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Bicentral oxidation of nitrosolic acids: synthesis of 1,1-dinitroalkanes

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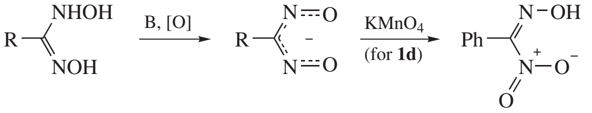
***gem*-Dinitrozo compounds are cleanly oxidized into the *gem*-dinitro analogues on treatment with formic acid/hydrogen peroxide system.**

The chemical oxidation of mono-*C*-nitroso to *C*-nitro alkanes[1] was previously performed using CrO_3/AcOH,[2] NO,[3] N_2O_4,[4] N_2O_5,[4(c),5] air,[6] ozone,[7] aq. H_2O_2/AcOH,[8] aq. H_2O_2/HNO_3,[9] $H_2O_2/(CF_3CO)_2O$,[10] MCPBA,[11] aq. HNO_3,[12] aq. HNO_3/AcOH,[13] conc. HNO_3,[14] aq. NaOCl/$Bu_4N{\cdot}HSO_4$/benzene,[15] periodic acid[16] and iodosylbenzene[17] as the reagents.

gem-Dinitroso compounds have been known since 1905, when Wieland[18] first described the isolation of a blue crystalline salt **1a** from a complex mixture of products obtained by the disproportionation of *N*-hydroxy amidoxime **2a** under basic conditions (Scheme 1). Since then analogous anionic α,α-dinitroso compounds **1a–d**, termed also as nitrosolates or dinitrosomethanides, were prepared from *N*-hydroxy amidoximes **2a–d** by disproportionation or, more recently, by periodate oxidation.[19]



2a–d **1a–d** **3**

a R = H **b** R = Me **c** R = Et **d** R = Ph

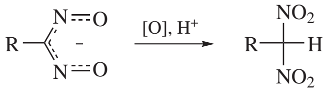
Scheme 1

The corresponding acids, termed as nitrosolic acids by Wieland, were shown to exist for a short time in solutions on cooling. However, their attempted isolation resulted in decomposition. In contrast, salts **1** are sufficiently stable and can be isolated. Both the acids and their anions are blue coloured. Their structure was determined by a series of chemical degradation,[18(b),(c)] UV,[19(b),(c)] ^{1}H and ^{13}C NMR[20] and X-ray crystallographic studies.[20,21] The polarography of some salts has been investigated[19] and the p*K* values[19(c)] of a series of acids have been determined. The single literature precedent[22] demonstrates the susceptibility of α,α-dinitroso compounds anions to oxidation, *viz.,* the oxidation of one NO group to NO_2 group in compound **1d** was performed with $KMnO_4$ in the presence of a base to give the corresponding nitrolic acid **3** (see Scheme 1). On the other hand, oxidation of nitrolic acids using N_2O_4[23] or nitric acid[24] afforded 1,1-dinitroalkanes.

With this knowledge, we explored an intriguing possibility of the one-step preparation of 1,1-dinitroalkanes from nitrosolates **1**. 1,1-Dinitroalkanes are of great interest as intermediates in the synthesis of highly nitrated compounds[25] and nitrogen heterocycles.[26]

Our research in this area is focused on the hydrogen peroxide oxidation. Present strategy was based on our previous observation[27] that the oxidative activity of hydrogen peroxide mixtures depended on its concentration, amount as well as manner of its addition to the reactant.

Here, we describe the new oxidation of nitrosolates **1**[†] with *in situ* generated peroxy acids affording 1,1-dinitroalkanes **4** (Scheme 2).



1a–d **4a–d**

a R = H **b** R = Me **c** R = Et **d** R = Ph

Scheme 2

Preliminary experiments (Table 1) showed that oxidation of nitrosolate **1a** with a mixture of H_2O_2 and strong inorganic acids provided only low yields (up to 10%) of dinitromethane **4a**. The most of the starting nitrosolate was lost in the hydrolytic

Table 1 Oxidation of compounds **1a–d** with H_2O_2/strong acid mixtures.

