Synthesis of Diazeniumdiolates from the Reactions of Nitric Oxide with Enolates

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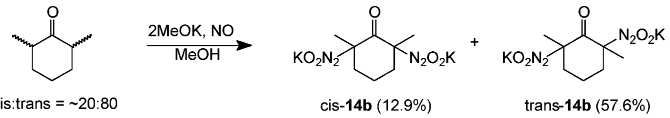
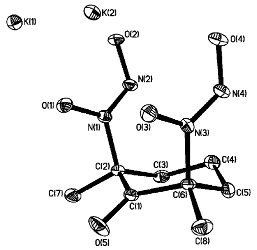


cis:trans = ~20:80

cis-**14b** (12.9%)

trans-**14b** (57.6%)



Reactions of nitric oxide with enolates derived from aliphatic methyl ketones containing α-methylene or α-methine groups and with enolates derived from α,α′-dimethylene or α,α′-dimethine ketones yield mono- or bis(diazeniumdiolate) products. Diazeniumdiolation occurs in the following order: α-methine > α-methylene > α-methyl. The amount of the base used alters the extent of diazeniumdiolation and the course of the reaction. Mono- and bis(diazeniumdiolate)-substituted methyl ketones are cleaved in the presence of excess base before and after the subsequent diazeniumdiolation of the α-methyl group. Similar to the trihalogenated methyl groups in the base-assisted halogenation reactions of methyl ketones, the bis(diazeniumdiolate)-substituted α-methylene and α-methyl groups act as leaving groups in the presence of excess base. The reaction of nitric oxide with a (∼20:80, cis/trans) mixture of 2,6-cyclohexananone yields the cis and trans isomers of 2,6-dimethylcyclohexanone-2,6-bis(diazeniumdiolate) in 12.9% and 57.6% yield. Single-crystal X-ray diffraction data determined for potassium *cis*-2,6-dimethylcyclohexanone-2,6-bis(diazeniumdiolate), *cis*-**14b**, reveal that the $N_2O_2^-$ substituent is planar with considerable delocalization of a double bond over the anionic four-atom group. Except for one of the diazeniumdiolate products, namely, potassium propanoate 2,2-bis(diazeniumdiolate), **8b**, all are stable in neutral and basic aqueous media. Compound **8b** slowly decomposes in neutral aqueous solution releasing nitrous oxide and nitric oxide gases but is stable in basic aqueous media. Differential scanning calorimetry data measured for the diazeniumdiolate products indicate that they decompose exothermally with most of them undergoing explosive decomposition at moderately high temperatures (181−274 °C).

Introduction

Although in many of its reactions nitric oxide behaves as monomeric oxidant or reductant, it undergoes a kinetically important pressure- and temperature-dependent dimerization. The electrophilic dimer is significant in that it has been structurally[1,2] and spectroscopically[3] characterized at low temperatures, and it is kinetically important in NO's reactions with

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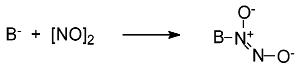
bromine, chlorine, oxygen, and hydrogen.[4] Many nucleophiles add bimolecularly to two NO's to give new sulfur, oxygen, and nitrogen bonds to one of the nitrogens of the nitric oxide dimer, with the resulting adduct being a diazeniumdiolate ($B-N^+(O^-)=N-O^-$) (eq 1).[5]



$$B^- + [NO]_2 \longrightarrow B-N^+(O^-)=N-O^- \qquad (1)$$

Invariably, the products adapt the *Z*-geometry as shown above, contrary to theoretical results which predict the products could also exist in the *E* geometry.[6] A more recent study has shown that the *Z* to *E* conversion can be accomplished in the case of the O^2-2-bromoethyl ester of a primary amine–diazeniumdiolate by trapping the *E*-isomer by cyclization.[7]

In general, N-bound diazeniumdiolates decompose in aqueous media releasing nitric oxide and are useful as nitric oxide donors in biomedical research.[8] Underscoring their importance, considerable recent attention is directed toward the synthesis of this class of nitric oxide donors. Modified polymers and nanoparticles that are capable of releasing nitric oxide at varying rates under physiological conditions have also been developed, and some of them have proved valuable building blocks in the preparation of thromboresistant sensors.[9]

On the basis of their thermal decomposition behavior, C-diazeniumdiolate compounds can be considered as high energy density materials (HEDM). Similar to the traditional explosives such as TNT, RDX, and HMX,[10] diazeniumdiolate-substituted compounds also derive energy from the oxidation of the carbon backbone during their decompositon. We attribute the exothermal decomposition behavior of the diazeniumdiolate compounds to the similarity of the diazeniumdiolate group to the nitro substituents in the explosives. We also believe suitably modified C-diazeniumdiolates may prove useful propellants as their thermal properties can be altered by the choice of nitrogen-rich cations such as hydrazinium, guanidium etc. In addition, the diazeniumdiolate salts can be expected to have lower vapor pressure because of their ionic nature, which is also an important requirement for a propellant.

Recently, we have shown that C-bound tris(diazeniumdiolates) synthesized from acetone, pinacolone, acetophenone or 1,3-biacetylbicyclo[1.1.1]pentane, and that the tris(diazeniumdiolate) species are both nitric oxide donors and decompose exothermally.[11,12]

Reactions of nitric oxide with carbanions were originally reported by Traube more than a century ago[13] and have been extended to a series of carbanions derived from ketones by Yandovskii et al. several decades later.[14–16] Traube's characterization of products, performed with techniques available in the 1890s, need careful scrutiny. Nevertheless, the phenomenological core of his results remains remarkably accurate. In contrast, many subsequent researchers have not isolated the diazeniumdiolate salts as formed but have converted them into their corresponding O-alkyl esters ($-N^+(O^-)=N-OR$) and have characterized the alkylated products. The reported yields of the alkyl esters are low, leaving open the question of possible formation of more than one diazeniumdiolate salt in the reactions.

