JOC The Journal of Organic Chemistry

Article

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E versus *Z* Diazeniumdiolation of Acetoacetate-Derived Carbanions

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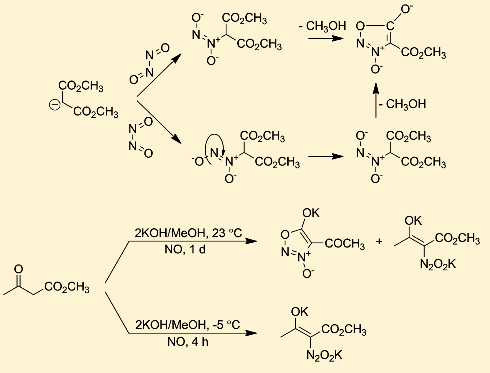
Supporting Information

ABSTRACT: Nitric oxide adds to methyl acetoacetate in the presence of KOH in methanol at room temperature to form potassium acetylsydnonate *N*-oxide (**K1**) with an (*E*)-diazeniumdiolation and potassium acetate diazenium diolate (**K$_2$2**) from a (*Z*)-diazeniumdiolation. A study of the reaction with LiOH, NaOH, and NMe$_4$OH and with ethyl acetate substrate reveals that the temperature of the reaction greatly influences the nitric oxide reactivity. At 23 °C, nitric oxide adds to give both *E* and *Z* products, whereas at −5 °C the gas reacts almost exclusively to give *Z* addition. The (*Z*)-diazeniumdiolation products, namely, the alkali metal and NMe$_4^+$ salts of methyl and ethylbutenoate-2-diazeniumdiolate-3-hydroxylate (**3**$^{2-}$ and **4**$^{2-}$), are isolated in good yields. The alkali metal salts are not amenable for recrystallization because of their ready decomposition in aqueous solutions. However, [NMe$_4$]$_2$[MeC(O)C(N$_2$O$_2$)CO$_2$Me] is readily recrystallized from a methanol/acetonitrile solvent mixture. The crystals are unambiguously characterized by X-ray crystallography. NMR spectra for all of the **3**$^{2-}$ and **4**$^{2-}$ salts reveal the presence of two isomers in aq solutions. But the structure of the NMe$_4^+$ salt contains only one of the isomers. Our attempts to cyclize the isolated and purified butenoatediazeniumdiolates from the (*Z*)-diazeniumdiolation to the *E*-containing sydnonate products were unsuccessful. TGA/DSC data for all of the products demonstrate the thermal instability of the salts at high temperatures. The salts decompose exothermally possibly with the release of N$_2$O among other gases.

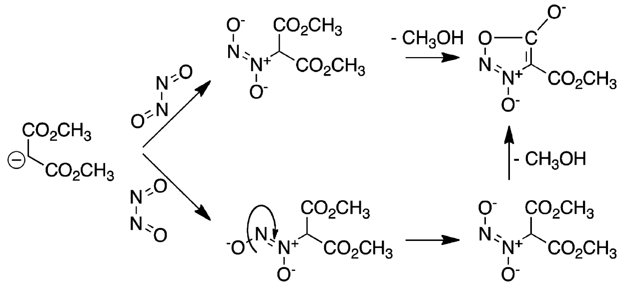


INTRODUCTION

Nitric oxide (NO) is a stable free radical that readily dimerizes to give a kinetically important ON−NO-bound dimer.[1] It is stubbornly unreactive with substrates such as olefins except when any one of the gases O$_2$, NO$_2$, or N$_2$O$_3$ is present in at least catalytic amounts.[2−6] However, NO readily reacts with a variety of dialkylamines[7] and enolates,[8] forming (NO)$_2$-addition products. Significantly, the reactions with dialkylamines rarely yield nitrosoamines,[9] and the kinetics of NO addition to diisopropylamine and pyrrolidine imply bimolecular addition of NO at high concentrations of the gas.[10] In addition, a thorough IR and UV−vis spectroscopic investigation of the heterogeneous reaction between NO gas and a series of manganese(II) porphyrinate complexes at 90 K also indicates the presence of dimeric NO, *cis*-(NO)$_2$.[11] Yet another facet of the NO reactivity with organic substrates and alkaline sulfites is that the products formed contain cis (*Z*) geometry for the −N$_2$O$_2^-$ groups.[7,8,12−14] This observation lends credence to a theoretical claim that NO exists predominantly as the dimeric singlet *cis*-(NO)$_2$ ($^1A_1$).[15] These calculations also predict three other shallow NO dimers of slightly higher energy, namely, a triplet *cis*-(NO)$_2$ ($^3B_2$) and two *trans*-(NO)$_2$ species (^1A_g and ^3A_u). IR and Raman spectroscopic data measured for NO at low temperatures prove the existence of the singlet *cis*-(NO)$_2$, but there is a scarcity of experimental data for the trans isomers.[16,17] However, we have previously reported synthetic observations that point to either the direct addition of *trans*-(NO)$_2$ to form an *E* or *anti*-N$_2$O$_2^-$ intermediate or the addition of *cis*-(NO)$_2$ to form a *Z* or *cis*-N$_2$O$_2^-$ intermediate. The latter is proposed to subsequently tautomerize into the *E anti*-N$_2$O$_2^-$ intermediate in the eventual formation of sydnonate N-oxide products. In both cases, the final (*E*) anti-N$_2$O$_2^-$ intermediate cyclize into forming the sydnone *N*-oxide product (Scheme 1).[18,19]

The reactions of nitric oxide with carbanions derived from dimethyl malonate,[18,19] terminal alkynes,[20] and benzyl

