The Chemistry of Exciting Tetraazidomethane

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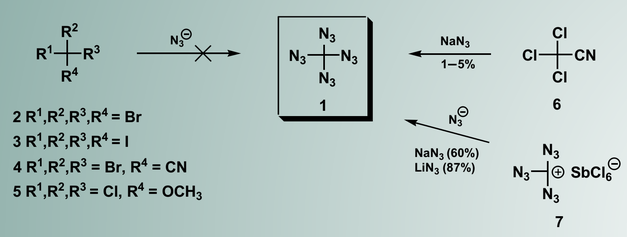
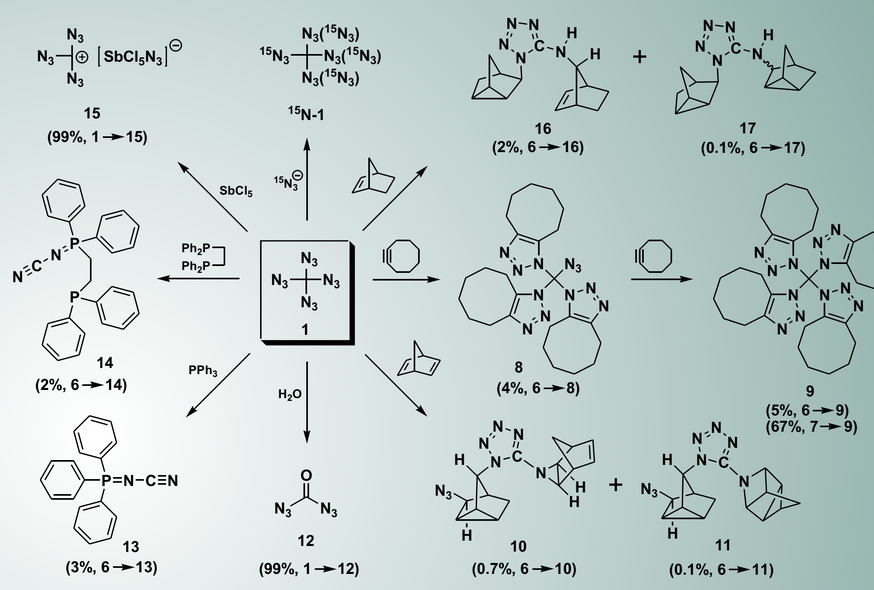
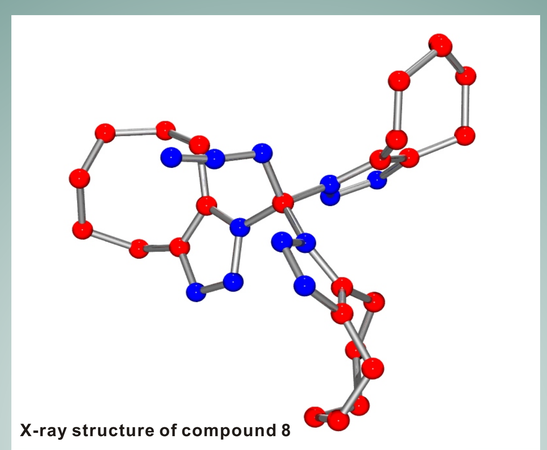
In order to study highly energetic material, several homoleptic polyazides of the type $M(N_3)_n$ have been prepared and characterized.[1]