To understand the nitric oxide reaction chemistry with carbanions and to synthesize potentially HEDM compounds, we set out to study the reactions of nitric oxide with carbanions derived from ketones containing primary, secondary, and tertiary α-protons. We observe that the reactions with ketones follow the pathway of common nucleophilic addition reactions. The diazeniumdiolate salts formed can be purified under appropriate conditions as will be described. Here, we report the reactions of nitric oxide with 2-butanone, 2-pentanone, 3-pentanone, 3-methyl-2-butanone, 3-methyl-2-pentanone, and 2,6-dimethylcyclohexanone in the presence of alkali methoxides and the characterization of their products by spectroscopic data, elemental analysis, and thermal analysis.

Results and Discussion

The reactions of nitric oxide with the ketones were carried out in a glass high-pressure reaction vessel with strict exclusion of oxygen and nitrogen dioxide. The presence of oxygen in the reaction mixture leads to the formation of several oxidation products rendering subsequent purification cumbersome or impossible. We have also observed that the reactions of the ketones with ca. 2.5 atm of nitric oxide progress more rapidly at lower temperatures (ca. −20 °C) than at room temperature. The solvent for these reactions is ideally methanol as it reacts comparatively slowly or not at all with nitric oxide under these conditions.

In a typical reaction, 1 equiv of the substrate is added to a freshly prepared solution of 1–5 equiv of sodium or potassium metal dissolved in absolute methanol. The solution is cooled in an ice–salt bath, degassed, and pressurized with nitric oxide to 2–2.5 atm with vigorous stirring at ca. −20 °C. The reaction ensues with a rapid absorption of nitric oxide in the first 6 h and subsides after 12 h. The reaction mixture is allowed to warm

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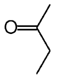
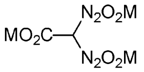
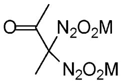
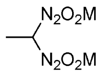
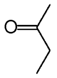
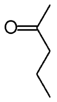
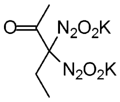
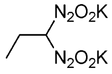
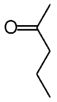
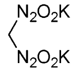
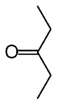
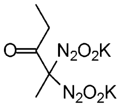
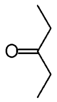
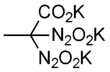
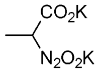
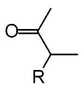
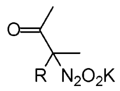
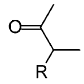
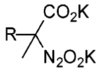
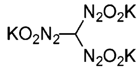
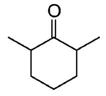
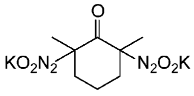
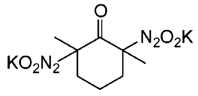
TABLE 1. Reactions of Nitric Oxide

entry	substrate	reaction conditions	products (yield%)		
1		2MeOM, MeOH, NO a: M = Na; b: M = K	 **1a** (2.8%) **1b** (2.0%)	 **2a** (41.2%) **2b** (61.0%)	 **3a** (~3%) **3b** (~2%)
2		5MeOM, MeOH, NO	**3a** (66.0%) **3b** (70.5%)		
3		2MeOK, MeOH, NO	 **4b** (48.2%)	 **5b** (18.3%)	**1b** (10.3%)
4		5MeOK, MeOH, NO	 **6b** (~17%)	**5b** (71.2%)	**1b** (10.2%)
5		2MeOK, MeOH, NO	 **7b** (8.3%)	other uncharacterized products	
6		4MeOK, MeOH, NO	 **8b** (24.9%)	 **9b** (8.6%)	**3b** (57.4%)
7		1MeOK, MeOH, NO	 **10b** (70.1%, R = Me) **11b** (61.1%, R = Et)		
8		4MeOK, MeOH, NO	 **12b** (63.5%, R = Me) **13b** (57.2%, R = Et)	**6b** (4%)	 (30%)
9	 cis:trans = ~20:80	2MeOK, MeOH, NO	 cis-**14b** (12.9%)	 trans-**14b** (57.6%)	

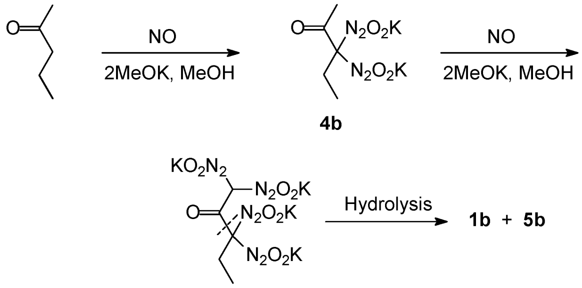
to room temperature after the first 6 h and stirred under pressurized nitric oxide (2−2.5 atm) until no significant gas absorption is observed (about 48 h) to ensure the completion of the reaction. The precipitated product, if any, is purified by recrystallization from water− or aqueous alkali hydroxide−methanol/ethanol solvent mixtures. In some reactions, most of the products remain in solution and are separated by the rotary evaporation of the filtrate and recrystallization. Table 1 summarizes the reactions studied and includes structures of the products and their numbering. In general, the isolated yields of products from the reactions with potassium methoxide are higher. There may be two reasons for this: first, the enolates prepared from potassium methoxide under these conditions are clear solutions, whereas those derived from sodium methoxide are cloudy suspensions; second, the potassium products may have less solubility and so the final recrystallization yields improve. In the former, the difference in yields may reflect different solution chemistry during the reaction, and in the latter, they may reflect the outcome of the purification. We favor the latter since these reactions are often allowed to run for long periods of time and until no additional NO is absorbed. As will be discussed below, some of the reactions also form the alkali salts of acetate. Since the potassium salts of the carboxylates are more soluble in methanol than the sodium salts, the diazeniumdiolated products are more readily freed from potassium acetate.

In all of the reactions, the diazeniumdiolate products are isolated as alkali metal salts and no esterification is observed.

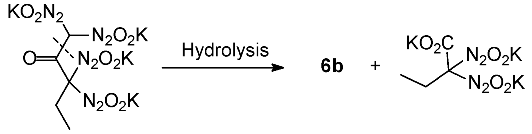
Although the reactions were carried out under strictly anaerobic conditions, no such efforts were taken to exclude small amounts of water from the reaction medium. We attribute the presence of water in the reaction medium and the weakly acidic nature of the acid form of the diazeniumdiolate substituents to the absence of esterification of the products.