Scheme 1

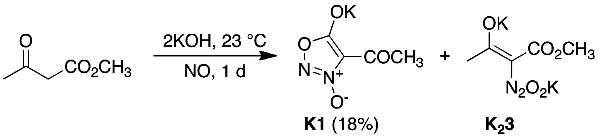


Received: May 23, 2012
Published: August 1, 2012

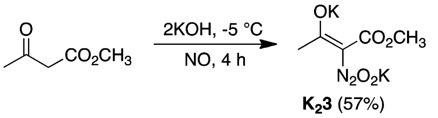
cyanide[18,21] are the only substrates that have been studied for such reactions until date. A closely related family of 3-hydroxysydnoneimines has been known in the literature for over 40 years.[22] These compounds are synthesized from the nitrosylation of *N*-(nitriloalkyl)hydroxylamines, RCH(CN)-NHOH. The intermediate nitrosohydroxylamine, RCH(CN)-N_2O_2H, is similarly suggested to undergo intramolecular condensation to form the hydroxysydnoneimines.[22] In the context of the various physiological roles played by nitric oxide, it is desirable to establish its reactivity. Therefore, we were interested in determining the mode of addition of nitric oxide to carbanions. Specifically, we sought to determine if it is possible to distinguish between *cis*- or *trans*-$(NO)_2$ addition to give *Z* or *E* diazeniumdiolation products, respectively. Toward this goal, we have now studied the reactions of nitric oxide with methyl and ethyl acetoacetates under a variety of conditions. The acetoacetates are particularly suitable as they contain a highly acidic methylene group but only one α-carboxylate group. We hoped that the proposed cyclization step in the formation of the sydnonate *N*-oxide may be less favored than in the malonate reaction and that hence it may be possible to isolate intermediary species. As we discuss below, although we were able to isolate the corresponding *cis*-$N_2O_2^-$-substituted product and a mixture of both cis- and trans-$(NO)_2$ addition products, there is no evidence for the conversion of the (*Z*)-diazeniumdiolated acetoacetate into the corresponding E sydnonate-N-oxide. We have also studied the thermal properties of the new compounds as both diazeniumdiolate and sydnonate-N-oxide products are known to exhibit exothermic decomposition properties.[8,12,19]

■ RESULTS AND DISCUSSION

The reaction of nitric oxide with methyl acetoacetate and 1 equiv of KOH in methanol solvent at room temperature (23 °C) for 24 h yields a mixture of products, eq 1. Slow recrystallization of the crude product from 0.1 N aq KOH readily forms potassium 4-acetylsydnone *N*-oxide (**K1**) as the first crop. On further standing, a mixture of potassium acetatediazeniumdiolate, $CH_2(N_2O_2K)CO_2K$ (**K**$_2$**2**), and potassium oxalate is formed. Several recrystallizations were necessary to separate the diazeniumdiolate from the latter salt. On the other hand, the above reaction carried out at −5 °C for 4 h yields potassium methyl 2-butenoate-3-hydroxylate-2-diazeniumdiolate, $MeC(OK)C(N_2O_2K)CO_2Me$ (**K**$_2$**3**), as the major product (eq 2) with less than 2% of sodium acetate and the sydnonate *N*-oxide impurities. The impurities are readily removed when the dried precipitate is washed with methanol. However, we are unable to recrystallize **K**$_2$**3** from methanol, water, 0.1 N aq KOH, or 0.5 N aq KOH as it undergoes slow decomposition in solution. In neutral aqueous media, the product decomposes to form potassium acetate and potassium oxalate. In basic aqueous solutions **K**$_2$**3** is hydrolyzed, and over a period of 5 d, **K**$_2$**2** and potassium acetate are formed. Nearly quantitative conversion into the two salts is achieved from aq. KOH solutions containing at least 1 equiv of KOH (eq 3) as described in the Experimental Section. Recrystallization was also attempted by the slow evaporation of water under a steady flow of N_2 gas over several days with both the neutral and basic aq solutions of **K**$_2$**3**, and similar decompositions were observed.



(1)



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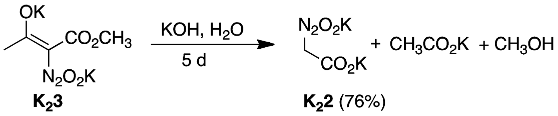


(3)

Unlike **K**$_2$**3**, salts **K1** and **K**$_2$**2·H**$_2$**O** are quite stable in aqueous solution at neutral and basic pH's. UV−vis, IR, and NMR spectroscopic data and single-crystal X-ray diffraction characterize the salts unambiguously. The UV−vis spectrum measured for **K1** exhibits three intense peaks at 206, 239, and 290 nm arising from $\pi \rightarrow \pi^*$ transitions.[19] **K**$_2$**2** exhibits a single absorption at 249 nm consistent with the presence of the diazeniumdiolate functional group.[12] Crystallographic structural data establish anti and cis geometry for the N_2O_2 fragment in **K1** and **K**$_2$**2**, respectively. Views of the anions are shown in Figure 1. Although the compounds are unusual and novel, the structures themselves are comparable to previously reported structures of sydnonate *N*-oxides and diazeniumdiolates.[12,18,19,23,24] On the other hand, the characterization of **K**$_2$**3** relies on more indirect spectroscopic data and elemental analysis data. The IR spectrum measured for **K**$_2$**3** exhibits a strong absorption at 1342 cm^{-1} attributable to the $(ONNO)_{sym}$ vibration.[25] Solutions of the salt in 0.1 N aq KOH exhibit an intense absorption at 263 nm in its UV−vis spectrum, although the elemental analysis data indicate one diazeniumdiolate substituent. The relatively low energy of the chromophore compared to other monodiazeniumdiolates, 248 nm, suggests that as with other polydiazeniumdiolates with 258 and 264 nm for bis- and tris(diazeniumdiolates), respectively,[12,26] the vicinal carboxylate in **K**$_2$**3** also results in a red-shifted Stark effect. The ^1H NMR spectrum for **K**$_2$**3** in 0.1 N KOD (D_2O) exhibits two pairs of singlets at 3.61 and 3.60, and 2.28 and 1.77 ppm. The

