Nitrogen-Rich Compounds

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The Exciting Chemistry of Tetraazidomethane**

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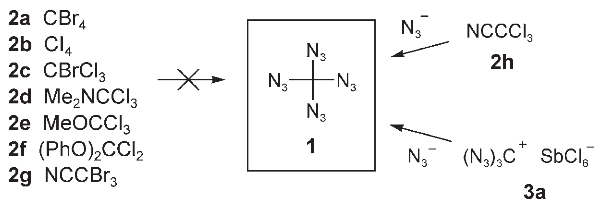
Dedicated to Professor Adalbert Maercker on the occasion of his 75th birthday.

The chemistry of "isocentric" polyazides has experienced a renaissance in recent years.[1] Numerous homoleptic azides[2a–g] of the type $M(N_3)_n$ as well as derivable salts[2g–j] have been prepared and characterized to investigate the properties of highly energetic materials. Amazingly, the organic representative tetraazidomethane (**1**) has not been synthesized until now, even though its structure had already been calculated at the B3LYP/6-311+G* level of theory.[3] The properties of triazidomethane, which is accessible from bromoform by simple nucleophilic substitution,[4,5] support the expectation that **1** should be highly explosive, and thus that isolation of this homoleptic azide would be a challenge. We report herein two routes to prepare **1** as well as some of its succeeding reactions, some of which are rather surprising.

Our efforts to generate **1** from halide compounds **2a**–**c** were unsuccessful (Scheme 1).[6] Treatment of precursors **2d**–**g**,[7] bearing donor or acceptor substituents, with different azide-transfer reagents also gave no hint of formation of **1**.[6] For example, **2f** and sodium azide afforded diazido(diphenoxy)methane in 86% yield, but the latter could not be transformed into **1**. In contrast, treatment of **2h** with sodium azide in acetonitrile (50°C/18 h), followed by workup (dilution with water/*n*-pentane, followed by extraction and drying) and addition of cyclooctyne[8] (−20°C/5 h) as well as chromatographic separation led to the trapping product **4b** in 5% yield (Schemes 1 and 2). At shorter reaction times of the cyclooctyne, the intermediate product **4a** can be obtained in 4% yield. Both **4a** and **4b** were characterized by the usual spectroscopic methods as well as by single-crystal X-ray structure analyses (Figure 1).[9] Compound **1** can be isolated by preparative gas chromatography (packed column, 1 m, OV 101, 80°C) as a colorless liquid (see the *Safety Precautions*) after conversion of **2h** with sodium azide and workup.[10] We estimate a boiling point of approximately 165°C for **1** because its retention time in gas chromatography is intermediate between those of *n*-nonane and *n*-decane. As a part of the spectroscopic characterization of **1** (Table 1), the GC–MS(EI) data point to a dissociation to the triazidocarbenium ion[11] ($M = 138$). Thus, **1** differs from other azides that



Scheme 1. Attempts to prepare tetraazidomethane (**1**).

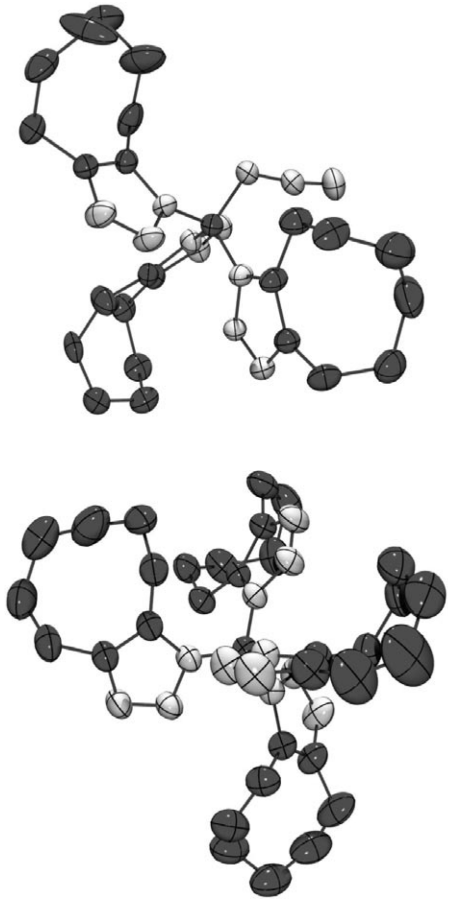


Figure 1. Molecular structures of cycloadducts **4a** (top) and **4b** (bottom).