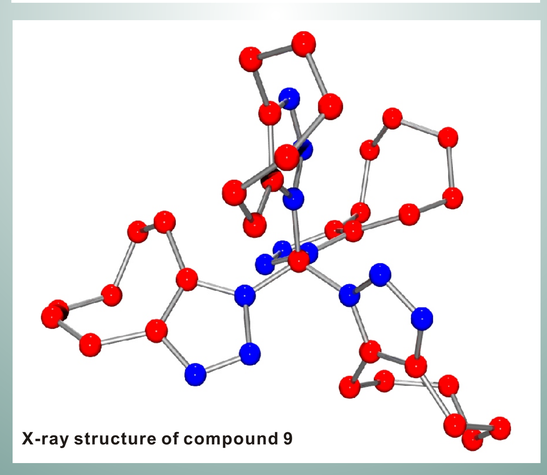


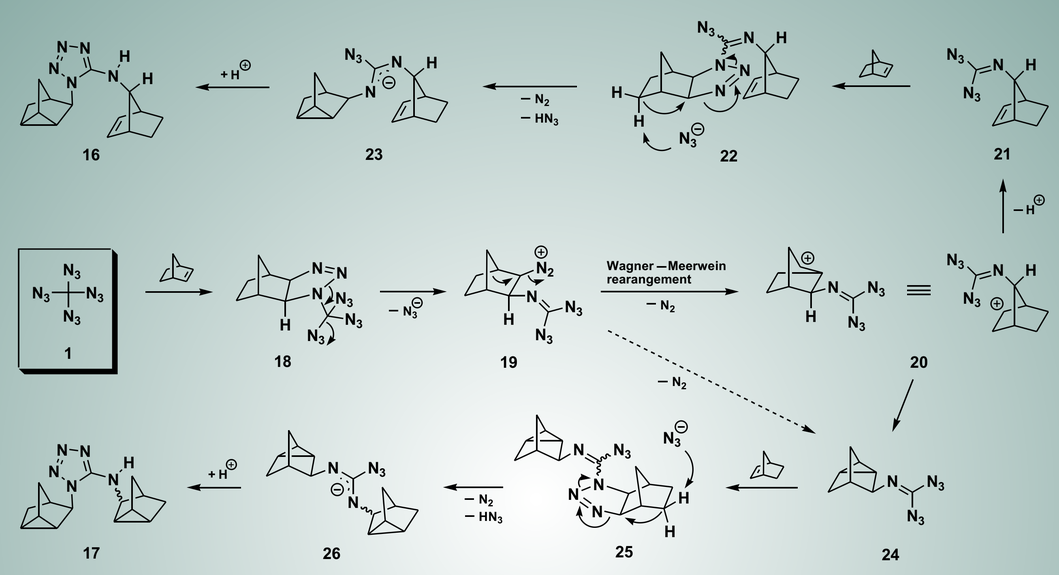
However, the organic compound $C(N_3)_4$ **1** is still missing. Our attempts to synthesize tetraazidomethane **(1)** starting with tetrabromomethane **2**, tetraiodomethane **3**, tribromoacetonitril **4**[2], trichloro(methoxy)methane **5**[3], or similar substrates and azide transfer reagents were unsuccessful. But treatment of inexpensive trichloroacetonitrile **6** with sodium azide led to the title compound **1**, in low yield (ca. 5%, 1% after GC). The tetraazide **1**, which can be isolated by gas chromatography as an extremely explosive and dangerous colorless liquid, is also accessible by the reaction of triazidomethylium hexachloroantimonate **(7)**[4] with dry NaN_3 or LiN_3 in CD_3CN. In these cases, the NMR yield of **1** amounted to 60% or 87%, respectively.



Tetraazidomethane **(1)** is characterized by its IR, MS, ^{13}C NMR, and ^{15}N NMR data as well as its trapping products **8** and **9** formed in the presence of cyclooctyne. In wet chloroform, **1** was easily hydrolyzed to yield **12**, whereas treatment with triphenylphosphine or 1,2-bis(diphenylphosphino)-ethane led to the simple products **13**[5] or **14**, respectively. Ionic exchange processes of azide could be observed for **1** in the presence of labelled azide ion or antimony pentachloride in dry CD_3CN by spectroscopy. On the other hand, surprising products were obtained in several cases, for example, if **1** was reacted with norbornene to give **16** and **17**.