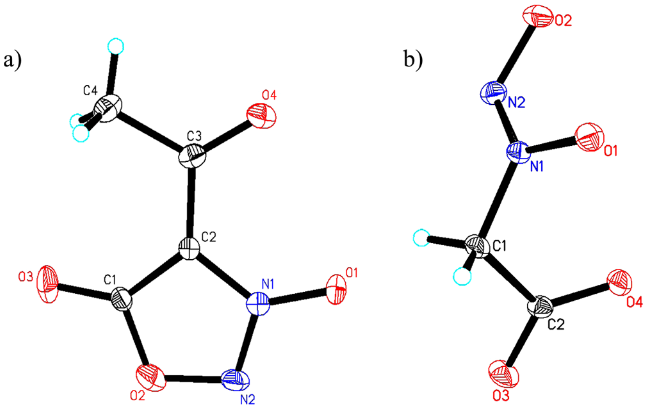


Figure 1. Views of 1^- (a) and 2^{2-} (b). In this and the following figures, the hydrogen atoms are represented as unlabeled open circles. The rest of the atoms are drawn as thermal ellipsoids of 50% probability. Selected bond distances (Å) in 1^-: C2−N1, 1.3930(13); N1−O1, 1.2579(11), N1−N2, 1.3193(13); N2−O2, 1.3861(14), C1−O2, 1.3720(14), C2−C3, 1.4439(14); C3−O4, 1.2300(13). Selected bond angles (deg) in 1^-: C1−C2−N1, 125.48(9); O1−N1−N2, 118.72(9); O1−N1−C2, 129.65(9); C2−N1−N2, 111.63(9); N1−N2−O2, 106.90(8); O2−C1−C2, 107.59(9); C1−C2−C3, 129.62(9).

ratio of the two pairs is identical at 1:1.63. Similarly, the proton-decoupled ^{13}C spectrum exhibits two sets of five peaks indicating the presence of two isomers in solution. The proton-coupled ^{13}C spectrum reveals that the two pairs of the peaks at 53.4, 53.2, 27.5, and 26.2 ppm are methyl groups. Therefore, the spectra are assigned to arise from two isomers of structure $CH_3C(OK)C(N_2O_2K)CO_2CH_3$. However, the spectra are insufficient for the assignment of the geometry of the diazeniumdiolate substituent or for determining the nature of the two species in solution. Therefore, we extended the study to ethyl acetoacetate and to reactions in the presence of sodium, lithium and tetramethylammonium hydroxides. The reactions of methyl acetoacetate with the bases at −5 °C give similar results forming the respective **3**$^{2-}$ salts. The reactions of ethyl acetoacetate with nitric oxide in the presence of KOH and NaOH at −5 °C form the respective monodiazeniumdiolates. Both of them exhibit similar UV−vis, IR and NMR spectra as **K$_2$3**. Fortunately, the tetramethylammonium salt of **3**$^{2-}$ crystallizes from methanol/acetonitrile solvent mixtures allowing for its complete structural characterization.

The room-temperature reactions of nitric oxide with the acetoacetates and the various bases were also studied. The reactions proceed similarly as the reaction with KOH, but the fractional crystallization of the sydnonate *N*-oxide and acetatediazeniumdiolate salts is more difficult. The products are contaminated with each other, as well as the alkali acetate and oxalate salts.

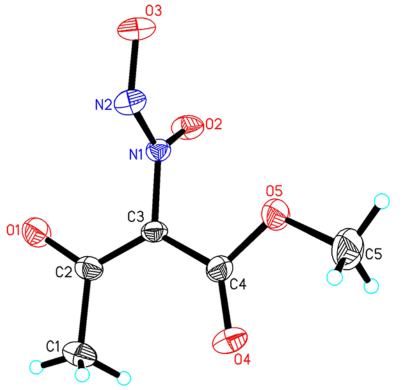
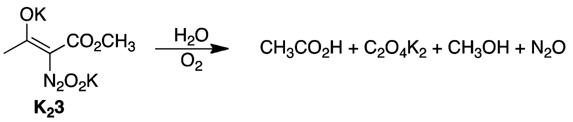


Figure 2. View of **3**$^{2-}$ in **[NMe$_4$]$_2$3·3H$_2$O·MeOH**.

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Anions in K$_2$2·H$_2$O and [NMe$_4$]$_2$3·3H$_2$O·MeOH

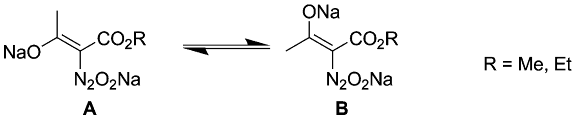
K$_2$2·H$_2$O		[NMe$_4$]$_2$3·3H$_2$O·MeOH	
C1−N1	1.4577(8)	C3−N1	1.4382(11)
N1−N2	1.2906(8)	N1−N2	1.2878(11)
N1−O1	1.3068(7)	N1−O2	1.2934(10)
N2−O2	1.2925(7)	N2−O3	1.2934(10)
C1−C2	1.5321(9)	C3−C2	1.3955(13)
		C2−O1	1.2617(12)
		C3−C4	1.4324(13)
N1−C1−C2	112.13(5)	N1−C3−C4	117.29(8)
N2−N1−O1	123.98(5)	N2−N1−O2	122.51(7)
N1−N2−O2	114.31(5)	N1−N2−O3	114.44(8)
N2−N1−C1	116.25(5)	N2−N1−C3	117.53(8)
O1−N1−C1	119.38(5)	O2−N1−C3	119.96(7)
		C2−C3−C4	125.57(8)