Entry	Reagents and conditions	Yields of dinitroalkanes (%)			
		4a	**4b**	**4c**	**4d**
1	30% H_2O_2 + 56% HNO_3, –5 °C → room temperature	6	4	2	traces
2	50% H_2O_2 + 56% HNO_3, –5 °C → room temperature	4	3	5	0
3	50% H_2O_2 + 100% HNO_3, –5 °C → room temperature	traces	3	6	0
4	30% H_2O_2 + 50% H_2SO_4, –10 °C → room temperature	2	traces	traces	6
5	30% H_2O_2 + 96% H_2SO_4, –10 °C → room temperature	5	traces	traces	traces
6	50% H_2O_2 + 96% H_2SO_4, –10 °C → room temperature	8	4	traces	2
7	50% H_2O_2 + $KHSO_5$ + 10% H_2SO_4, –10 °C → room temperature	10	11	7	14
8	50% H_2O_2 + $KHSO_5$ + 50% H_2SO_4, –10 °C → room temperature	3	7	5	5

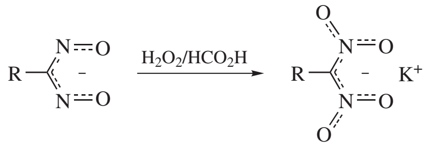
[†] Potassium nitrosolates **1a–c** were used, whereas phenyl analogue **1d** was applied in the form of silver salt as the corresponding potassium salt is unknown.

process, and if too great excess of the oxidizing mixture was used, the only product was a gas. Similar results were observed for the oxidation of compounds **1b–d**.

We attributed the low yields of the oxidation with H_2O_2/HNO_3 and H_2O_2/H_2SO_4 to the Nef reaction[28] that proceeded when salts of the forming nitro compounds were exposed to strong acid. We supposed that application of a mixture of H_2O_2 with weaker organic acids could be more successful. We reasoned that during the use of an acid weaker than dinitroalkanes (the pK_a values[29] are: dinitromethane, 3.60; dinitroethane, 5.21; dinitropropane, 5.53), both oxidized precursor and forming product would exist as anions that should prevent the Nef reaction.

Organic peroxy acids are the weak acids having pK_a values *ca.* 3.5–4 units greater than those of the parent acids.[30] The published[30] pK_a values for HCO_3H and $MeCO_3H$ are 7.10 and 8.2, respectively. Therefore, they could be anticipated to be the competent oxidants.

In fact, exposure of potassium nitrosolate **1a** to the mixture of 95% H_2O_2 (pK_a 11.6)[30] with Ac_2O gave dinitromethane salt **5a** in moderate yield (Table 2, entry 1; Scheme 3). The use of more diluted H_2O_2 (Table 2, entries 2, 3), as well as the mixtures of hydrogen peroxide with acetic acid (Table 2, entries 4–6) led to lower yields.



1a–d **5a–d**

a R = H **c** R = Et
b R = Me **d** R = Ph

Scheme 3

We supposed that moving to a stronger carboxylic acid could provide more active peroxy species. In fact, the oxidation of potassium nitrosolate **1a** using a mixture of hydrogen peroxide and formic acid gave product **5a**[‡] in yields as high as 71–86% (Table 2, entries 6, 7).

Investigating scope and limitations of our procedure we found that salts **1b** or **1c** when treated with HCOOH/80% H_2O_2 transformed into the desired dinitromethyl derivatives **5b** and **5c** in 85% and 76% yields, respectively. However, attempted oxidation of Ag-salt **1d**[†] under these conditions failed to give any of dinitro compounds. On the other hand, similar oxidation in the presence of K_2HPO_4 provided the desired K-salt **5d** in 47% yield.

Compounds **4** and **5** were identified by elemental analyses, ^1H, ^{13}C and ^{14}N NMR spectral data[31] and infrared absorption spectra,[32] which were consistent with the data described recently.

Table 2 Oxidation of **1a** with *in situ* organic peroxy acids.

Entry	Reagents and conditions	Yield of **5a** (%)
1	95% H_2O_2 + Ac_2O, –5 °C → 35 °C	53
2	80% H_2O_2 + Ac_2O, –5 °C → 35 °C	48
3	50% H_2O_2 + Ac_2O, –5 °C → 35 °C	32
4	95% H_2O_2 + AcOH, 0 °C → 35 °C	29
5	80% H_2O_2 + AcOH, 0 °C → 35 °C	25
6	50% H_2O_2 + AcOH, 15 °C → 55 °C	26
7	80% H_2O_2 + HCOOH, 15 °C → 45 °C	86
8	50% H_2O_2 + HCOOH, 15 °C → 60 °C	71
9	35% H_2O_2 + HCOOH, 15 °C → 65 °C	58

