Hexanitroisobutene Dianion Salts**

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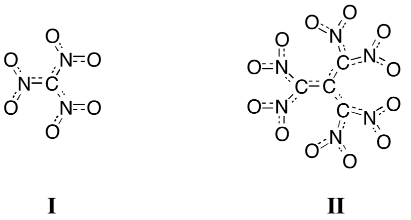
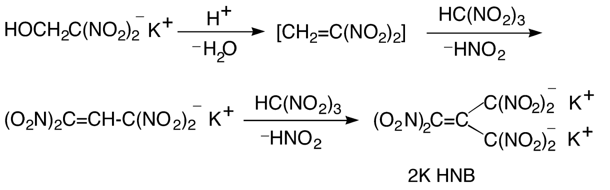
The trimethylenemethane dianion and its analogs have generated considerable interest during the last three decades, in both theoretical organic chemistry (Y-conjugation, Y-aromaticity)[1–12] and synthetic organic chemistry (ligand design).[13–15] Driven by our current interest in "dendritic" Y-conjugated anions,[16, 17] we pursued the synthesis of the hexanitroisobutene (HNB) dianion ($C_4(NO_2)_6^{2-}$; compound **II** in Scheme 1).



Scheme 1. Sample Y-conjugated anions.

Use of a "direct" synthetic approach to HNB, via nitration of dilithium trimethylenemethanide,[2] was rejected because of the obvious problems associated with the simultaneous introduction of six nitro groups onto a chemically labile trimethylenmethane system. An alternative approach (which includes a sequence of addition–elimination reactions, that start from the potassium salt of 2,2-dinitroethanol as the 1,1-dinitoethylene precursor[18] and trinitromethane) was successful (Scheme 2). A similar approach was previously employed for the synthesis of substituted 1,1,3,3-tetranitropropanes[18] and 1,1,3-trinitropropene salts.[19] The only difference in our case was that the elimination of HNO_2 proceeds simultaneously and does not require the addition of bases.[19]



Scheme 2. Addition–elimation synthetic procedure.

After recrystallization from water, HNB salts can be prepared as large, deep-ruby colored crystals (which contain a single coordinated water molecule in the case of dipotassium salt 2K HNB). HNB salts are thermally unstable and tend to decompose slowly even at room temperature. The structure of the HNB dianion is depicted in Figure 1.

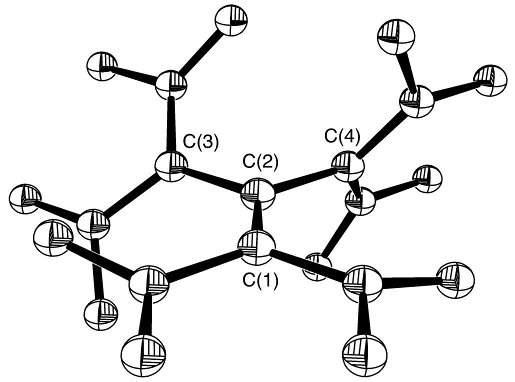


Figure 1. ORTEP representation of the HNB dianion.

The HNB dianion is a nonplanar system. Specific conformations of the anion vary from one salt to another but certain structural features remain intact. Thus, in all salts, the main plane of the molecule (C(1)-C(2)-C(3)-C(4) in Figure 1) is preserved. Dinitromethylene fragments are twisted on various angles in relations to this central plane. The C(1)–C(2) bond distance in the dipotassium salt (2K HNB · H_2O) is 1.34 Å, which is very close to a typical C=C bond distance (see the Supplementary Material). In this salt, the C(1) dinitromethylene fragment is almost coplanar to the main plane of the molecule. The other two dinitromethylene fragments (C(3) and C(4)) are twisted by substantial angles (63.5° and 40.2°, respectively).

UV/Vis spectra of the HNB salts vary from one solvent to another—an indication of the conformational mobility of the HNB dianion in solution. Thus, UV/Vis spectra of 2K HNB in acetone have two distinct absorption maxima: at 370 (19400) and 508 nm (13600 $mol\,L^{-1}cm^{-1}$). In water, these maxima shifted to 368 (21300) and 478 nm (7100 $mol\,L^{-1}cm^{-1}$), respectively. The existence of two absorption peaks in the UV/Vis spectra is a typical feature of conjugated 1,1-dinitrocabanion systems (such as 1-(*R*)-3,3-dinitropropene salts), which was attributed in the past to the presence of two types of rotamers (conjugated and nonconjugated) in solution.[20] Indeed, we found that the sum of integral intensities of these two peaks in the UV/Vis spectra of HNB salts remains constant in different solvents.