Single-crystal diffraction data for [(**NMe$_4$**)]$_2$**3** reveal that it is a monodiazeniumdiolate and that the $-N_2O_2^-$ group is of *Z* geometry (Figure 2) as in other known diazeniumdiolates.[10,12,13,26] The metrical parameters (Table 1) associated with the diazeniumdiolate substituent do not reveal substantial differences from those of **2**$^{2-}$. However, bonds C2−O1, C2═C3, and C3−C4 of the 2-butenoate-3-hydroxylate backbone exhibit significant anomalies. Whereas the C−O bond is significantly shorter than a typical C−O single bond, C2═C3 is ca. 0.2 Å longer than a C═C double bond, and C3−C4 ca. 0.1 Å shorter than a C−C single bond. In addition the four atoms are also coplanar. Together, these data suggest delocalization of the enolate and diazeniumdiolate negative charges, and the C═O and C═C double bonds over the **3**$^{2-}$ dianion. As could be expected, the mean plane passing through atoms C1, C2, O1 and C3 atoms and that of the $-N_2O_2^-$ substituent dissect at an angle (91.6°) close to 90°. The observed delocalization of charges and bonds renders the C═C bond prone to hydrolysis under both acidic and neutral conditions in aqueous media. **K$_2$3** undergoes oxidative hydrolysis in aqueous solutions under atmospheric conditions over several days to form acetic acid, potassium oxalate and methanol while also releasing nitrous oxide gas (eq 4). The hydrolysis is completed in 1 h if the solution is heated to 80 °C. Nitrous oxide was identified by the IR spectrum, which exhibits strong absorptions at 2236, 2203, 1297, and 1272 cm^{-1} as described in the Experimental Section. Significantly, the spectrum does not contain any peaks attributable to NO or NO$_2$ gases. The formation of the rest of the products is verified by the ^1H and ^{13}C NMR spectra measured for a solution of **K$_2$3** in D_2O (heated at 80 °C for 1 h).



(4)

Concentrated solutions of salts of **3**$^{2-}$ are sufficiently stable for at least 1 h in D_2O, whereas those of the sodium and potassium salts of **4**$^{2-}$ are quite unstable. Therefore, the NMR spectra for the salts of **4** were measured in 0.1 N NaOD/D_2O and 0.1 N KOD/D_2O, respectively. As a representative case, the spectra for salts of **K$_2$3** were also measured in 0.1 N KOD/D_2O. The spectra are identical to those measured in D_2O. The NMR spectra are valuable in estimating the percentage of the two isomers. We were particularly interested to see if the N═N bond is responsible for the observed tautomerism as it would help explain the formation of sydnonate *N*-oxides. The second possibility is tautomerism due to the C═C bond. The relatively well-localized N═N double bond in **3**$^{2-}$ and the longer and delocalized C═C bonds suggest that the latter bond may be more readily rotated than the N═N bond. ^1H NMR spectra measured for **K$_2$3** in 0.1 N KOD (D_2O) at temperatures 6, 20, and 50 °C reveal that neither the ratio of the isomers nor their chemical shifts change significantly at those temperatures. We interpret this observation as evidence for the absence of any exchange of tautomers in solution. In agreement with that conclusion, we are unable to cyclize both **3**$^{2-}$ and **4**$^{2-}$ under a variety of conditions to salts of acetylsydnonate *N*-oxide. Therefore, we conclude that the two sets of proton and carbon peaks observed in the ^1H and ^{13}C NMR spectra for both **3**$^{2-}$ and **4**$^{2-}$ must be due to tautomerism involving the C═C double bond. The two tautomers can be represented by structures **A** and **B**. The crystallographic structural data reveals that there is only one of the tautomers (**A**) present in the solid state structure of $[\mathbf{NMe_4}]_2\mathbf{3}$. On the basis of the overall similarity of the IR spectra, we propose that all of the various salts of $\mathbf{3}^{2-}$ and $\mathbf{4}^{2-}$ contain only one of the tautomers, specifically, tautomer **A**. The ratio of the tautomers in aq or aq KOH solutions of the salts of $\mathbf{3}^{2-}$ are 1:1.63 for the sodium and potassium salts, 1:2 for the lithium salt, and 1:1.73 for the NMe_4^+ salt. The unique ratio for the lithium salt can be ascribed to strong metal−ligand coordination between the Li^+ cations and the enolate and diazeniumdiolate oxygen atoms of $\mathbf{3}^{2-}$. Such interactions are less pronounced or negligible in the K^+, Na^+, and NMe_4^+ salts. In comparison, the ratio of 1:1.26 observed for the K^+ and Na^+ salts of $\mathbf{4}^{2-}$ is significantly different, and the difference may be due to the presence of the sterically bulkier ethyl group.



The formation of salts of $\mathbf{3}^{2-}$ and $\mathbf{4}^{2-}$ from the reactions of methyl and ethyl acetoacetates and the bases with nitric oxide at −5 °C implies that nitric oxide adds exclusively as the *cis*-$(NO)_2$ isomer. The formation of salts of $\mathbf{1}^-$ at higher temperatures (23 °C) as a coproduct along with those of $\mathbf{3}^{2-}$ reveals that both formal cis- and *trans*-$(NO)_2$ additions take place at higher temperatures. The temperature difference may reflect competition of mechanisms with either carbanion addition of $(NO)_2$ with stepwise addition of two NO's to the carbanion.

Diazeniumdiolates of secondary amines and others have useful reactivity as nitric oxide or nitroxylate donors.[27] Therefore, we also tested the new diazeniumdiolates for such behavior following literature methods.[28,29] The salts release neither NO nor NO^- in aqueous solutions as judged by the reductive nitrosylation of manganese(III)porphyrins. Nitroxyl has been proposed to be a rapid and efficient reductive nitrosylating agent for these porphyrins and their absence here suggests either that the N−N bond in the diazeniumdiolate is retained in the product or that the diazeniumdiolate is unable to reduce the Mn(III). The salts of $\mathbf{3}^{2-}$ and $\mathbf{4}^{2-}$ appear to lose the diazeniumdiolate moiety on protonation as N_2O gas as discussed above.

