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Synthesis and ^{15}N NMR Characterization of 4,5-Dicyanoimidazol-2-yl-pentazole

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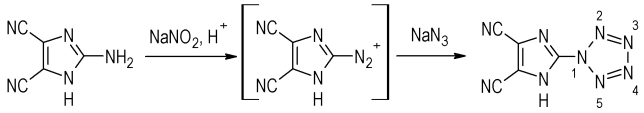
In the last few decades, pentazole derivatives have received a great deal of attention as they are important intermediates in the synthesis of all-nitrogen compounds[1-2]. In order to continue the search for novel energetic pentazole derivatives, 4,5-dicyanoimidazol-2-yl-pentazole (DCIP) was designed and synthesized from 2-amino-4,5-dicyanoimidazole by introducing 4,5-dicyanoimidazolyl group to the pentazole ring. The structure of the pentazole compound was characterized by ^{15}N NMR spectroscopy.

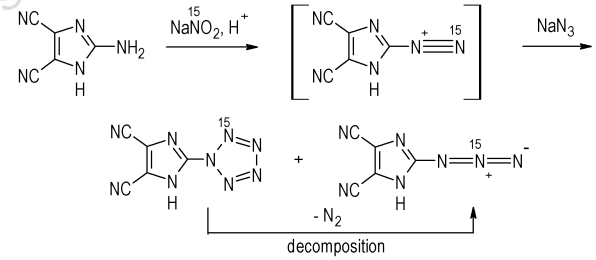
The synthesis of DCIP: 2-amino-4,5-dicyanoimidazole (1.291 g) was dissolved in a solution of mineral acid and water, and a solution of sodium nitrite (0.76 g) in 2 mL of water was added dropwise at 0 ℃. The above mixture was stirred for 30 min, and cooled to −40 ℃, then a solution of sodium azide (0.71 g) in 10 mL of 50% aqueous methanol was added dropwise. After continuous stirring for 1 h at −40 ℃, the mixture was filtrated and dried at −40 ℃ to give yellow powder (Scheme 1). When sodium nitrite or sodium azide was replaced by ^{15}N labeled sodium nitrite or ^{15}N labeled sodium azide in the above synthesis, sample Ⅰ and sample Ⅱ was obtained, respectively. The ^{15}N NMR of DCIP was determined using deuterated methanol as solvent and nitromethane as external standard.



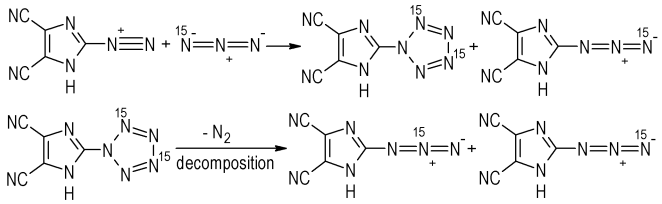
Scheme 1 Synthetic route of DCIP

^{15}N NMR results show for sample Ⅰ that the signals of δ −23.57 and δ −143.97 are obtained at −40 ℃, and the signal of δ −23.57 is disappeared when the sample is heated to 20 ℃. It may conclude that sample Ⅰ consists of the N2/5 ^{15}N labeled pentazole and N_β ^{15}N labeled 2-azido-4, 5-dicyanoimidazole (ADCI)[3] (Scheme 2), and δ −23.57 and δ −143.97 can be assigned to N2/5 of DCIP and N_β of ADCI, respectively.

Similarly, for sample Ⅱ, the signals of δ 7.39, δ −23.57 (N2/5), δ −139.15 and δ −143.97 (N_β) are detected at −40 ℃, and two signals of δ 7.39 and δ −23.57 (N2/5) are disappeared when the sample is heated to 20 ℃. It indicates that sample Ⅱ consists of the N2/5 and N3/4 ^{15}N labeled pentazole and N_γ ^{15}N labeled ADCI, N_β ^{15}N labeled ADCI was formed when the decomposition of pentazole occurred[3] (Scheme 3), and δ 7.39 and δ −139.15 can be assigned to N3/4 of DCIP and N_γ of ADCI, respectively. In addition, the decomposition of DCIP in the synthesis and ^{15}N NMR analyses was confirmed by the signal of N_β of ADCI detected at −40 ℃.



Scheme 2 Mechanism of the reaction using ^{15}N labeled $NaNO_2$



Scheme 3 Mechanism of the reaction using ^{15}N labeled NaN_3

In summary, it is found that the ^{15}N NMR chemical shifts of DCIP are −23.57 (N2/5) and 7.39 (N3/4), and are agreement with the ^{15}N NMR chemical shifts of *p*-dimethylaminophenylpentazole (−27.1 (N2/5) and 4.9 (N3/4)) reported[4].

Key words: organic chemistry; 4,5-dicyanoimidazol-2-yl-pentazole; synthesis; characterization

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