^{13}C NMR spectroscopy shows the equivalence of the dinitromethylene groups of the HNB dianion in solution (on the NMR timescale). The ^{13}C NMR spectrum of 2K HNB in $[D_6]$DMSO has only two signals: at $\delta = 135.3$ (dinitromethylene groups) and $\delta = 127.9$ (C(2)). These chemical shifts are very close to those observed in a similar system, the potassium salt of 1,1,3 trinitropropene ($\delta = 134.0$, 127.5, and 127.1 in $[D_6]$DMSO). Again, as in the case of the trinitromethanide

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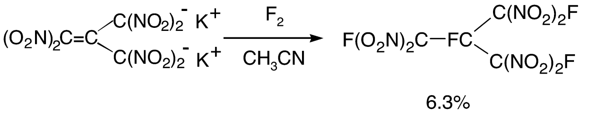
anion (compound **I** in scheme 1),[16, 17] either the barriers of rotation of the three dinitromethylene groups in HNB dianion are too small to be detected by this method or the anion assumes an averaged symmetrical conformation in solution. Similar behavior was reported for the tris(diphenylmethylene) dianion and related systems.[3, 8]

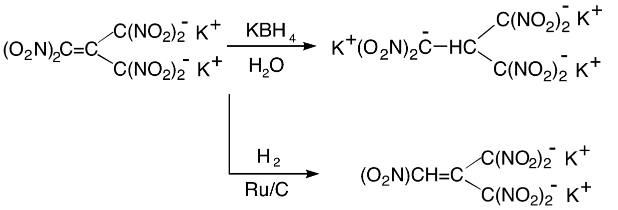
Quantum mechanical calculations show that the central carbon atom (C(2); see Figure 1 and the Supplementary Material) is postively charged, whereas the peripheral carbon atoms (C(1), C(3), and C(4)) are negatively charged. These features suggest that HNB salts can react with both nucleophilic and electrophilic agents. Unfortunately, many of the tested reactions of HNB salts proceed with the fragmentation of the carbon skeleton. Only fluorination and hydrogenation of the HNB salts were successful.

Direct fluorination of the HNB salts with elemental fluorine gave the expected, fully fluorinated product, tris(fluorodinitromethyl)fluoromethane, albeit in a low (6.3 %) yield (Scheme 3).



Scheme 3. Fluorination of HNB.

Hydrogenation of HNB salts can be achieved using elemental hydrogen (5 % Ru/C) or tetrahydroborate reagents. Catalytic hydrogenation of 2K HNB yielded a substitution product, the dipotassium salt of 2-dinitromethyl-1,1,3-trinitropropene (Scheme 4). Reduction with sodium borohydride gave the normal addition product, the tripotassium salt of tris(dinitromethyl)methane, together with the above-mentioned dipotassium salt.



Scheme 4. Hydrogenation of HNB.

In summary, we have synthesized salts of a new, fully nitrated Y-conjugated system, the hexanitroisobutene dianion. It is expected that this dianion will be useful in ligand design similar to other known Y-conjugated anions with a rich coordination chemistry, such as the hexacyanoisobutene dianion.[14, 15]

Experimental Section

Caution: all salts of polynitrocompounds should be handled as potential explosives; therefore use proper protective measures.

Dipotassium salt of hexanitroizobutene (2K HNB), monohydrate: The potassium salt of 1,1-dinitroethanol (4.1 g, 23 mmol) was added incrementally with stirring to a solution of trinitromethane (5.0 g, 33 mmol) in water (20 mL). The temperature was maintained below 25 °C during the addition. The reaction mixture was stirred for an additional 2 h and then left overnight at room temperature. Deep-ruby colored crystals of 2K HNB · H_2O were collected by filtration and were washed with a small amount of ethanol. An additional portion of the crystals was obtained from filtrate by adding KCl (1.6 g). The total yield of 2K HNB · H_2O was 1.8 g (19 %). The salt can be recrystallized from warm water (45 °C). Elemental analysis: calcd for $C_4N_6O_{12}K_2 \cdot H_2O$: C 11.43, N 20.00, K 18.57, H_2O 4.29; found: C 11.29, N 19.45, K 18.62, H_2O 4.29. IR (Ge): $\tilde{\nu} = 1220\,cm^{-1}$ [$C(NO_2)_2^-$]. Other analytical data are presented in the text.