We also examined the thermochemical properties of the new products by thermogravimetric and differential scanning calorimetric analysis. As is common for sydnonate *N*-oxides and diazeniumdiolates, the new products also exhibit explosive decomposition properties.[8,12,14,18,19,23] The TGA and DSC data (Table 2) for the products were measured under a steady flow of N_2 gas in partially sealed aluminum cups. Except for $[NMe_4]_2\mathbf{3}\cdot H_2O$, all of them explode if the sample size was greater than 2 mg, popping the covers of the sample cups. Therefore, smaller amounts (ca. 0.5−1 mg) were taken for the studies. The DSC data reveal that the compounds are stable on heating up to more than 150 °C and with Δ*H* in the range of 990−2101 J g^{-1}. The decomposition is accompanied by the mass loss in the range of 33.7 to 86.7%. We speculate that nitrous oxide is lost in each of the decompositions although it is not possible to satisfactorily explain the mass loss for all of the products. It is likely that the sample may be insufficiently decomposed due to the nonavailability of oxygen and also due to the observed explosiveness. However, the data clearly show that the NMe_4^+ salt is the least exothermic and that the sydnonate *N*-oxide is the most exothermic. The sydnonate-N-oxide salt is also stable up to ca. 250 °C and decomposes at sharply at 270 °C. Similarly, the alkali salts of $\mathbf{3}^{2-}$ and $\mathbf{4}^{2-}$ also exhibit sharp exothermic decomposition at high temperatures.

Table 2. Thermal Decomposition Data

compd	DSC T_{Onset}, °C	T_{max}, °C	Δ*H*, J/g	TGA Δ*m*, %
K1	270	273	2101	−54.0[a]
$\mathbf{K_22\cdot H_2O}$	308	312	1550	−35.8[a]
$\mathbf{K_23}$	269	271	1086	−64.3[a]
$\mathbf{Na_23}$[b]	226, 250	231, 262	2018	−33.7[c]
$\mathbf{Li_23\cdot 0.67MeOH\cdot 0.33H_2O}$	198	203	1277	−59.1[a]
$\mathbf{[NMe_4]_23\cdot H_2O}$	159	170	990	−86.3[c]
$\mathbf{K_34}$	280	282	1578	−37.2
$\mathbf{Na_34}$	237	264	1882	−37.5

[a] Sample exploded. [b] Two overlapping peaks. [c] Broad weight loss at ca. 100 − 300 °C.

■ CONCLUSIONS

On the basis of the products formed, it is clear that nitric oxide formally adds as *cis*-$(NO)_2$ to carbanions formed from methyl and ethyl acetoacetates at low temperatures (−5 °C) and as both *cis*- and *trans*-$(NO)_2$ at room temperature. It also appears that once formed the diazeniumdiolate substituent prefers the cis geometry, and it does not undergo N=N rotation to form the anti-isomer. In contrast, the C=C double bond involving the enolate and diazeniumdiolate-substituted carbons exhibit rotation resulting in two tautomers in solution. The products are explosive due to the presence of the N_2O_2 grouping.

■ EXPERIMENTAL SECTION

Caution! Although we did not experience any explosions in the course of this research, we recommend great caution. All products may be explosive and must be manipulated behind splash shields. TGA/DSC measurements must be carried out with less than 2 mg samples to avoid damage to the instrument.

Reagents were purchased from commercial vendors and used as received. The reactions with nitric oxide were carried out using a nitric oxide reactor described previously.[12] The removal of solvents is achieved using a rotary evaporator. All products from reactions with nitric oxide were isolated as solids and dried in a vacuum oven at room temperature overnight. The UV−vis spectra were measured in water or 0.1 N aq KOH or aq LiOH or aq NaOH or aq NMe_4OH solutions. The NMR spectra were measured in either D_2O or 0.1 N KOD/D_2O or 0.1 N $NaOD/D_2O$ on a 600 MHz NMR spectrometer. The D_2O solutions contained DSS-d_6 (0.1% w/v) as internal calibration standards. Carbon chemical shift assignments, where possible, were made by measuring their proton coupled spectra, direct ^{13}C, which are included in the Supporting Information. The IR spectra were measured as powder on an FTIR instrument equipped with an ATR. Only strong IR bands are listed here. Decomposition of some of the products in aqueous media was followed by measuring the IR spectra for the gases released using a gas cell.

Thermogravimetric and differential calorimetric data were measured on a TGA/DSC instrument in the 25−500 °C temperature region. These data, which include their melting/decomposition temperatures, are included in Table 2. A steady flow of nitrogen gas was maintained as reaction gas. Approximately, 1 mg of the sample was placed in partially sealed aluminum cups. Melting point data are given in Table 2.

Potassium Acetylsydnonate *N*-Oxide (K1). A solution of KOH (85% w/w, 6.6 g, 0.100 mol) in methanol (100 mL) taken in a glass pressure bottle was cooled in an ice−salt bath for 30 min and treated with methyl acetoacetate (5.805 g, 0.05 mol). The colorless cloudy mixture was degassed by applying reduced pressure (−20 psi) and filling with N_2 gas six times with stirring. Then the ice−salt bath was removed, and the reaction mixture was allowed to warm to room temperature (23 °C). The clear pale yellow solution was pressurized with nitric oxide to 38 psi (2.7 atm). The solution turned yellow as the reaction progressed. The solution was repeatedly pressurized with nitric oxide. Rapid absorption occurred in the first 2 h, but the reaction mixture was stirred overnight while maintaining a nitric oxide pressure of at least 30 psi. The reaction mixture was cooled and degassed as described above, and the precipitated pale yellow powder was filtered and washed with cold methanol (10 mL).