The reactions of nitric oxide with 2-butanone and 2-pentanone, entries 1 and 3 of Table 1, in the presence of 2 equiv of potassium methoxide yield products containing two diazeniumdiolate substituents at the α-methylene carbon, namely, potassium 2-butanone-3,3-bis(diazeniumdiolate) (**2b**) and potassium 2-pentanone-3,3-bis(diazeniumdiolate) (**4b**), respectively, as the major products. The hydrolytically cleaved byproducts potassium acetate-2,2-bis(diazeniumdiolate) (**1b**) and potassium ethane-1,1-bis(diazeniumdiolate) (**3b**) are isolated from the 2-butanone reaction and **1b** and potassium propane-1,1-bis(diazeniumdiolate) (**5b**) are isolated from the 2-pentanone reaction in lower yields. The corresponding reactions with sodium methoxide yield the analogous sodium salts. From the nature of the products formed and their yields, it is clear that the α-methylene group in the two ketones are more readily substituted in comparison to the α-methyl groups. Compounds **2a**, **2b**, and **4b** are quite stable toward hydrolytic decomposition in neutral aqueous media, and do not undergo hydrolytic cleavage. The ^{1}H NMR spectra measured for **2a**, **2b**, and **4b** in D_2O exhibit exchange of the peak due to the acetyl-methyl group indicating the acidic nature of these protons.

The reactions of nitric oxide with 2-butanone and 2-pentanone, entries 2 and 4 of Table 1, in the presence of 5 equiv of potassium methoxides yield the hydrolytically cleaved products **3b** and **5b**, respectively. ^{1}H NMR spectra measured for the crude product obtained from the reaction of 2-butanone also reveal the presence of small amounts of **1b** (~1%) and **6b** (~1%) indicating the diazeniumdiolation of the α-methyl group and subsequent hydrolytic cleavage of the tetrakisdiazeniumdiolated 2-butanone. Similarly, a considerable proportion of the crude product from the 2-pentanone reaction also constitutes **1b** and **6b**, in 10% and 17%, respectively. The product distribution in the 2-butanone reaction suggests that in the presence of more than two equiv of the base, the excess base accelerates the hydrolytic cleavage of the initially formed bis(diazeneniumdiolates), to form **3b** instead of assisting successive diazeniumdiolation of the α-methyl group. In the reaction of 2-pentanone, however, significant diazeniumdiolation of **4b** occurs at the α-methyl group (10.3% vs 2%). Since there is no significant difference with respect to electronic and steric effects, we speculate that the higher solubility of **4b** in the reaction medium must be responsible for the discrepancy. Compound **4b**, once formed, may not be immediately precipitated unlike **2b**, and therefore, would undergo subsequent diazeniumdiolation at the α-methyl group.



(2)



(3)

The tetrakisdiazeniumdiolated product, potassium 2-pentanone-1,1,3,3-tetrakis(diazeniumdiolate) (eq 2), formed as intermediate, however, must have undergone hydrolytic cleavage at the carbonyl group as shown in eq 2 to form **1b** and **5b**. The isolation of **6b** from the reaction indicates that the hydrolytic cleavage also occurs on the methyl side of the carbonyl group (eq 3). But we were unable to isolate the corresponding carboxylate, namely, potassium butanoate-2,2-bis(diazeniumdiolate). We speculate that this product could be unstable in aqueous media similar to the analogous propanoate derivative **8b** (see later) and would have decomposed precluding its isolation. On the basis of the higher percentage of isolated **5b**, we propose that the hydrolytic cleavage along the propyl side of the carbonyl group (eq 2) is preferred for unknown reasons. The preferential cleavage of the propyl−carbonyl bond is also reflected in the formation of **5b** in the reaction with 2 equiv of the base (entry 3).

The reaction of nitric oxide with 2-butanone is in agreement with Traube's original report of the reaction in the presence of an unspecified amount of sodium methoxide. Traube[13] has speculated that the hygroscopic, amorphous, and free-flowing powder obtained from the reaction could be **2a**, even though his attempts to purify the product by recrystallization have led to the formation of **3a**.

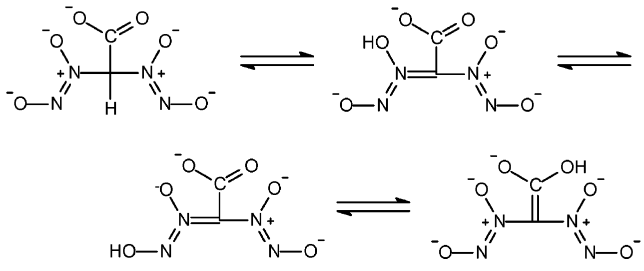
On the basis of the products isolated from the reactions of both 2-butanone and 2-pentanone, we conclude that the use of more than 2 equiv of the bases invariably leads to the hydrolytically cleaved products **3a**, **3b**, **5a**, and **5b** together with **1a**, **1b**, and **6b** and the alkali acetates. The preferential cleavage of **2a**, **2b**, and **4b** over complete diazeniumdiolation of the ketones is consistent with the base-assisted reaction of nitric oxide with acetone.[11]

Reactions of 3-pentanone and 4-heptanone, which contain two chemically identical α-methylene groups, are more complex. The reaction of nitric oxide with 3-pentanone in the presence of 2 equiv of potassium methoxide, entry 5 in Table 1, yields potassium 3-pentanone-2,2-bis(diazeniumdiolate) (**7b**) in low yield (8.3%). The precipitate formed in large amount, containing the bulk of the products, undergoes slow decomposition in both neutral and basic aqueous media and could not be characterized satisfactorily. We speculate that the product is probably potassium 3-pentanone-2,2,4,4-tetrakis(diazeniumdiolate). It is likely that the two α-methylene groups in the symmetric 3-pentanone undergo diazeniumdiolation forming the tetrakis(diazeniumdiolate), which is unstable in aqueous media undergoing hydrolytic cleavage at the carbonyl group. Both neutral and basic solutions of the precipitate decompose while continuously releasing a gas on standing at room temperature. IR characterization of the gas reveals that the gas released is a mixture of nitrous oxide and nitric oxide. We have previously observed a similar decomposition behavior with two potassium methanetris(diazeniumdiolate) salts.[12]

Similar to **2a**, **2b**, and **4b**, compound **7b** which also contains a carbonyl group is quite stable toward hydrolytic cleavage at the carbonyl group in neutral aqueous media. However, the ^{1}H NMR spectrum measured for **7b** in D_2O exhibits exchange of the peak due to the α-methylene group indicating the acidic nature of these protons as seen in **2a**, **2b**, and **4b**. The observed stability of the carbonyl group-containing diazeniumdiolates in neutral media in contrast to their hydrolysis in basic media suggests that basicity of the medium is the requirement for the hydrolysis.