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[+] Single-crystal X-ray diffraction analyses.

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Table 1: Selected physical data of **1** as well as the azides **3a**, **5**, and **7**.[a]

1: Colorless, highly explosive liquid; IR (CCl_4): $\tilde{\nu}=2125\ cm^{-1}$; ^{13}C NMR ($CDCl_3$): $\delta=102.5$ ppm (s); ^{13}C NMR (CD_3CN): $\delta=103.5$ ppm (s); ^{13}C NMR ([D$_6$]DMSO): $\delta=101.7$ ppm (s); ^{15}N NMR (CD_3CN): $\delta=-276.7$ (d, $^1J=15.6$ Hz, N_α), -145.1 (d, $^1J=6.9$ Hz, N_γ), -143.3 ppm (dd, $^1J=15.6$ Hz, $^1J=6.9$ Hz, N_β); GC–MS (EI, 70 eV): m/z (%): 138 (60) $[M-N_3]^+$, 54 (84), 42 (100); HR-MS (ESI): m/z: 180.0812 (calcd 180.0801).

3a: ^{13}C NMR (CD_3CN): $\delta=176.6$ ppm (s); ^{15}N NMR (CD_3CN): $\delta=-239.8$ (d, $^1J=16.9$ Hz, N_α), -157.9 (dd, $^1J=16.9$ Hz, $^1J=4.6$ Hz, N_β), -116.6 ppm (d, $^1J=4.6$ Hz, N_γ).

5: ^{13}C NMR ($CDCl_3$): $\delta=161.6$ ppm (s); ^{13}C NMR (CD_3CN): $\delta=162.6$ ppm (s); ^{13}C NMR ([D$_6$]DMSO): $\delta=160.3$ ppm (s); ^{15}N NMR (CD_3CN): $\delta=-257.3$ (d, $^1J=15.5$ Hz, N_α), -145.5 (dd, $^1J=15.5$ Hz, $^1J=5.5$ Hz, N_β), -137.9 ppm (d, $^1J=5.5$ Hz, N_γ).

7: ^{13}C NMR (CD_3CN): $\delta=106.5$ ppm (s).

[a] The data of the products **4a**,**b**, **6**, **8**, **9a**,**b**, and **10a**,**b** are collected in the Supporting Information. ^{13}C NMR: 100.6 MHz; s (singlet) refers to the absence of $^{13}C,^1H$ coupling in each case. ^{15}N NMR: 40.5 MHz; CH_3NO_2 as external standard; δ values resulting from measurements with natural isotopic abundance; multiplicities and J values are based on $^{15}N,^{15}N$ coupling in compounds with isotopically labeled azido groups.

also do not show a signal for molecular ion under these conditions of measurement but instead produce a signal that can be explained by the loss of N_2. However, mass spectra of **1** recorded in ESI mode showed the molecular-ion peak.