The combined filtrate was rotary evaporated to a small volume (ca. 20 mL) and cooled in an ice bath for 1 h. The microcrystalline solid formed was filtered and washed with cold methanol (10 mL). The solids were combined and dried under reduced pressure at room temperature overnight. The dried solid (6.75 g) was recrystallized from 0.1 N aq KOH (50 mL) by slow evaporation. The first crop of crystals formed after 3 d was filtered, washed with methanol/water (50:50) solvent mixture (10 mL) and methanol successively, and dried. Yield: 1.650 g (18%). IR ($\mathrm{cm^{-1}}$): 1723 s ($\nu_{\mathrm{C=O}}$, $\mathrm{CH_3CO}$), 1631 s ($\nu_{\mathrm{C=O}}$, $\mathrm{CO_2}$), 1448 s, 1376 s, 1355 s, 1202 ($\nu_{\mathrm{C-O}}$, $\mathrm{CO_2}$). ^{1}H NMR (600 MHz, D_2O): δ 2.42 (s). ^{13}C NMR (151 MHz, D_2O): δ 191.7 (q, ^2J = −6.1 Hz), 171.0, 106.9, 29.7 (q, J = 128.8 Hz). Anal. Calcd for $C_4H_3N_2O_4K$: C, 26.37; H, 1.66; N, 15.38. Found: C, 26.28; H, 1.68; N, 15.14. $\lambda_{\max}$ (ε) in water: 206 nm (9066 $\mathrm{M^{-1}\,cm^{-1}}$), 239 nm (10844 $\mathrm{M^{-1}\,cm^{-1}}$), 290 nm (10,931 $\mathrm{M^{-1}cm^{-1}}$). From the filtrate on further standing, a mixture of crystals of **$K_2$2·H_2O**, **$K_2$3** and potassium oxalate formed. **$K_2$2·H_2O** is more readily synthesized from **$K_2$3** (see the following discussion).

Potassium Methyl 2-Butenoate-2-diazeniumdiolate-3-hydroxylate ($K_2$3). Product **$K_2$3** was isolated when the above reaction was carried out with KOH (85% w/w, 6.6 g, 0.100 mol) and methyl acetoacetate (5.805 g, 0.05 mol) in methanol (100 mL) as described above for **K1** but at −5 °C in an ice−salt bath. The reaction was stopped after 4 h as there was no significant absorption of nitric oxide after 4 h, and the precipitate formed was filtered, washed with ice-cold methanol (10 mL), and dried. The dried product was further washed with methanol (30 mL) by stirring at room temperature for 30 min. The undissolved solid was filtered and dried. Yield: 7.210 g (57%). IR ($\mathrm{cm^{-1}}$): 1645 s ($\nu_{\mathrm{C=O}}$, $\mathrm{CO_2Me}$), 1500 s, 1342 s ($\nu_{\mathrm{N=N}}$), 1310 s, 1242 ($\nu_{\mathrm{C-O}}$, $\mathrm{CO_2Me}$). ^{1}H NMR (600 MHz, D_2O): δ 3.61 (s, 1.86H), 3.60 (s, 1.14H), 2.28 (s, 1.14H), 1.77 (s, 1.86H). ^{13}C NMR (151 MHz, D_2O): δ 188.0, 189.5, 171.5, 169.6, 113.6, 113.3, 53.4 (q, ^1J = 147.1 Hz), 53.2 (q, ^1J = 147.1 Hz), 27.5 (q, ^1J = 127.6 Hz), 26.2 (q, ^1J = 127.6 Hz). UV−vis in 0.1 N aq KOH, $\lambda_{\max}$ (ε): 263 nm (21669 $\mathrm{M^{-1}\,cm^{-1}}$). Anal. Calcd for $C_5H_6N_2O_5K_2$: C, 23.80; H, 2.40; N, 11.10. Found: C, 23.76; H, 2.42; N, 10.88.

Sodium Methyl 2-Butenoate-2-diazeniumdiolate-3-hydroxylate ($Na_2$3). The product was synthesized from NaOH (97% w/w, 4.124 g, 0.100 mol) and methyl acetoacetate (5.805 g, 0.05 mol) in methanol (100 mL) and nitric oxide as described above for **$K_2$3**. Yield: 7.560 g (69%). IR ($\mathrm{cm^{-1}}$): 1642 s ($\nu_{\mathrm{C=O}}$, $\mathrm{CO_2Me}$), 1497 s, 1355 m, 1331 s, 1223 ($\nu_{\mathrm{C-O}}$, $\mathrm{CO_2Me}$). ^{1}H NMR (600 MHz, D_2O): δ 3.61 (s, 1.86H), 3.60 (s, 1.14H), 2.28 (s, 1.16H), 1.77 (s, 1.84H). ^{13}C NMR (151 MHz, D_2O): δ 188.0, 187.6, 171.5, 169.6, 113.6, 113.3, 53.4 (q, ^1J = 146.1) δ 53.2 (q,^1J = 146.1 Hz), 27.5 (q, ^1J = 127.7 Hz), 26.1 (q, ^1J = 127.7 Hz). $\lambda_{\max}$ (ε) in 0.1 N aq NaOH: 265 nm (22129 $\mathrm{M^{-1}\,cm^{-1}}$). Anal. Calcd for $C_5H_6N_2O_5Na_2$: C, 27.29; H, 2.75; N, 12.73. Found: C, 26.65; H, 2.67; N, 12.58.

