Communications

New Synthesis and Nitrination of 1,2-Bis(5-aminotetrazol-1-yl)ethane

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Received October 31, 2011, Accepted December 7, 2011

Key Words: Tetrazole, Nucleophilic substitution, Energetic materials, Nitrination, Nitrogen-rich

Tetrazole derivatives, which have high nitrogen content, belong to an interesting class of heterocycles that could be applied to a variety of high energy density materials (HEDMs). Particularly, aminotetrazole-based energetic materials have attracted considerable interest due to their high thermal stabilities and large positive heats of formation. Moreover, they are anticipated to be quite insensitive, extremely powerful, and produce less pollutants when explode.

Recently, 1,2-bis(5-nitroiminotetrazol-1-yl)ethane (3) and its energetic salts3 have been prepared in good yields (Scheme 1). The development of 1,2-bis(5-aminotetrazol-1-yl)ethane (2)5a,b has been extended by the utilization of an excellent in situ method that involves reactions of cyanogen azide6 and ethylene diamine. Nitrination of aminotetrazole 2 using 100% nitric acid produced 3. The synthesis of nitroiminotetrazole salts provided a straightforward approach to highly energetic salts, which exhibit attractive physical properties, such as good thermal stabilities, high densities, and good heats of formation.4

1-Substituted 5-aminotetrazole derivatives were prepared by the treatment of potassium 5-aminotetrazolate with an alkyl halide.7 There are several reports in the literature describing in situ generation of 1-substituted 5-aminotetrazoles via alkylation of 5-aminotetrazole with alkyl halides. However, selective alkylation of aminotetrazoles is not possible because of the competitive formation of 1- and 2-alkylated-5-aminotetrazoles.5a These isomers were separable in very low yields by crystallization or column chromatography. 1-Substituted 5-aminotetrazoles could be efficiently prepared using cyanogen azide.5a,b,d However, cyanogen azide is highly toxic and is not convenient to handle.5a,b In this work, we present a new synthetic scheme for compound 2 without using toxic cyanogen azide and introduce an efficient preparation of 3 for easy scale-up.

The synthesis of 2 results from a nucleophilic substitution reaction between 2 equivalent of sodium 5-aminotetrazolate and 1 equivalent of 1,2-dibromoethane (Scheme 2).5a,8 However, three isomers, 2, 1-(5-aminotetrazol-1-yl)-2-(5-aminotetrazol-2-yl)ethane (6), and 1,2-bis(5-aminotetrazol-2-yl)ethane (ratio = 1:3:1), from this reaction were formed as was reported in the literature.5a,c Separation of the three isomers was accomplished based on the difference of aqueous solubility. 2 was isolate in 11% yield through a very rapid filtration from refluxing suspension with a small amount of water.

To improve the yield, we searched for a new route for compound 2. 1-(2-Chloroethyl)-5-aminotetrazole (5) can be prepared by chlorination of 1-(2-hydroxyethyl)-5-aminotetrazole, which was synthesized from sodium 5-aminotetra-

Scheme 1. Synthesis and reaction of 3.

Scheme 2. Synthesis of 2.
zolate and 2-chloroethanol. Under the same conditions for alkylation, 5 was reacted with sodium 5-aminotetrazolate in aqueous solution. Separation of the two isomeric products (2:6 = 1:1) led to the 2 in 14% of yield. The experiments showed that water was a suitable separation solvent, whereas other solvents, namely, acetone, acetonitrile, ethanol, and DMSO/water did not give a good result in the isolation of 2. These isomers could be separated in aqueous solution but much of the product was lost.

Since the separation of 2 and 6 required a great deal of effort and caused a loss of a substantial portion of products, nitration with 100% nitric acid preceeded with a mixture. The solution was obtained from compound 2, which was present as a mixture with 6.

After nitration, a white solid was obtained along with oily unknown compounds. This oil was removed with a Pasteur pipette and the crude white solid was washed several times with water. Fortunately, the white solid was proved to be pure compound 3 by $^1$H, and $^{13}$C NMR spectroscopy. Our NMR analyses were in good agreement with the reported values.

In conclusion, we developed a new nontoxic method for the preparation of 2 from 5 and sodium 5-aminotetrazolate with 14% yield. The alkylation of sodium 5-aminotetrazolate using 1,2-dibromoethane was performed by following the experimental procedure by Barmin et al. and modifying the separation method. The production yield for 2 was 11%. Highly energetic compound 3 could be synthesized by nitration from 2, which was present as a mixture with 6 in good yield. Our new synthetic scheme without using highly toxic cyanogen azide may enable us to produce a large quantity of the compound 3 and to apply it to various military applications.

**Safety Precautions.** While we have experienced no difficulties with the impact instability of the 1,2-bis(5-aminotetrazol-1-yl)ethane (2) and 1,2-bis(5-nitroiminotetrazol-1-yl)ethane (3), Manipulations must be carried out in a hood behind a safety shield. Eye protection and leather gloves must be worn. Extreme caution should be exercised at all times during the synthesis, characterization, and handling of any of these materials, and mechanical actions involving scratching or scraping must be avoided.