The reaction of nitric oxide with 3-pentanone in the presence of 4 equiv of potassium methoxide, entry 6 in Table 1, also yields a precipitate which undergoes slow decomposition in aqueous media as evidenced by the release of nitrous oxide and nitric oxide. The precipitate is washed with boiling methanol and then recrystallized from 0.1 N aqueous potassium hydroxide, as microcrystals of potassium propanoate-2,2-bis(diazeniumdiolate), **8b**, in 24.9% yield. From the methanol washings and the filtrate of the reaction mixture, potassium propanoate-2-diazeniumdiolate **9b** and **3b** are separated in 8.6% and 57.4%, respectively, as described in the Experimental Section. The formation of **8b** and **9b** indicates that both α-methylene groups undergo diazeniumdiolation with the formation of the tris- and tetrakisdiazeniumdiolates, $CH_3C(N_2O_2K)_2COCH(N_2O_2K)CH_3$ and $CH_3C(N_2O_2K)_2COC(N_2O_2K)_2CH_3$. The reactivity pattern observed is comparable to that with 4-heptanone. As will be reported elsewhere, the reaction with 4-heptanone forms potassium butanoate-2-diazeniumdiolate resulting from the hydrolysis of an unstable tetrakisdiazeniumdiolated heptanone intermediate.[17]

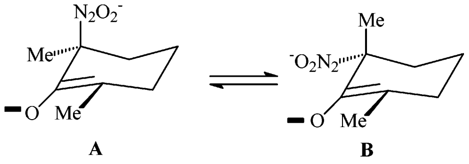
Compound **8b** undergoes slow decomposition in aqueous media at neutral pH, but is stable in slightly basic solutions. In contrast, the mono(diazeniumdiolate) **9b** and the other monocarboxylate-bis(diazeniumdiolate) **1b** are quite stable in neutral and basic aqueous media. The higher stability of **1b** could be attributed to the possible existence of two additional tautomeric structures as shown below.



The reactions of nitric oxide with 3-methyl-2-butanone and 3-methyl-2-pentanone, entry 7 in Table 1, in the presence of 1 equiv of potassium methoxide yield monodiazeniumdiolated products potassium 3-methyl-2-butanone-3-diazeniumdiolate (**10b**) and potassium 3-methyl-2-pentanone-3-diazeniumdiolate (**11b**), respectively. The reactions in the presence of 2−4 equiv, entry 8 in Table 1, of the base yield the diazeniumdiolated alkanoates, potassium iso-butanoate-2-diazeniumdiolate (**12b**) and 2-methylbutanoate-2-diazeniumdiolate (**13b**), respectively, together with **6b** and potassium methanetris(diazeniumdiolate). These reactions are again similar to those of 2-butanone and 2-pentanone in that diazeniumdiolation occurs preferentially at the α-tertiary carbon than at the more acidic α-primary carbon and in that hydrolytic cleavage of the monodiazeniumdiolated products competes with subsequent diazeniumdiolation of the α-methyl group.

The reaction of nitric oxide with a cis and trans isomeric mixture (∼20:80) of 2,6-dimethylcyclohexanone in the presence of 2 equiv of potassium methoxide, entry 9 in Table 1, proceeds smoothly yielding the *cis*- and *trans*-α,α′-bisdiazeniumdiolated products also in ratio of 20:80, without the formation of any byproducts. One of the products, namely, potassium *cis*-2,6-dimethylcyclohexanone-2,3-bis(diazeniumdiolate), *cis*-**14b**, is readily recrystallized from water as colorless crystals, and the trans isomer (*trans*-**14b)** is isolated as a highly hygroscopic white powder. The cis isomer is poorly soluble in methanol whereas the trans isomer is freely soluble in methanol. The difference in solubility allows for the facile separation of the two isomers. Both isomers are stable in neutral and basic aqueous media.

We propose that this reaction also involves the formation of the 2,6-dimethylcyclohexanone anion in the first deprotonation followed by monodiazeniumdiolation and that subsequently the second α-methine group undergoes deprotonation to form another carbanion which can also exist as the corresponding enolate. The enolate intermediate undergoes another diazeniumdiolate addition to form a mixture of *cis*- and *trans*-**14b**. Due to the proposed involvement of the enolate intermediate, one may expect a 50:50 ratio of the cis and trans isomers. The observed 20:80 ratio of the products reveals stereoselectivity in the second diazeniumdiolation and appears to be inconsistent with the mechanism. However, a precedence similar to the observed stereoselectivity is known in the literature for the 2,6-dimethylcyclohexenolate anion:[18,19] the protonation of the anion is known to form a mixture of a 92:8, cis/trans mixture of 2,6-dimethylcyclohexanone.[19] Similarly, the stereoselectivity in this reaction is most likely due to the face selectivity of the second addition of $[NO]_2$ to either the axial or equatorial $[N_2O_2^-]$ monodiazeniumdiolate enolate **A** and **B**.



Addition to the top face of **A** or to the bottom face of **B** will yield the minor isomer *cis*-**14b**. Addition to the bottom face of **A** or to the top face of **B** will yield the major isomer *trans*-**14b**. The addition of electrophiles to enolates derived from 2,6-dimethylcyclohexane are known to exhibit strong solvent and cation selectivities due to cation interaction with the enolate oxygen,[18] and this effect can be expected to be even larger for the dianion equilibrium between **A** and **B.**[19] Coordination or chelation of the potassium cation with an enolate oxygen and a diazeniumdiolate would stabilize **B**, and electrophilic addition to the less sterically encumbered top face could then account for *trans*-**14b** as the major product. While the origin of this stereoselectivity remains somewhat speculative, the two isomers are the only examples of α,α′-bis(diazeniumdiolate)-substituted ketones known to-date.