Lithium Methyl 2-Butenoate-2-diazeniumdiolate-3-hydroxylate ($Li_2$3·$^2/_3$MeOH·$^1/_3$$H_2O$). LiOH·$H_2O$ (4.2 g, 0.100 mol) was dissolved in boiling methanol (100 mL). The solution was cooled to room temperature and treated with methyl acetoacetate (5.805 g, 0.05 mol). Subsequent steps were carried out as described above for **$K_2$3** except for the following modification. After the filtration of the precipitated white powder, the filtrate was rotary evaporated to ca. 30 mL and the cloudy solution cooled in an ice bath for 1 h. The microcrystalline product formed was filtered, mixed with the first crop, and dried. The dried product was washed with methanol (30 mL), filtered and dried. The product is characterized as **$Li_2$3·$^2/_3$MeOH·$^1/_3$$H_2O$** on the basis of elemental analysis and NMR data. Yield: 8.120 g (75%). IR ($\mathrm{cm^{-1}}$): 1643 s ($\nu_{\mathrm{C=O}}$, $\mathrm{CO_2Me}$), 1461 s, 1331 m, 1254 ($\nu_{\mathrm{C-O}}$, $\mathrm{CO_2Me}$). ^{1}H NMR (600 MHz, D_2O): 3.62 (s, 1.98H) 3.60 (s, 1.02H), 3.34 (s, 2H), 2.29 (s, 1.02H), 1.79 (s, 1.98H). ^{13}C NMR (151 MHz, D_2O): δ 188.3, 188.2, 171.4, 169.9, 113.0, 112.8, 53.5 (q, ^1J = 147.2 Hz), 51.6 (q, ^1J = 142.4 Hz), 27.5 (q, ^1J = 127.7 Hz), 25.9 (^1J = 127.7 Hz). $\lambda_{\max}$ (ε) in 0.1 N aq LiOH: 263 nm (22539 $\mathrm{M^{-1}\,cm^{-1}}$). Anal. Calcd for $C_{5.67}H_{9.33}N_2O_6Li_2$: C, 31.60; H, 4.37; N, 13.01. Found: C, 31.46; H, 4.44; N, 12.88.

Tetramethylammonium Methyl 2-Butenoate-2-diazeniumdiolate-3-hydroxylate ($[NMe_4]_2$3). The product was synthesized from $NMe_4OH·5H_2O$ (7.25 g, 0.040 mol) and methyl acetoacetate (2.320 g, 0.02 mol) in methanol (100 mL) and nitric oxide as described above for **$K_2$3**. The product did not precipitate as the alkali metal salts. The reaction mixture was rotary evaporated to ca. 30 mL and treated with acetonitrile (100 mL). The cloudy solution was allowed to stand in refrigerator (5 °C) overnight when colorless crystals of the product formed. The crystals were separated by filtration. On standing further, a second crop was obtained. Single crystal X-ray diffraction data reveal that the salt is a trihydrate methanolate, whereas elemental analysis data for dried crystals is consistent as the monohydrate. Yield: 5.170 (74%). IR ($\mathrm{cm^{-1}}$): 1646 s ($\nu_{\mathrm{C=O}}$, $\mathrm{CO_2Me}$), 1524 s, 1304 m, 1213 ($\nu_{\mathrm{C-O}}$, $\mathrm{CO_2Me}$). ^{1}H NMR (600 MHz, D_2O): δ 3.61 (s, 1.90H), 3.59 (s, 1.10H), 3.17 (s, 24H), 2.28 (s, 1.10H), 1.79 (s, 1.90H). ^{13}C NMR (151 MHz, D_2O): δ 187.9, 187.3, 171.5, 169.5, 113.6, 113.4, 57.9 (q, ^1J = 145.1 Hz), 53.3 (q, ^1J = 146.7 Hz), 53.1 (q, ^1J = 146.7 Hz), 27.5 (q, ^1J = 127.3 Hz), 26.1 (q, ^1J = 127.3 Hz). $\lambda_{\max}$ (ε) in 0.1 N aq NMe_4OH: 265 nm (22379 $\mathrm{M^{-1}\,cm^{-1}}$). Anal. Calcd for $C_{13}H_{32}N_4O_6$, %: C, 45.87; H, 9.47; N, 16.46. Found: C, 45.40; H, 9.48; N, 16.18.

Potassium Ethyl 2-Butenoate-2-diazeniumdiolate-3-hydroxylate ($K_2$4). Product **$K_2$4** was isolated when the reaction was carried out with KOH (85% w/w, 6.6 g, 0.100 mol) and ethylacetoacetate (6.5 g, 0.05 mol) in ethanol (100 mL) as described above for **$K_2$3**. The precipitate formed was filtered, washed with ice-cold methanol (10 mL) and dried. The dried product was further washed with methanol (30 mL) by stirring at room temperature for 30 min. The undissolved solid was filtered and dried. Yield: 8.240 g (62%). IR ($\mathrm{cm^{-1}}$): 1649 s ($\nu_{\mathrm{C=O}}$, $\mathrm{CO_2Me}$), 1501 s, 1325 s, 1310 s, 1241 ($\nu_{\mathrm{C-O}}$, $\mathrm{CO_2Et}$). ^{1}H NMR (600 MHz, 0.1 N KOD/D_2O): δ 4.08 (m, 2H), 2.28 (s, 1.33H), 1.77 (s, 1.67H), 1.21 and 1.19 (t, ^1J = 7.1, 7.0 Hz, 3H). ^{13}C NMR (151 MHz, 0.1 N KOD/D_2O): δ 188.8, 187.3, 171.2, 169.3, 114.0, 113.6, 62.4 (t, ^1J = 143.4 Hz), 62.2 (t, ^1J = 146.4 Hz), 27.5 (q, ^1J = 127.2), 26.2 (q, ^1J = 127.9), 16.6 (t, ^1J = 126.5 Hz). $\lambda_{\max}$ (ε) in 0.1 N aq KOH: 264 nm (24545 $\mathrm{M^{-1}\,cm^{-1}}$). Anal. Calcd for $C_6H_8N_2O_5K_2$: C, 27.06; H, 3.03; N, 10.52. Found: C, 26.88; H, 2.92; N, 10.27.