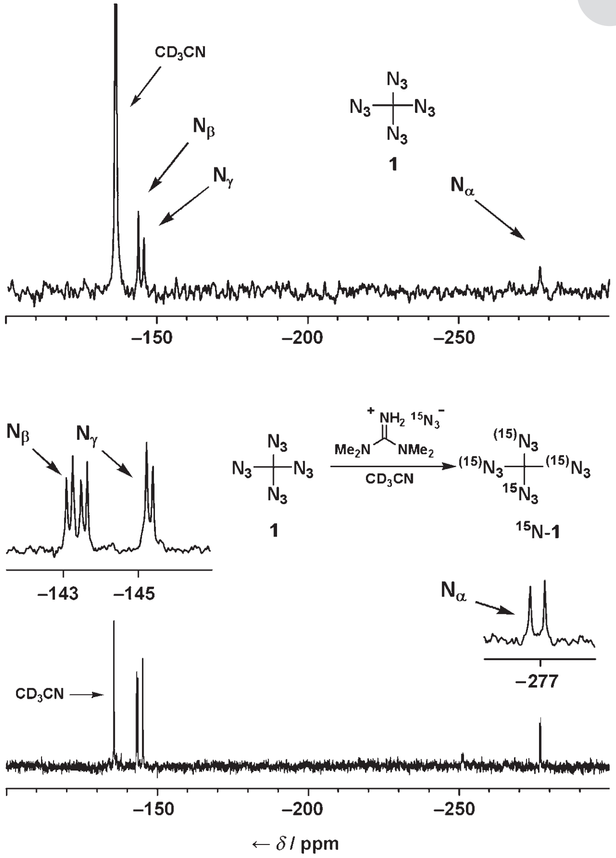
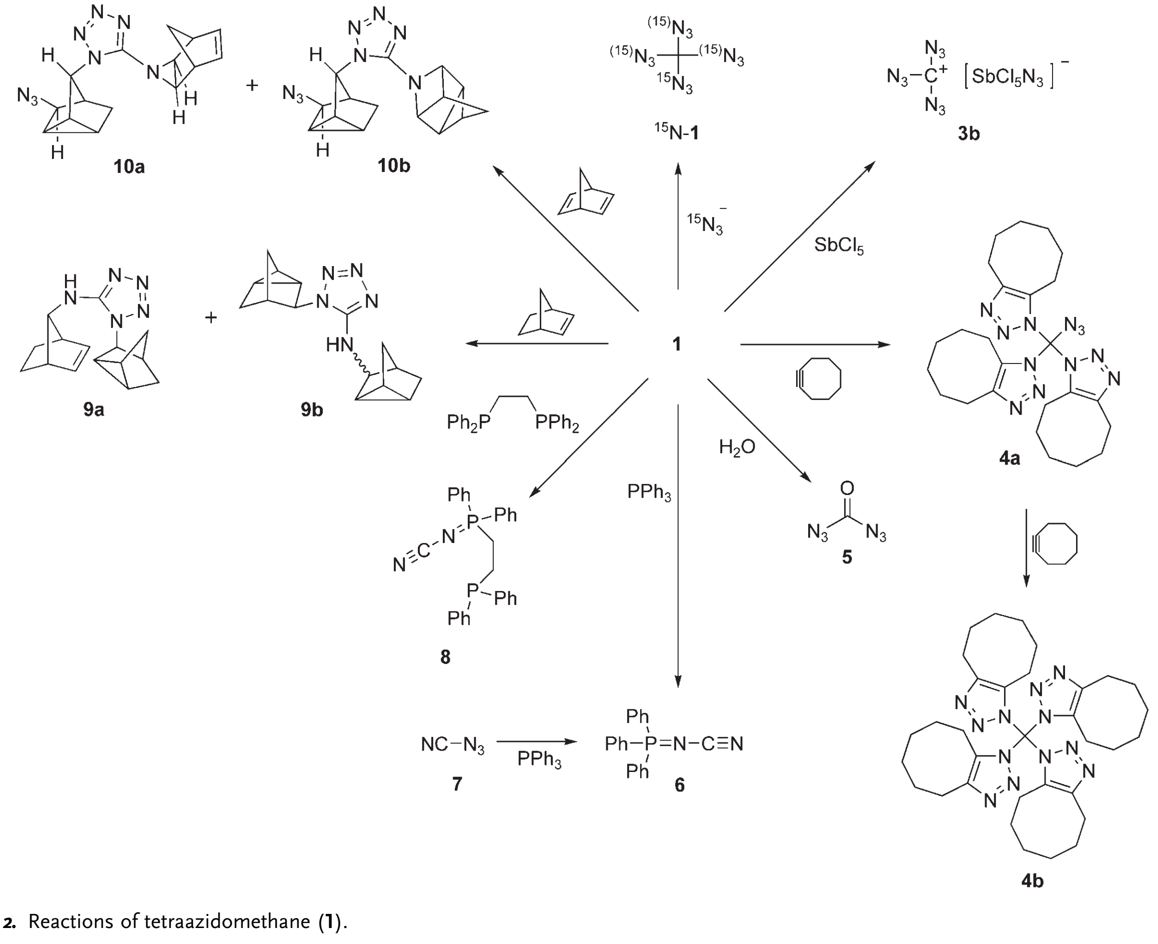


Figure 2. ^{15}N NMR spectra of **1** with natural isotopic abundance and ^{15}N-**1** with threefold ^{15}N-labeled azido groups (see also Table 1).



Scheme 2. Reactions of tetraazidomethane (**1**).