Preliminary reactions performed with cyclopentanone and cyclohexanone appear to form ring-opened bis(diazeniumdiolates), although we have not been able to purify and characterize the products.

Mechanism. In the reactions with enolates derived from ketones, nitric oxide appears to add solely to carbon. The origin of this regioselectivity, as well as the *E*/*Z* stereochemistry in

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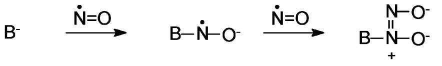
the resulting diazeniumdiolate, most likely has to do with the nature of the electrophile. Two common mechanisms for the addition are shown below in eqs 4 and 5. A recent theoretical analysis suggests that the dimer pathway is more likely.[5c] Drago et al. have favored the dimeric addition pathway to explain the formation of *N*-diazeniumdiolates in the reactions of secondary amines, since these reactions produced higher yields of diazeniumdiolates at −78 °C.[5a,b] Clearly, our results are consistent with exclusive addition to the carbon of the diazeniumdiolate. We note that addition to the oxygen is expected to give an *O*-ester of Angeli's salt, R−O−N(O)═NO⁻, a very unusual but not unprecedented species. Our preliminary observation that the current reactions progress more rapidly at −20 °C than at room temperature is also in favor of the dimeric addition of nitric oxide.



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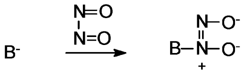

(5)

On the basis of the products isolated from the reactions of nitric oxide with the α-primary, α-secondary, and α-tertiary methyl ketones studied, we propose that diazeniumdiolation is favored in the order: α-CH > α-CH_2 > α-CH_3. The observation is consistent with the well-known ease of formation and nucleophilicity of the enolates generated from the respective α-groups in that order.[20] We propose the following mechanism for the reactions with α-methyl ketones.

The cleavage of the polydiazeniumdiolated intermediate formed in the above reactions is reminiscent of the haloform reaction,[20] in which methyl ketones undergo hydroxide-assisted decarbonylation after the halogenation of the α-methyl group. Similarly, the bis- and trisdiazeniumiumdiolated α-methyl groups and bisdiazeniumdiolated α-methylene groups also act as leaving groups in the present reactions.

Structure and Characterization. The new products are characterized by IR, NMR and UV−vis spectral data and elemental analysis. Compounds **2a**·$2H_2O$, **3b**·$2H_2O$, and *cis*-**14b** have also been characterized by single-crystal X-ray diffraction data. The crystal structures of **14b** is described here and the rest are reported elsewhere.[21]

The cyclohexanone ring in *cis*-**14b** adopts the chair conformation with the two diazeniumdiolate substituents occupying the axial sites of the 2,6-tertiary carbons as shown in Figure 1. The two diazeniumdiolate substituted carbon atoms are asymmetric. From the relative orientation of the four substituents around each of the carbon atoms, the compound is identified as the cis isomer.

The $N_2O_2^-$ groups are nearly planar and the N−N and N−O bond distances are in the narrow range 1.293(2)−1.311(2) Å (Table 2), indicating extensive charge and double bond delocalization similar to those in other structurally characterized C-diazeniumdiolates.[11,17,21−27] The two substituents are roughly parallel to each other with the dihedral angle between the mean planes passing through them being 18.13(7)°. The leaning of the two planes toward each other is perhaps due to their interaction with the cations. The potassium ions are surrounded by eight oxygen atoms of three neighboring diazeniumdiolate groups with the associated K−O distances being in the range 2.739(1)−3.079(1) Å (Table S3, Supporting Information) resulting in a three-dimensional network.

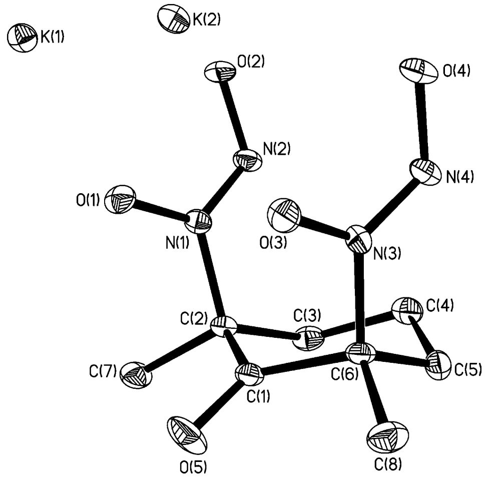

FIGURE 1. View of the anion and cations in the crystal structure of **14b**. Hydrogen atoms are omitted for clarity.

TABLE 2. Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) Associated with the Diazeniumdiolate Substituents in 14b

C(2)−N(1)	1.487(2)	N(1)−N(2)	1.295(2)
N(1)−O(1)	1.311(2)	N(2)−O(2)	1.297(2)
C(6)−N(3)	1.491(2)	N(3)−N(4)	1.293(2)
N(3)−O(3)	1.308(2)	N(4)−O(4)	1.299(2)
C(2)−N(1)−N(2)	117.79(13)	C(2)−N(1)−O(1)	117.06(13)
O(1)−N(1)−N(2)	125.13(13)	N(1)−N(2)−O(2)	113.47(13)
C(6)−N(3)−N(4)	117.89(13)	C(6)−N(3)−O(3)	116.83(13)
O(3)−N(3)−N(4)	125.27(13)	N(3)−N(4)−O(4)	113.37(13)
O(1)−N(1)−N(2)−O(2)	1.3(2)	O(3)−N(3)−N(4)−O(4)	−1.3(2)