The structure of **5c** was ultimately confirmed by single crystal X-ray crystallography[33] using a sample recrystallized from water.[§]

General view of molecule of **5c** is presented in Figure 1. An asymmetric unit cell consists of half of dinitropropane-potassium salt which occupies special position (on the mirror plane). Each potassium cation is coordinated with eight oxygen atoms. Both nitro groups of the anion are equally involved in coordination, and negative charge is delocalized over NO_2–C–NO_2 moiety that is nearly planar (mean deviation is 0.034 Å). The C(1)–N(1)[N(1A)] bonds [1.3807(11) Å] are shorter than C_{sp^2}–NO_2 single bonds for neutral molecules (1.40–1.46 Å).[34] The lenghts of eight K···O contacts vary in the range of 2.72–2.93 Å which corresponds to normally observed distances.[34] Cation–anion interactions link molecules to the layers parallel to *ab* crystallogrphic plane while the layers are connected to each other by ordinary van der Waals interactions between ethyl groups.

In conclusion, we have developed a simple and efficient method for the oxidative synthesis of α,α-dinitroalkanes, compounds of significant synthetic interest. To the best of our knowledge, this is the first example of oxidative formation of

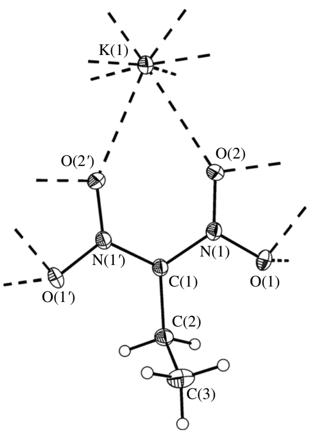


Figure 1 ORTEP view of molecule of **5c**. The displacement ellipsoids are drawn at 50% probability level.

[‡] *General procedure for the synthesis of* gem-*dinitroalkane K-salts* **5**. Potassium salt of dinitrosomethanide **1a** (1.12 g, 10 mmol) was added very slowly to a stirred solution of formic acid (5 ml) in 80% H_2O_2 (10 ml) at 15 °C, maintaining the temperature of the solution below 18 °C (**Caution!** The reaction is exothermic and potentially explosive). Stirring was continued at this temperature for 30 min and then the mixture was heated to 45 °C. The reaction mixture was diluted with water and left on stirring at 0 °C for 2 h. The precipitated solid was collected by filtration. The filtrate was concentrated, and the precipitation was repeated. The two crops were combined and crystallized from H_2O. After filtration and washing with water, the yellow solid was dried under vacuum to give the product **5a** (1.24 g, 86%); mp 207 °C (explosion!) [lit., 207–208 °C (decomp.)]. All compounds described in this paper gave satisfactory physico-chemical data. **Caution!** Compounds **1a–d** and **5a–d** are sensitive to heat, sparks, friction, and impact, hence, fluoroplastic spatulas should be used. Grounding straps, thick gloves, and a face shield should be worn during all manipulations.

[§] *Crystal data for* **5c**. Crystals of $(C_3H_5N_2O_4)^-K^+$ are monoclinic, space group $P2_1/m$: $a = 4.1938(3)$, $b = 7.7949(6)$ and $c = 9.7764(8)$ Å, $\beta = 99.161(2)°$, $V = 315.52(4)$ Å^3, $Z = 2$, $M = 172.2$, $d_{calc} = 1.812$ g cm^{-3}, $\mu = 0.797$ mm^{-1}. 3401 reflections were collected on a SMART 1000 CCD diffractometer [λ(MoKα) = 0.71073 Å, graphite monochromator, ω-scans, $2\theta < 58°$] at 120 K. The structure was solved by the direct methods and refined by the full-matrix least-squares procedure in anisotropic approximation. 889 independent reflections ($R_{int} = 0.0203$) were used in the refinement procedure that was converged to $wR_2 = 0.0533$ calculated on F^2_{hkl} [GOF = 1.018, $R_1 = 0.0229$ calculated on F_{hkl} using 832 reflections with $I > 2\sigma(I)$].

CCDC 779124 contains 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. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2010.

α,α-dinitromethylene moiety; earlier preparation of α,α-dinitroalkanes has been limited to the nitration reaction.

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