for by assuming that under non-acidic conditions, the nucleophile first attacks reversibly one nitrile group. According to the structure of the nucleophile, the reaction can be (path *B*), or not (path *A*), followed by an irreversible reaction. Then a judicious choice of reactants could lead to chemoselective reactions proceeding either by an attack of the nitrile group followed by elimination of an aldehyde molecule or by ring opening of the epoxide followed by elimination of two hydrogen cyanide molecules. As we have already shown that the reaction of piperidinium dithiocarbamate salts **2** with *gem* dicyanoepoxides **1** leads to *meso*-ionic dithioles **3** (according to path *A*), it was of interest to test a very similar reactant such as triethylammonium dithiocarbamates salts **8**. In this case we can imagine that an intermediate **9** related to **5** could evolve irreversibly to give the dithiole **11** and the aldehyde RCHO. We should like to report in this communication that this is in fact the case.

A solution of *gem* dicyanoepoxide **1** in tetrahydrofuran (THF) is added slowly to a suspension of triethylammonium dithiocarbamate salts **8** [R^1 = p-ClC_6H_4, C_6H_5, p-$MeOC_6H_4$, p-MeC_6H_4, p-$N(Me)_2C_6H_4$, $N(Me)_2$] and refluxed for 2 to 12 h. After the usual workup, the dithioles **11** are recrystallized in ethanol (yield: 46–80%). Structural assignments of compound **11** were based on ^1H and ^{13}C NMR, IR spectra as well as satisfactory high resolution mass spectra and elementary analysis.†

In summary we have shown that the primary attack of a convenient binucleophilic reagent on a nitrile group of the epoxides **1** leads selectively to a 5-*exo*-tet ring opening of **1**. To our knowledge, the compounds **11** obtained during this reaction are the first 1,3-dithioles bearing the enaminonitrile functionality. As such derivatives are related to the important class of 4-cyano-5-amino imidazoles (purines precursors[4]), it would be of interest to compare these two classes of compounds. Moreover, suitable R^1 substituents makes the dithioles **11** attractive starting material for the design of new extended tetrathiafulvalene derivatives bearing push–pull substituents.[5] We are now extending the scope of the reaction to other functionalized epoxides and looking for the characterization of the postulated intermediates **9** and **10**. The synthesis of extended tetrathiafulvalenes from **11** is also underway.

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† *Selected spectroscopic data* for **11**; (R^1 = p-ClC_6H_4): IR ν_{max}/cm^{-1} (Nujol) 3400–3100br and 2200s; ^1H NMR ($CDCl_3$ + CF_3CO_2H) δ 7.20 (m, 4H); ^{13}C NMR ($CDCl_3$ + CF_3CO_2H); δ 188.6 (s), 154.1 (s), 138.4 (t), 132.7 (d), 132.2 (t), 112.8 (s), 61.8 (s). High resolution mass spectrometry $M^{+\cdot}$: 267.7625; calc.: 267.7575. The p-chlorobenzaldehyde resulting from the fragmentation of **10** was characterized by comparison of its spectra with a commercial sample.