Spectroscopic Data. The IR spectra of the diazeniumdiolate products are characterized by intense absorptions in the 1400−1100 cm^{-1} region.[11,12,25,26,28] Similar to $K_3[CH(N_2O_2)_3]$ and $[H_2NEt_2][Et_2NN_2O_2]$, the present spectra exhibit one or two strong absorption bands in the 1405−1350 cm^{-1} region attributable to the $\nu(ONNO)_{sym}$ mode vibration of the $N_2O_2^-$ group.[11,28] The spectra of the diazeniumdiolate substituted ketones **2a**·$2H_2O$, **2b**·MeOH, **4b**·$^1/_2H_2O$, **7b**, **10b**, **11b** and **14b** exhibit strong $\nu(CO_2)_{asymm}$ absorptions in the 1712−1735 cm^{-1} region. Similarly, characteristic absorptions due to the carboxylate groups are present in the spectra of carboxylates **1a**·$2H_2O$, **1b**·H_2O, **8b**·H_2O, **9b**·$^1/_2$EtOH, **12b**·$^1/_2H_2O$ and **13b**·$1^1/_2H_2O$. The $\nu(CO_2)_{sym}$ vibrations are observed in the 1649−1670 cm^{-1} region for the α,α-bis(diazeniumdiolate)-substituted carboxylates **1a**·$2H_2O$, **1b**·H_2O, and **8b**·H_2O, and those of the rest of the

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TABLE 3. DSC Data for the Diazeniumdiolate Products

compd	T_{onset}, °C	T_{max}, °C	ΔH, cal/g	total ΔH, kcal/mol
1a·$2H_2O^a$	207	218		
2a·$2H_2O^a$	194	198		
2b·CH_3OH^a	181	189		
3a·$^1/_2CH_3OH$	225	236	−189	−36.67
3b·H_2O^a	202	204		
4b·$^1/_2H_2O$	181	190	−237	−66.91
5a·H_2O	220	238	−220	−49.74
5b	245	249	−341	−82.01
7b	212	216	−1104	−74.50
8b·H_2O^b	101, 198	104, 205	−157, −301	−149.49
9b·$^1/_2EtOH^c$	274	292	−643	−150.01
10b^c	199	204	−310	−57.11
11b	206	214	−354	−70.18
12b·$^1/_2H_2O$	266	270	−155	−34.79
13b·$1^1/_2H_2O^c$	264	276	−175	−44.84
cis-**14b**^{c}	245, 280	283, 288	−214	−69.09
trans-**14b**^{b}	211, 273	223, 283	−248	−55.62

[a] Explodes, ΔH undetermined. [b] Exhibits two exotherms. [c] Also exhibits an endotherm: **9b**·$^1/_2EtOH$ at 72 °C, **10b** at 155 °C, **13b** at 104 °C and *cis*-**14b** at 72 °C.

carboxylates with just one α-diazeniumdiolate substituent are observed in the 1605−1625 cm^{-1} lower energy region.

The UV−vis spectra measured for the compounds are indicative of the number of diazeniumdiolate substituents on a single carbon atom. The spectra were measured for aqueous solutions of the compounds except for **8b**·H_2O, which undergoes slow decomposition at neutral aqueous solutions. The spectrum for **8b**·H_2O was measured in 0.1 N aq. KOH. The spectra reveal an absorption due to the $\pi-\pi^*$ transition expected for the $-N_2O_2^-$ group, and those of diazeniumdiolate substituted ketones also exhibit a shoulder at ~235 nm due to the $\pi-\pi^*$ transitions associated with the keto groups. Monodiazeniumdiolates exhibit an absorption in the 246−251 nm region, and bis(diazeniumdiolates) excluding the cis and trans isomers of **14b** exhibit an absorption in the 255−259 nm region; the intensities of the bands are approximately twice those of the bands of the monodiazeniumdiolates.

The ^1H and ^{13}C NMR spectra are illustrative of the electronegative inductive influence of the diazeniumdiolate substituents as has been observed previously.[11] Consistent with the trend, the ^1H and ^{13}C signals due to the methine groups of the α,α-bis(diazeniumdiolates) are shifted downfield in comparison to those of the mono(diazeniumdiolates).

Thermal Properties. Differential scanning calorimetry data obtained for the new compounds reveal the explosive nature of the compounds (Table 3). Most of them undergo rapid exothermic decomposition in the 181−290 °C region. In comparison to the bis(diazeniumdiolate) substituted compounds, the mono(diazeniumdiolate) compounds decompose less violently. The thermal decomposition behavior of the present series of compounds is consistent with that observed for other diazeniumdiolate substituted compounds.[11,12,25,26] The DSC data further demonstrates the thermal instability and high energy content of the $-N_2O_2^-$ substituents.

Conclusion. With the complicated reactivity pattern described in this paper, it is not surprising that nitric oxide's reactions with ketones have been largely unexplored. The addition of nitric oxide to the enolates generated from the ketones contained in Table 1 suggests Lewis acid/base chemistry. Although specific rules to delineate which products will form under a specific set of conditions is difficult to formulate at this point, it is clear that there are specific substrate preferences for the observed diazeniumdiolations which follow the trend α-CH > α-CH_2 > α-CH_3 for the ketones. In general, the products described in the paper are stable white crystalline salts whose chemistry will be the subject of future studies.

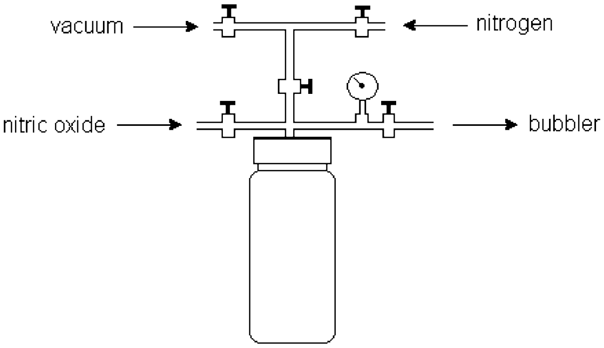

FIGURE 2. Nitric oxide reactor.

Experimental Section

General Methods. The reagents and solvents used were reagent grade and used as supplied. Nitric oxide gas was obtained from Scott Specialty Gases and was purified by passing through a column packed with sodium hydroxide pellets.