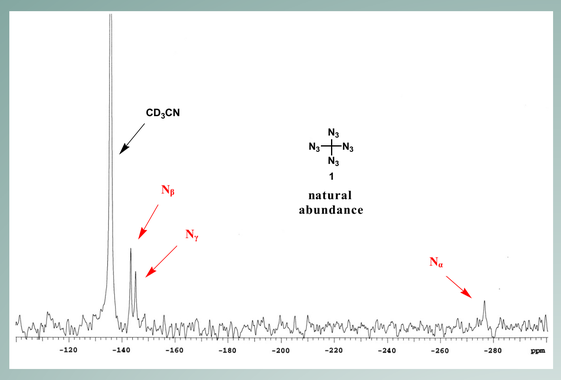


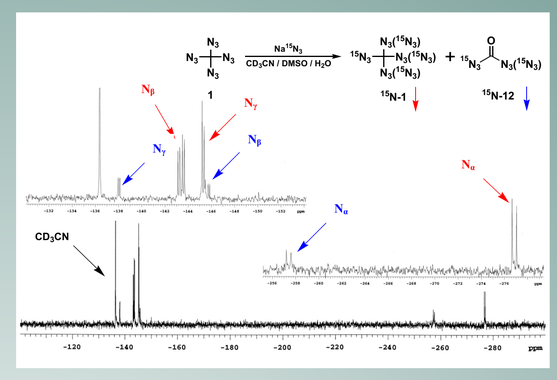




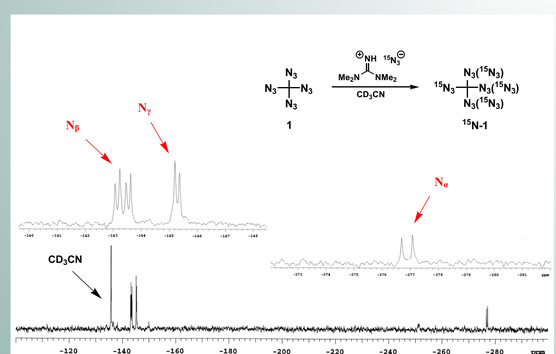
Possible mechanism for the formation of 16 and 17:

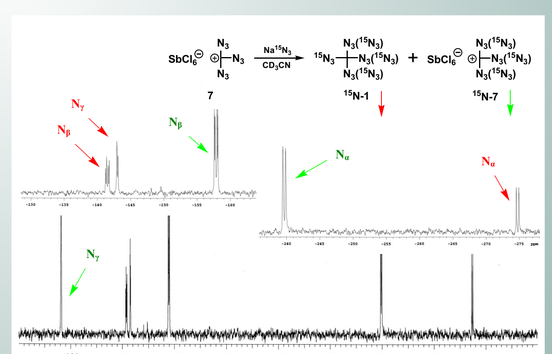
First tetraazidomethane (**1**) and norbornene form the *exo*-product **18** by 1,3-dipolar cycloaddition followed by a fragmentation reaction to give **19**. Loss of nitrogen and Wagner–Meerwein rearrangement lead to the carbenium ion **20** that can yield the norbornene derivative **21** on deprotonation. Thereafter, *exo*-cycloaddition at a second molecule of norbornene should yield dihydrotriazole **22** which is able to generate the intermediate **23** by 1,3-elimination via deprotonation and loss of a second molecule of nitrogen. Finally, tetrazole **16** is formed on cyclization and protonation of **23**. Deprotonation of **20** can alternatively lead to **24** which is also accessible directly from **19**. The diazide **24** should react with norbornene via the intermediates **25** and **26** to give the final product **17** as described before analogously.



