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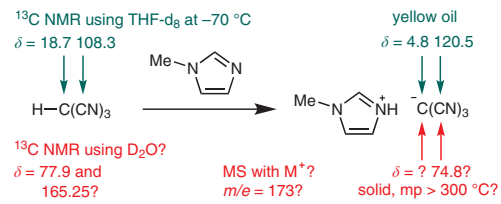
Tricyanomethane and its Salts with Nitrogen Bases: A Correction of Sixteen Reports

Klaus Banert*
Manfred Hagedorn

Chemnitz University of Technology, Organic Chemistry, Strasse der Nationen 62, 09111 Chemnitz, Germany
klaus.banert@chemie.tu-chemnitz.de

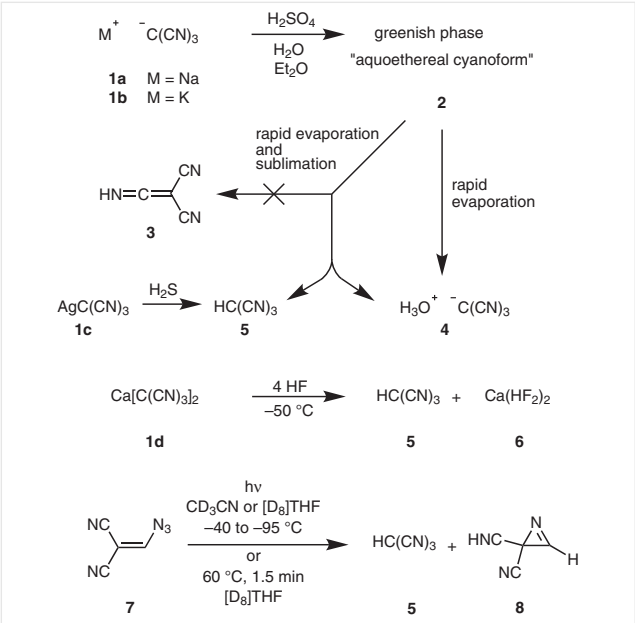


Received: 29.03.2019
Accepted after revision: 10.05.2019
Published online: 05.06.2019
DOI: 10.1055/s-0037-1611846; Art ID: st-2019-b0182-l

Abstract A series of 16 articles, dealing with formation of tricyanomethanide salts from nitrogen bases (amines) and tricyanomethane, turned out to be wrong because no tricyanomethane or similar compounds are used and no tricyanomethanide salts are prepared. This statement is based mainly on the recently published spectroscopic data and depicted spectra, which are completely incompatible with the claimed structures. Some of the tricyanomethanide salts are now synthesized from nitrogen heterocycles and tricyanomethane or other precursors. The corresponding products show plausible spectroscopic data and physical properties, which are entirely different to those previously reported.

Key words exclusion of structures, spectroscopic characterization, tricyanomethane, tricyanomethanide salts, unstable compounds

First attempts to prepare tricyanomethane (**5**), also called cyanoform, were reported as early as 1864,[1] but the syntheses could not be reproduced by other authors,[1c,2] and later it turned out that **5**, even if formed, would not have been able to survive the reaction conditions employed. In 1896, Schmidtmann treated sodium tricyanomethanide (**1a**) with dilute sulfuric acid, and, after addition of diethyl ether, he obtained a three-phase system, which included a greenish yellow middle layer **2** (Scheme 1).[3] This layer was claimed to contain **5**, however, first experiments to remove the solvents did not lead to characterizable products.[4] In 1963, Trofimenko utilized **1b**, repeated the synthesis of **2**, and called the product 'aquoethereal cyanoform'.[5] He was successful in liberating **2** from the solvents by rapid evaporation and sublimation and obtained unstable white crystals, to which he erroneously assigned the structure of ketenimine **3**. By treating **2** with tertiary amines, such as triethylamine or pyridine, or sterically shielded primary amines, Trofimenko et al. prepared 'amine salts of tricyanomethane'.[6] Dunitz et al. performed rapid evaporation of **2** without sublimation and isolated single crystals of hydronium tricyanomethanide (**4**) as confirmed by crystallographic X-ray diffraction studies.[7] In 2017, it turned out that Trofimenko's experiment did not lead to **3** because rapid evaporation and sublimation of **2** actually resulted in the isolation of a mixture of **4** and **5**.[8] Single crystals of cyanoform (**5**) were conveniently available under special conditions of vacuum sublimation and allowed structure verification by X-ray diffraction. Such single crystals could be handled at room temperature for a short time if moisture was excluded. However, **5** could not be characterized in solution by NMR spectroscopy at ambient temperature be-



Scheme 1 Reported syntheses of cyanoform (**5**)