Reactions with Nitric Oxide. Reactions of the ketones and alcohols with nitric oxide were performed using a slightly modified high-pressure reaction apparatus described in a previous report.[11] An Andrews Glass Co. Lab Crest high-pressure glass reaction bottle was fitted to the needle valve adapter of a gas manifold using a coupling assembly as shown in Figure 2. Throughout the reactor stainless steel couplings, adapters, and fittings were used, and seals were maintained with Viton O-rings. Pressure lines were established with $^1/_4$ in. Teflon tubing.

General Procedure for the Nitric Oxide Reactions. In a typical reaction, a solution of the appropriate alkali methoxide is prepared by slowly dissolving pieces of the alkali metal in absolute methanol (150 mL) under the blanket of nitrogen gas in a high-pressure reaction bottle. The substrate ketone is added to the solution, and the reaction bottle is attached to the gas manifold. The mixture is cooled in an ice−salt bath for 30 min and applied reduced pressure until the solution begins to boil. At this point, the reaction bottle is filled with nitrogen gas. The procedure is repeated three times, after which time the bottle is applied reduced pressure once again, and finally nitric oxide is admitted until the pressure reaches 2.5 atm. The gas inlet is closed and the reaction mixture is allowed to stand at the ice−salt bath temperature for 6 h with stirring. In the first 6 h, a rapid absorption of nitric oxide is observed and the nitric oxide gas inlet is frequently opened to maintain the pressure at 2.5 atm. After 6 h the reaction mixture is allowed to warm to room temperature and to continue to react with nitric oxide for 2 d. The excess nitric oxide is removed by opening the outlet to the bubbler and the reaction mixture is flushed with nitrogen gas for several minutes to remove any residual nitric oxide. In some of the reactions, the precipitate formed is filtered and dried under reduced pressure. In the rest, the cloudy reaction mixtures are rotary evaporated to a viscous solid. The products are purified by fractional crystallization of the precipitates from water/methanol/ethanol solvent mixtures. The crystallized products are dried at reduced pressure at room temperature overnight and stored in a desiccator since some of them absorb moisture over a period of several weeks.

Caution! The products described in this paper are explosive. Therefore, the crude product mixtures and recrystallized products must be handled in small amounts behind efficient shields.

Infrared spectra were obtained as KBr disks with an FTIR spectrophotometer. Proton and ^{13}C NMR spectra were measured in D_2O solvent containing DSS (0.1% w/v) as the internal standard on a 400 MHz NMR instrument. *J* values are given in Hz. UV−vis spectra were measured in water or in 0.1 N aq KOH solutions. Thermograms were obtained using a differential scanning calorimeter equipped with a cooling can for cooling measurements. Approximately 2 mg of the sample was placed in aluminum sample cups and crimped with a cover. The DSC runs were performed under a steady flow of argon gas and at a heating rate of 10 °C per min in the temperature range 25−500 °C.

Reaction of Nitric Oxide with 2-Butanone and 2 equiv of Sodium Methoxide (Entry 1, Table 1) Forming 2a·2H$_2$O. The reaction of 2-butanone (7.21 g, 0.1 mol) with nitric oxide in the presence of sodium methoxide (0.2 mol) in methanol (150 mL) was carried out by the general procedure. The precipitate (14.2 g) formed was dissolved in water (100 mL), and the solution was filtered and treated with methanol (10 mL). The solution was allowed to stand at 5 °C for 3 d. The large colorless crystals of sodium acetate 1,1-bis(diazeniumdiolate) dihydrate, **1a**·2H$_2$O,[11] formed were filtered and dried at room temperature. Yield: 0.8 g (2.8%) assuming 1 equiv of **1a** is formed from 1 equiv of the ketone. The filtrate was treated with methanol (50 mL), and the cloudy solution was allowed to stand at 5 °C overnight. The colorless crystals of **2a**·2H$_2$O formed were filtered and dried at room temperature. Yield: 11.2 g (41.2%). Anal. Calcd for $C_4H_{10}N_4O_7Na_2$: C, 17.64; H, 3.70; N, 20.59. Found: C, 17.63; H, 3.76; N, 20.79. IR (cm^{-1}): 3506 s, 3330−3270 b, 1729 s, 1670 w, 1457 m, 1420 w, 1360 s, 1341 s, 1293 s, 1220 s, 1199 s, 1121 s, 1101 m, 1006 w, 978 w, 944 s, 844 w, 771 s, 706 m, 630 m, 609 m, 680 m, 564 m, 531 w. ^{1}H NMR: 2.34 (s, 3H); 2.11 (s, 3H); ^{13}C NMR: 202.6, 98.6, 28.3 (q, *J* = 130.1 Hz), 21.4 (q, *J* = 133.2). λ_{max} (ϵ) in H_2O: 258 nm (13270 M^{-1} cm^{-1}).

The filtrate was rotary evaporated to dryness. The ^{1}H NMR spectrum of the white residue (∼1.5 g) revealed the presence of **2a** and sodium ethane-1,1-bis(diazeniumdiolate), **3a**, in a 1:2 ratio.

Reaction of Nitric Oxide with 2-Butanone and 5 equiv of Sodium Methoxide (Entry 2, Table 1) Forming 3a. To a freshly prepared solution of Na metal (5.75 g, 0.25 atom) in absolute methanol was added 2-butanone (3.6 g. 0.05 mol). The solution was allowed to react with nitric oxide. The reaction mixture was rotary evaporated to remove the solvent, and the white solid was dissolved in water (50 mL). The solution was filtered and allowed to evaporate slowly in a partially closed container for several days until the volume of the solution was ∼20 mL. The crystals of sodium ethane-1,1-bis(diazeniumdiolate), **3a**, formed were filtered and dried. Yield: 6.4 g (66.0%). Anal. Calcd for $C_2H_4N_4O_4Na_2$: C, 12.37; H, 2.08; N, 28.87. Found: C, 12.19; H, 2.11; N, 28.56. IR (cm^{-1}): 3002 w, 2924 w, 2854 w, 1444 w, 1411 s, 1400 m, 1369 s, 1312 m, 1258 s, 1237 m, 1215 s, 1176 m, 1101 m, 1064 m, 1035 m, 1009 m, 1003 m, 944 s, 745 m, 715 s, 618 w, 565 w, 517 m. ^{1}H NMR: 6.20 (q, 1H, *J* = 6.7), 1.89 (d, 3H, *J* = 6.6). ^{13}C NMR: 87.41 (d, *J* = 159.5 Hz), 17.92 (q, *J* = 131.1 Hz). λ_{max} (ϵ) in H_2O: 255 nm (15720 M^{-1} cm^{-1}). Additional crops of the product were obtained on further evaporation of the filtrate, but were contaminated with small amounts of sodium acetate, **1a** and **6a**.