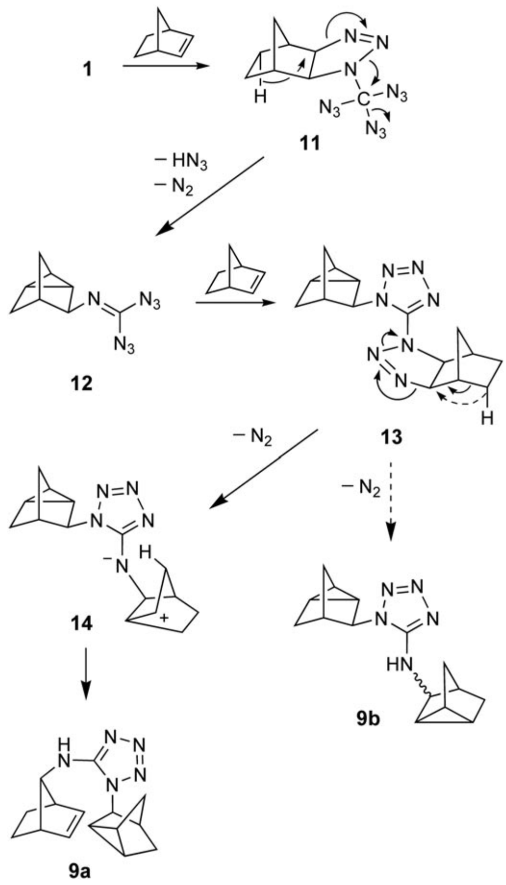
Furthermore, the ^{13}C NMR as well as ^{15}N NMR spectra (Figure 2) clearly proved that **1** is a compound with covalent bonding.

More than twenty years ago, an attempt to prepare 5-trichloromethyltetrazole by treatment of **2h** with ammonium chloride and an excess of sodium azide led to a serious explosion.[12] One of the causes that were supposed first was the isomerization of the tetrazole to its open-chained form, trichloromethylazidoazomethine.[13] However, it was later shown that 5-trichloromethyltetrazole prepared by a different method does not explode even on heating.[14] The formation of the dangerous azide **1** was possibly the cause of the explosion.

The reaction of the salt **3a**[11,15] with dry lithium azide or sodium azide in acetonitrile presented a further approach to the title compound **1** (Scheme 1). The yields are significantly higher for this method than for the synthesis of **1** from **2h**.[10] Nevertheless, the cheap and nonexplosive starting material **2h** is more suitable for preparative purposes, especially because the workup is less problematic and more reproducible than is the case with antimonate salts.

In wet chloroform, **1** reacted rather rapidly to give the carbonic acid derivative **5**[16] and hydrazoic acid almost quantitatively.[17,18] Further investigations showed that **1** in *n*-pentane was hydrolyzed considerably faster in the presence of dilute acids than in contact with aqueous base. The incorporation of an isotopic label into the azide **1** with $Na^{15}N_3$ in dry acetonitrile was unsuccessful. However, if water (2 vol%) and DMSO (5 vol%) were added, ^{15}N-**1** was detected instantaneously, but its formation was accompanied by the generation of ^{15}N-**5** (Table 1). When **1** in dry acetonitrile was treated with the reagent[19] $(Me_2N)_2C{=}NH_2^+\ {}^{15}N_3^-$, a slow exchange (5–7 days/20 °C) occurred, so that the signals of ^{15}N-**1** could be observed in the ^{15}N NMR spectrum without those of the hydrolysis product ^{15}N-**5** (Figure 2). Indeed, the dissociation of **1** is evidently assisted not only by protons but also by Lewis acids such as $SbCl_5$. Thus, **1** in acetonitrile could be transformed completely into the triazidocarbenium salt **3b** by addition of $SbCl_5$ (Scheme 2). We observed in the ^{15}N NMR spectrum not only the signals of ^{15}N-**1** but also the incorporation of the ^{15}N label into the excess triazidocarbenium ion when **3a** in acetonitrile was treated with a substoichiometric amount of $Na^{15}N_3$. Thereby, further evidence of the reversible dissociation of **1** in the presence of $SbCl_5$ is given.

Azides in which the N_3 group is directly connected with a strong acceptor unit (e.g., **3**, **5**, and **7**) show signals in their ^{15}N NMR spectra with increasing δ values in the order N_α, N_β, N_γ (Table 1).[20] In the case of compound **1**, the order N_α, N_γ, N_β is found instead, as is typical for simple alkyl and aryl azides.[20] Nevertheless, **1** undergoes reactions that differ from the pattern of simple azides. For example, treatment with PPh_3 yielded the simple product **6**,[10,21] which could also be prepared from **7** for comparison.[22] The reaction of **1** with $Ph_2PCH_2CH_2PPh_2$ led to the analogous compound **8**.[10] Neither with norbornene nor with norbornadiene did we get a simple 4,5-dihydro-1*H*-1,2,3-triazole as would be expected from a 1,3-dipolar cycloaddition. Instead, we isolated the 5-aminotetrazole derivatives **9a** and **9b**, as well as **10a** and **10b**, respectively,[10] whose formation can be explained only by multistep reaction mechanisms.[21] One suggestion for the formation of **9a** and **9b** is shown in Scheme 3.