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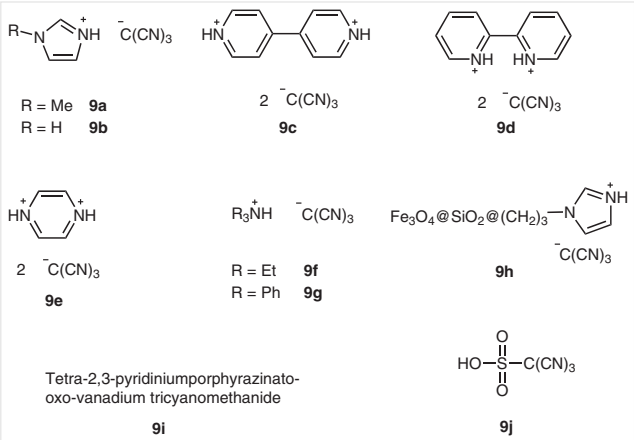
cause of rapid decomposition.[9] Furthermore, **5** was easily transformed into **4**, even when only trace amounts of water were present. In particular, mixtures of **4** and **5** underwent dynamic processes leading to extremely broad NMR signals at temperatures between −50 and 0 °C.[9] Consequently, even lower temperatures were necessary and resulted in sharp ^{13}C NMR signals with δ = 108.3 (CN) and 18.7 ppm (central carbon) for pure **5** in THF-d_8 at −70 °C.[8]

Tricyanomethane (**5**) was not only generated from **1a** or **1b** via **2**, but also by treating **1c** with pure, dry hydrogen sulfide,[10] or alternatively by reacting **1d** with an excess of anhydrous hydrogen fluoride,[11] and finally by photolysis or short-time thermolysis of azide **7**.[8] In the case of precursor **1d**, the products **5** and **6** could not be separated. Nevertheless, convincing spectroscopic characterization of **5** was possible.[11] When **7** was photolyzed in solution, the 2*H*-azirine **8** was formed besides **5**, whereas thermolysis of **7** led to **5** and small amounts of **4** only. Irradiation of **7** isolated in an argon matrix did not produce **5**, but ketenimine **3** and azirine **8** were formed instead.[8]

The chemistry of tricyanomethane (**5**) has been intensively investigated by many chemists in the course of more than 150 years.[4] Its gas-phase structure was analyzed by microwave spectroscopy[10] and photoelectron spectroscopy,[12] and the relative stabilities, spectroscopic features, and isomerization reactions of **3**, **5**, and other C_4HN_3 species were studied using quantum-chemical methods.[13] Especially, the acidic properties of **3** and **5** were discussed in detail.[5,14] Thus, **5** is mentioned in textbooks of organic chemistry as one of the strongest carbon acids.

Quite recently, a series of 16 articles by M. A. Zolfigol et al. presented the reaction of tricyanomethane (**5**) with amine bases to form the corresponding tricyanomethanide salts **9a**,[15a,f,g] **9b**,[15i,o] **9c**,[15c,h] **9d**,[15d,p] **9e**,[15m] **9f**,[15n] and **9g**;[15j] additionally, the magnetic silica-coated nanoparticles **9h**[15b,e] and the phthalocyanine-based vanadium derivative **9i**[15l] were described and the synthesis of **9j**[15k] from **5** and chlorosulfonic acid was reported (Scheme 2). The compounds **9a–j** were utilized as catalysts for various condensation reactions.[15]



Scheme 2 Tricyanomethanide salts **9a–i** and compound **9j** reported by M. A. Zolfigol et al.[15]

The following discrepancies are characteristics of all the 16 articles:

a) There are no pieces of information or references to the origin of **5**.[15] Consequently, the readers might erroneously assume that it is a commercial product. Nevertheless, nonsensical IR and NMR spectra of **5** are depicted in the publications or in the corresponding supplementary data.[15a,c,d,g,15i–o]

b) The shown IR spectra of alleged **5** do not present any signal of the C–H stretching vibration.[15a,c,d,15i–o] This contrasts with the IR data of pure **5** isolated in an argon matrix,[8] which indicated a stronger signal for C–H at 2927.6 cm^{-1} if compared with that of C≡N at 2268.1 cm^{-1}. The depicted IR spectrum of the substance claimed to possess the structure of **9h** does not include any signal of an aliphatic or aromatic C–H stretching mode, although the corresponding C≡N signal proves to be observable.[15b,e]

c) The shown NMR spectra of supposed **5** were measured with solutions in D_2O,[15g,i,j,l,m] despite the fact that **5** is extremely sensitive to water (see above),[8,9] which excludes NMR characterization of **5** using this solvent. Moreover, the ^{13}C NMR signals of **5** are claimed to appear at δ = 77.9 and 165.25 ppm.[15g,i,j,l,m] These data are not only completely different to the established chemical shifts of **5** (see above);[8,11] they also stand in flagrant contradiction to general rules, which describe the chemical shifts of cyano groups (δ = 110–125 ppm) and their shielding effects on adjacent carbon atoms.[16] The reported[15g,i,j,l,m] data of **5** are also incompatible with the known[8] ^{13}C NMR data of **4**.