Sodium Ethyl 2-Butenoate-2-diazeniumdiolate-3-hydroxylate ($Na_2$4). Product **$Na_2$4** was isolated when the reaction was carried out with NaOH (97% w/w, 4.124 g, 0.100 mol) and ethyl acetoacetate (6.5 g, 0.05 mol) in methanol (100 mL) as described above for **$K_2$3**. The precipitate formed was filtered, washed with ice-cold methanol (10 mL), and dried. The dried product was further washed with methanol (30 mL) by stirring at room temperature for 30 min. The undissolved solid was filtered and dried. Yield: 9.330 g (80%). IR ($\mathrm{cm^{-1}}$): 1639 s ($\nu_{\mathrm{C=O}}$, $\mathrm{CO_2Me}$), 1493 s ($\nu_{\mathrm{C-N}}$), 1325 s ($\nu_{\mathrm{N=N}}$), 1255 ($\nu_{\mathrm{C-O}}$, $\mathrm{CO_2Et}$). ^{1}H NMR (600 MHz, 0.1 N NaOD/D_2O: δ 4.10−4.06 (m, 2H), 2.28 (s, 1.33H), 1.77 (s, 1.67H), 1.21 and 1.19 (t, J = 7.1, 7.1 Hz, 3H). ^{13}C NMR (151 MHz, 0.1 N NaOD/D_2O): δ 188.9, 187.4, 171.2, 169.3, 114.0, 113.6, 62.5 (t, ^1J = 146.3 Hz), 62.3 (t, ^1J = 148.3 Hz), 27.5 (q, ^1J = 127.7 Hz), δ 26.2 (q, ^1J = 127.4 Hz), δ 16.64 (q, ^1J = 127.1 Hz). $\lambda_{\max}$ (ε) in 0.1 N aq NaOH: 263 nm (23341 $\mathrm{M^{-1}\,cm^{-1}}$). Anal. Calcd for $C_6H_8N_2O_5Na_2$, %: C, 30.78; H, 3.44; N, 11.97. Found: C, 30.86; H, 3.56; N, 11.73.

Potassium Acetatediazeniumdiolate ($K_2$2). Salt **$K_2$3** (2.532 g, 0.010 mol) was dissolved in 0.5 N aq KOH (50 mL) and the solution was allowed to evaporate slowly in a fume hood over 5 d. Colorless needles of **K1** formed after 2 d (0.250 g) were filtered off, and the filtrate allowed to stand further when large colorless crystals formed.

The crystals were filtered and washed with methanol/water (50:50) solvent mixture (10 mL) and methanol, and dried. Yield: 1.630 g (76%). IR (cm^{-1}): 1605 s ($\nu_{C=O}$, CO_2^-), 1379 s, 1306 s, 1253 (ν_{C-O}, CO_2^-). ^1H NMR (600 MHz, D_2O): δ 4.59 (s). ^{13}C NMR (151 MHz, D_2O): δ 175.9 (t, ^2J = 5.0 Hz), 65.1 (t, ^1J = 142.2 Hz). λ_{max} (ε) in water,: 249 nm (2207 M^{-1} cm^{-1}). Anal. Calcd for $C_2H_4N_2O_5K_2$: C, 11.21; H, 1.88; N, 13.07. Found: C, 11.16; H, 1.86; N, 12.94.

Decomposition of $K_2$3. About 0.1 g of **$K_2$3** taken in a 25 mL round-bottom flask was dissolved in 10 mL of water. The flask was secured with a septum and cooled in an ice bath. The flask and an IR gas cell were connected using a cannula, and the gas cell was vented through a mineral gas bubbler. The solution and the gas cell were thoroughly degassed by passing N_2 gas over a period of 30 min as the solution was cooled. Subsequently, the solution was slowly heated to ca. 80 °C and the bubbling of N_2 stopped. At 60 °C gas bubbles began to form. After the released gas was allowed to pass through the gas cell for 2 min, the cell was disconnected and an IR spectrum was measured. The spectrum consisted of intense absorptions at 2236, 2203, 1297, and 1272 cm^{-1} indicating that the gas is nitrous oxide.

X-ray Crystallography. The X-ray diffraction data were measured at 150 K on a Bruker SMART APEX II CCD area detector system equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube operated at 1.5 kW power (50 kV, 30 mA). Crystals were attached to a glass fiber using Paratone N oil. The detector was placed at a distance of 5.13 cm from the crystal during the data collection. The structures have been deposited with the Cambridge Crystallographic Data Center under the deposition nos. 882051, 882052, and 882053 for **1**, **2**, and **3**.

A series of narrow frames of data were collected with a scan width of 0.5° in ω or φ and an exposure time of 10 s per frame. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm.[21] The data were corrected for absorption effects by the multiscan method (SADABS). Crystallographic data collection parameters and refinement data are deposited as Supporting Information. The structures were solved by direct methods using the Bruker SHELXTL (V. 6.14) software package.[30] All non-hydrogen atoms were located in successive Fourier maps and refined anisotropically. The hydrogen atoms were also located on the difference Fourier maps and refined isotropically.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data (CIF) for **K1**, **$K_2$2·H_2O**, and **[N-(Me)$_3$]$_2$3·3H_2O·MeOH**. IR spectra (Figures S1−S8), ^1H and ^{13}C NMR spectra (Figures S9−S32), and TGA/DSC profiles (Figures S33−S40) for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

N.A. gratefully acknowledges support from the NASA-funded Wyoming Space Grant Consortium (NNG05G165H), and D.S.B. and I.P. acknowledge support from NSERC and the CRC.

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