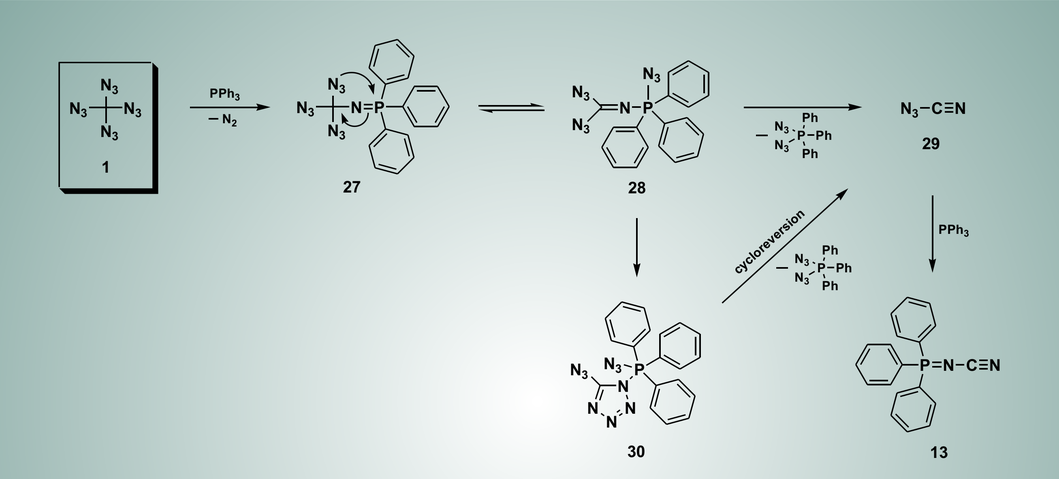


The ^{15}N NMR measurement was accomplished at 40 MHz in CD_3CN with CH_3NO_2 as standard. Using tetraazidomethane (**1**) with natural abundance of isotopes (0.37% ^{15}N), three broad singlet ^{15}N NMR signals were observed. Obviously, $^{15}N,^{15}N$ coupling could only be investigated with the help of ^{15}N-labelled tetraazidomethane (^{15}N-**1**). Treatment of **1** in CD_3CN with $Na^{15}N_3$ in H_2O/DMSO led to the ^{15}N NMR signals of ^{15}N-**1** and ^{15}N-**12** measured as doublets or doublets of doublets. Thus, these signals were easily assigned to N_α, N_β, and N_γ of the covalent azides ^{15}N-**1** and ^{15}N-**12**. According to the chemical shifts, the order of the signals was different for the alkyl azide **1** (N_α / N_γ / N_β) and the azides **7**, **12**, or **29** (N_α / N_β / N_γ), in which the azido unit is connected with an electron-withdrawing group. For comparison, the diazide ^{15}N-**12** was also prepared by another method.





If **1** in dry CD_3CN was treated with tetramethylguanidinium ^{15}N-azide, the exchange reaction to generate ^{15}N-**1** was slow (5–7 days at room temperature) but not accompanied by hydrolysis to give ^{15}N-**12**. On the other hand, the reaction of triazidomethylium hexachloroantimonate (**7**) with labelled sodium azide ($Na^{15}N_3$) in dry CD_3CN was very rapid at room temperature. A mixture of ^{15}N-**1** and ^{15}N-**7** was formed in this case indicating that obviously dissociation of ^{15}N-**1** to yield ^{15}N-**7** is a rapid process likewise. In a control experiment, the natural abundance ^{15}N NMR spectrum of **7** was also measured.



Possible mechanism for the formation of 13 from 1:

Treatment of tetraazidomethane (**1**) with an excess of triphenylphosphine (0°C, dry *n*-pentane/CH_2Cl_2) should generate the intermediate **27** in a Staudinger reaction. Migration of an azido group can lead to the species **28** which is able to give the cyano compound **29** directly by β-elimination. Alternatively, **29** can be formed from **28** via cyclization to yield tetrazole **30** followed by cycloreversion. Finally a second Staudinger reaction should transform **29** into the known[5] triphenylphosphoranylidenecyanamide **13**. As shown in a control experiment, independently prepared **29**[6] reacted with triphenylphosphine to produce **13**.

References

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Acknowledgment

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