d) The ^{13}C NMR data of presumed tricyanomethanide salts **9a–g**[15a,c,d,15f–j,15m–o] are totally incompatible[17] with the corresponding chemical shifts of similar or identical salts, which are commercially available or reported in the literature.[18] For example, the δ values of the cyano groups are allegedly found at 70.0 for **9d**,[15d] 74.8 (**9a**),[15a] 136.3 (**9f**),[15n] 152.6 (**9e**),[15m] and 166.4 ppm (**9b**).[15i] The central carbon of the tricyanomethanide unit was characterized with δ = 41.9 for **9g**,[15j] 50.1 (**9c**),[15c] 63.0 (**9d**),[15d] 69.6 (**9b**),[15i] 120.9 (**9f**),[15n] and 130.1 ppm (**9e**).[15m] Clearly, these data are far away from plausible chemical shifts of cyano groups, and the high-field signal of the central carbon atom (δ = 4–6 ppm) is missing in all cases of tricyanomethanide salts **9**.[15] Moreover, it is remarkable that entirely different chemical shifts were presented for the same tricyanomethanide species in distinct salts, δ = 70.0–166.4 ppm for the cyano groups and δ = 41.9–130.1 ppm for the central carbon.

We prepared **9a** and **9c** from single crystals of **5** and 1-methylimidazole and 4,4′-bipyridine, respectively, as well as **9b** and **9d** from **2** and imidazole or 2,2′-bipyridine.[19] Furthermore, we conveniently synthesized **9a–d** from **1b** and the corresponding amine hydrochlorides by salt metathesis reactions using a procedure which was analogously utilized

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in the literature.[18,20] The ^{13}C NMR spectra of the products indicated signals with δ = 120.5 (cyano groups) and 4.8 ppm (central carbon of the tricyanomethanide unit) in all four cases.[19] Thus, we obtained plausible ^{13}C NMR data of tricyanomethanide salts **9a–d** that are very close to those of similar compounds, reported in the literature,[18,20] but differ drastically from the data published by Zolfigol et al.[15,19]

e) Standard mass spectra (EI, 70 eV)[15j,n] were also utilized by Zolfigol et al. to analyze alleged compounds **9**. However, the depicted spectra indicated a very high number of signals, and the characteristic signals were not extractable without strong doubts; nevertheless, the desired $[M]^+$ signal with low intensity was always picked out.[15a,c,d,15f–h,15j,k,m,n] In the cases of **9a**,[15a,f,g] **9c**,[15c,h] **9d**,[15d] **9e**,[15m] **9f**,[15n] and **9g**,[15j] however, the data include the corresponding signal of $[M]^+$, which is based on the total mass of the salt, i.e., the sum of the (di)cation mass and the mass of the anion(s). But detection of cations and anions at the same time is impossible as shown generally[21] and also for similar imidazolium, pyridinium, and ammonium tricyanomethanides.[18]

f) Not only spectroscopic data of **9** but also physical properties, presented by Zolfigol et al.,[15] differ extensively from data reported by other authors. Whereas Trofimenko described **9f** as an oil,[6] Zolfigol et al.[15n] claimed isolation of **9f** as a yellow solid with a melting point of 136–138 °C. We obtained **9a** as a yellow oil with a melting point slightly below room temperature;[19] in great contrast, Zolfigol et al. characterized **9a** as a pale-pink solid with m.p. > 300 °C.[15a,f,g] While we measured a melting point of 210–215 °C for **9c**,[19] Zolfigol et al. described the same compound with m.p. > 300 °C.[15c] Finally, we established that **2** or pure **5** did not react with the very weak base triphenylamine. But Zolfigol et al. claimed a conversion of these precursors to produce **9g** with 97% yield.[15j]

In summary, it turned out without any doubt that Zolfigol et al.[15,22] did not utilize tricyanomethane (**5**) nor salts of type **1** or compounds **2** or **4** as substrate in their syntheses [see points b) and c)], and they did not prepare any tricyanomethanide salt **9** or product with a tricyanomethyl group [points d), e), and f)]. Moreover, their real experiments cannot be clarified because they did not give any information about the origin of the presumed tricyanomethane (**5**) [see point a)]. Consequently, all described[15,22] condensation reactions, catalyzed by alleged tricyanomethanide salts **9**, are totally unclear and cannot be reproduced by other researchers. It is therefore clear that fundamental corrections are necessary for all 16 articles, or these reports should be withdrawn.

Acknowledgment

We thank Dr. Nader G. Khaligh for fruitful discussions, Jana Buschmann, Philipp Denkmann, and Christopher Mohrig for some experiments with **5** and **9**, and Dr. Andreas Ihle for his help in connection with the manuscript.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611846.

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