Scheme 3. Possible reaction mechanism for the formation of products **9a** and **9b** (the sequence of the single steps is arbitrary; the second *exo*-cycloaddition at norbornene can lead also to a diastereomer of **13**).

Safety Precautions: Tetraazidomethane (**1**) is extremely dangerous as a pure substance. It can explode at any time—without a recognizable cause. Less than a drop of this compound isolated by gas chromatography is able to destroy completely not only the glass trap but also the vacuum Dewar flask of the cooling bath. Therefore, the isolated substance should only be diluted by vapor deposition of a solvent behind a safety shield rather than by manual handling (with a pipette or syringe). However, solutions of **1** can also lead to an explosion after mechanical stress (swivel closure) or after evaporation of a volatile solvent, for example, in a pipette. Finally, it should be considered that **3**, **5**, and **7** are also explosive azides.

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[6] We treated **2a–c** with reagents such as NaN_3 in *N,N*-dimethylformamide or acetonitrile and tributylhexadecylphosphonium azide in different solvents. The starting materials **2d–g** were reacted with these reagents as well as $(Me_2N)_2C{=}NH_2^+\ N_3^-$ in CH_2Cl_2 or acetonitrile and HN_3 in chloroform.

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[9] Crystallographic data for **4a**: $C_{25}H_{36}N_{12}$, $M=504.66$, monoclinic, space group $P2_1/c$, $Z=4$, $a=11.1484(6)$, $b=11.0673(5)$, $c=21.2600(13)$ Å, $\beta=90.153(5)°$, $V=2623.1(2)$ Å^3, $\rho_{calcd}=1.278\ g\,cm^{-3}$, $T=298$ K, crystal size $0.40\times0.35\times0.20$ mm^3, $R=0.0605$ $(I>2\sigma(I)$, $Rw=0.2078$, GOF $=1.023$. Crystallographic data for **4b**: $C_{33}H_{48}N_{12}$, $M=612.83$, triclinic, space group $P\bar{1}$, $Z=4$, $a=12.250(4)$, $b=12.373(4)$, $c=22.192(5)$ Å, $\alpha=81.041(9)$, $\beta=82.336(9)$, $\gamma=85.500(11)°$, $V=3287.1(18)$ Å^3, $\rho_{calcd}=1.238\ g\,cm^{-3}$, $T=298$ K, crystal size $0.30\times0.30\times0.30$ mm^3, $R=0.0762$ $(I>2\sigma(I)$, $Rw=0.2545$, GOF $=1.048$. CCDC-619288 and -619287 (**4a** and **4b**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[10] Because the yield of **1** could not be determined by weighing (see the Safety Precautions), the integration of the ^{13}C NMR signal (without decoupling, delay of 60 s between the pulses) relative to those of weighed amounts of CCl_4, CBr_4, and tetrachloroethene was used. This resulted in a yield of 1–2% for the synthesis of **1** from **2h** including isolation by gas chromatography and a yield of 60–87% for the generation of **1** from **3a** and NaN_3 or LiN_3 without workup. As the method described above for determination of the yield is very laborious and inaccurate, the yields of the stable succeeding products of **1** (Schemes 1 and 2) were based on precursor **2h**. Thus, we obtained **6** in 3% yield (based on **2h**) as well as **8** in 2%, **9a** in 2%, **9b** in 0.1%, **10a** in 0.7%, and **10b** in 0.1% yield.

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[17] The sensitivity of **1** to hydrolysis may be the reason that Cu^I-catalyzed treatment with terminal alkynes (click chemistry) according to the Sharpless protocol[18] was not successful. However, variants of this click reaction in water-free solvents have also hitherto failed.

[18] Review on click reaction (azide/alkyne): V. D. Bock, H. Hiemstra, J. H. van Maarseveen, *Eur. J. Org. Chem.* **2006**, 51–68.

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