Fluorination of 2K HNB: A suspension of 2K HNB (4.2 g, 10 mmol) in CH_3CN (100 mL) was fluorinated at 0 °C using 20 % F_2/N_2 until the reaction mixture became colorless. The reaction mixture was then poured into 500 g of an ice/water mixture and extracted with *n*-pentane (60 mL). The organic layer was separated and was washed several times with 5 % bicarbonate until the water layer became colorless. The organic layer was finally washed with water and dried over $MgSO_4$. The pentane was evaporated at normal pressure and the residue was distilled in vacuo (48 – 52 °C, 0.1 mm) to yield 0.25 g (6.3 %) of tris(fluorodinitromethyl)fluoromethane as a colorless liquid. Elemental analysis: calcd for $C_4F_4N_6O_{12}$: C 12.00, F 19.00, N 21.00; found: C 12.06, F 19.02, N 20.77. ^{19}F NMR (CCl_4, referenced against CF_3COOH): $\phi = 14.2$ (br m, 3F; $C(NO_2)_2F$), 87.9 (q, 1F, $J^3_{FF} = 14.8$ Hz; CF). IR (KBr): $\tilde{\nu} = 1310, 1645\,cm^{-1}$ [$C(NO_2)_2F$].

Hydrogenation of 2K HNB: a) A solution of 2K HNB · H_2O (0.62 g, 1.5 mmol) in water (25 mL) was hydrogenated at room temperature and normal pressure with a flow of H_2 using a 5 % Ru/C catalyst (1 g). The course of the reaction was monitored by UV/Vis spectroscopy. After the reaction was complete, the catalyst was removed by filtration and washed with water (3 × 15 mL). Combined water solutions were concentrated in vacuo to 5 mL. Cesium fluoride (0.5 g) was added to the solution. The orange precipitate was removed by filtration and was washed with small amounts of water and ethanol to yield dicesium 2-dinitromethyl-1,1,3-trinitropropene (0.2 g, 25 %). An analytical sample was recrystallized from hot water. Elemental analysis: calcd for $C_4HN_5O_{10}Cs$: C 8.79, H 0.37, N 12.82, Cs 48.72; found: C 8.98, H 0.41, N 12.85.77, Cs 47.9. ^1H NMR (D_2O): $\delta = 7.75$ (s; $CHNO_2$). UV/Vis (acetone): λ'_{max} (ε) = 370 (17500); λ''_{max} (ε) = 456 nm (25600 $mol\,L^{-1}cm^{-1}$). b) A solution of potassium borohydride (0.2 g, 3.7 mmol) in water (1 mL) was added with stirring to a solution of 2K HNB · H_2O (1.0 g, 2.4 mmol) in water (37 mL) at room temperature. The reaction mixture was stirred at that temperature for an additional 30 min and then was diluted with methanol (250 mL). The precipitate was filtered and was then washed with ethanol to yield 0.45 g (45 %) of the tripotassium salt of tris(dinitromethyl)methane, analyzed as dipotassium monocesium salt after a partial cation exchange with CsF in water. Elemental analysis: calcd for $C_4HN_6O_{12}K_2Cs$: C 8.96, H 0.19, N 15.67, K 14.55, Cs 24.81; found: C 8.63, H 0.31, N 15.77, K 14.19, Cs 23.60; ^1H NMR (D_2O): $\delta = 7.18$ s (CH). IR (KBr): $\tilde{\nu} = 1240, 1520\,cm^{-1}$ [$C(NO_2)_2^-$]. UV/Vis (H_2O): λ_{max} (ε) = 373 (30500 $mol\,L^{-1}cm^{-1}$).

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Superacid-Catalyzed Selective Formylation–Rearrangement of Isoalkanes with Carbon Monoxide to Branched Ketones**

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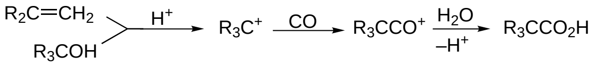
Thomas Mathew, and Eric R. Marinez

The acid-catalyzed carbonylation of olefins or alcohols to branched aliphatic acids (neo-acids) is known as the Koch–Haaf reaction.[1] It involves the intermediate formation of a trivalent alkyl cation (carbenium ion) which then alkylates CO to the corresponding acyl cation to produce, upon hydrolysis, the branched carboxylic acid (Scheme 1).



$$\left.\begin{array}{l}R_2C{=}CH_2\\R_3COH\end{array}\right\rangle \xrightarrow{H^+} R_3C^+ \xrightarrow{CO} R_3CCO^+ \xrightarrow[-H^+]{H_2O} R_3CCO_2H$$

Scheme 1. Koch–Haaf reaction of alkenes and alcohols, $R = CH_3$.

Hopff and Nenitzescu et al.[2a] reported in 1936 that when carbon monoxide was treated with isobutane in the presence of an excess of $AlCl_3$, a mixture of products was obtained, including 31% of methyl isopropyl ketone (MIPK) besides some *tert*-butyl isopropyl ketone and pivalic acid. Nenitzescu subsequently suggested that MIPK was formed by reaction of CO with the intermediately formed *tert*-butyl cation, followed by hydride transfer from the pivaloyl cation to give pivalaldehyde, which then rearranged to MIPK.[2b] The aluminum halide-catalyzed conversion of saturated hydrocarbons with carbon monoxide, however, as reported by Nenitzescu et al., usually gives complex mixtures of products, containing carboxylic acids and ketones.[3]

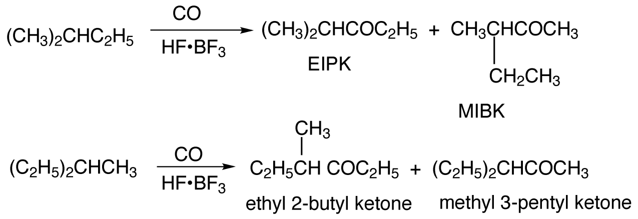
In contrast, Sommer et al.[4] treated CO with alkanes with superacidic $HF \cdot SbF_5$ as a catalyst and obtained exclusively Koch–Haaf carboxylic acid products. After studying the superelectrophilic activation of carbon monoxide and its reaction with adamantane, we reported[5] in 1988 that both the Koch type carboxylation as well as a distinctly different direct formylation to give 1-formyladamantane take place. Whereas the Koch-carboxylation involves initial formation of the 1-adamantyl cation, the formylation reaction proceeds by the activated formyl cation inserting into the tertiary C–H bond via a five-coordinate carbocation.

We now report the superelectrophilic formylation of isoalkanes, such as isobutane or isopentane (and their higher homologues), giving selectively and in high yield the corresponding rearranged branched ketones with no detectable (or minimal) branched acids, that is Koch products.[6] To achieve this remarkably efficient conversion superacids weaker than $HF \cdot SbF_5$ or $FSO_3H \cdot SbF_5$, such as $HF \cdot BF_3$ or $HF \cdot CF_3SO_3H \cdot BF_3$, are used, which do not readily oxidatively ionize isoalkanes to the corresponding alkyl cations (which would consequently lead predominantly to Koch carboxylation). They are, however, still strong enough to activate carbon monoxide to an efficient electrophilic formylating agent (that is the formyl cation protosolvated by the acid, $HCO^+ \cdots H^+A^-$). $HF \cdot BF_3$ was found to be particularly suitable to bring about the reaction. Illustrative of this in the experimental section is the example of the conversion of isobutane into MIPK (Scheme 2).

$$(CH_3)_3CH \xrightarrow[HF\bullet BF_3]{CO} \underset{\text{MIPK}}{(CH_3)_2CHCOCH_3}$$

Scheme 2. Carbonylation-rearrangement of isobutane.

Other isoalkanes containing tertiary CH groups, such as isopentane, isohexanes, or isoheptanes, react under related superacidic carbonylation conditions in a similar way to give the corresponding branched ketones (Scheme 3).



Scheme 3. Carbonylation-rearrangement of isopentane and 3-methyl pentane.

Isopentane for example is converted into methyl isobutyl ketone (MIBK) and ethyl isopropyl ketone (EIPK) in a ratio of 1:3. 3-Methylpentane gives ethyl 2-butyl ketone and methyl 3-pentyl ketone, respectively (4:1), as major products. The reaction is considered to involve electrophilic formylation of the tertiary CH bond of isobutane forming pivalaldehyde, which under the superacidic conditions rearranges to MIPK (Scheme 4).

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