Reaction of Nitric Oxide with 2-Butanone and 2 equiv of Potassium Methoxide (Entry 1, Table 1) Forming 2b·CH$_3$OH. A solution of potassium methoxide was prepared by dissolving potassium metal (7.8 g, 0.2 mol) in absolute methanol (150 mL). 2-Butanone (7.21 g, 0.1 mol) was added to the methoxide solution, and the mixture was allowed to react with nitric oxide. The precipitate (25.4 g) formed was dissolved in water (100 mL) and filtered. The solution was treated with methanol (10 mL) and allowed to stand at 5 °C for 3 d. The colorless crystals of hydrated potassium acetate-1,1-bis(diazeniumdiolate)[11] formed were filtered. After drying, the crystals were analyzed for **1b**·H$_2$O. Yield: 0.635 g (2.0%) assuming 1 equiv of **1b** is formed from 1 equiv of the ketone. To the filtrate was added methanol (50 mL), and the cloudy solution was allowed to stand at 5 °C overnight. The shiny crystals of **2b**·CH$_3$OH formed were separated by filtration and dried. Yield: 18.3 g (61.0%). Anal. Calcd for $C_4H_6N_4O_5K_2 \cdot CH_3OH$: C, 20.00; H, 3.36; N, 18.67. Found: C, 19.73; H, 3.26; N, 18.50. IR (cm^{-1}): 3540−3400 b, 3015 w, 2953 w, 1735 s, 1635 m, 1456 m, 1370 s, 1300 s, 1266 s, 1221 s, 1199 s, 1125 s, 1096 s, 1048 w, 1028 w, 1007 m, 970 m, 944 s, 929 s, 833 s, 778 s, 623 s, 616 m, 608 m, 570 s, 522 s, 450 w. ^{1}H NMR: 3.34 (s, 3H, C*H*$_3$OH), 2.34 (s, 3H), 2.11 (s, 3H). ^{13}C NMR: 202.6, 98.6, 51.6 (q, *C*H$_3$OH), 28.3 (q, *J* = 130.1), 21.4 (q, *J* = 133.2). λ_{max} (ϵ) in H_2O: 258 nm (13490 M^{-1} cm^{-1}).

The filtrate was rotary evaporated to dryness. The ^{1}H NMR spectrum of the white residue (∼0.8 g) revealed the presence of **2b** and potassium ethane-1,1-bis(diazeniumdiolate) (**3b**) in an ∼1:3 ratio.

Reaction of Nitric Oxide with 2-Butanone and 5 equiv of Potassium Methoxide (Entry 2, Table 1) Forming 3b·H$_2$O. To a freshly prepared solution of K (5 g, 0.128 mol) in methanol (100 mL) was added 2-butanone (1.80 g, 0.025 mol). The clear solution was allowed to react with nitric oxide. The precipitate formed (5.6 g) was dissolved in hot ethanol (100 mL) and quickly filtered. On cooling the filtrate, potassium ethane-1,1-bis(diazeniumdiolate) hydrate, **3b**·H$_2$O, crystallized out, and the crystals were filtered and dried. Yield: 4.3 g (70.5%). Anal. Calcd for $C_2H_6N_4O_5K_2$: C, 9.84; H, 2.48; N, 22.96. Found: C, 9.80; H, 2.53; N, 22.84. IR (cm^{-1}): 3386 b, 2999 w,1402 w, 1368 m, 1315 s, 1221 s, 1105 s, 1063 m, 1014 s, 938 s, 738 s, 708 s, 602 w, 523 w. ^{1}H NMR: 6.20 (q, 1H, *J* = 6.7), 1.89 (d, 3H, *J* = 6.7). ^{13}C NMR: 87.4 (d, *J* = 162.6), 17.9 (t, *J* = 131.5). λ_{max} (ϵ) in H_2O: 255 nm (15430 M^{-1} cm^{-1}). The filtrate was rotary evaporated to near dryness to obtain a white solid. A ^{1}H NMR spectrum measured for the white solid (∼0.6 g) in D_2O revealed the presence of **3b**, **1b**, and **6b** in ∼2:1:1 ratio.

Reaction of Nitric Oxide with 2-Pentanone and 2 equiv of Potassium Methoxide (Entry 3, Table 1) Forming 4b·$^1/_2$H$_2$O and 5b. To a solution of potassium methoxide (0.1 mol) in absolute methanol (150 mL) was added 2-pentanone (4.30 g, 0.05 mol). The clear solution was allowed to react with nitric oxide. The precipitate (2.5 g) was dissolved in aq KOH (0.1 N, 20 mL) and treated with ethanol (20 mL). A gas evolved from the solution, and the solution turned brown. On standing the solution for several days at 5 °C, colorless crystals of **1b**·H$_2$O formed. The crystals were filtered and dried. Yield: 1.6 g (10.2%) assuming one equivalent of **1b** is formed from 1 equiv of the ketone.

The filtrate from the reaction mixture was rotary evaporated to a small volume (ca. 20 mL). The viscous solution was dissolved in hot ethanol (100 mL) and quickly filtered to remove any insoluble material. The yellow solution was cooled to room temperature and allowed to stand at 5 °C overnight. The colorless crystals of potassium 2-pentanone-3,3-bis(diazeniumdiolate) hemihydrate, **4b**·$^1/_2$H$_2$O, formed were separated by filtration. Yield: 7.0 g (48.2%). Anal. Calcd for $C_5H_9N_4O_{5.5}K_2$: C, 20.62; H, 3.12; N, 19.25. Found: C, 20.72; H, 3.17; N, 19.06. IR (cm^{-1}): 3410 b, 2974 w, 2926 m, 2854 w, 1721s, 1713 s, 1357 s, 1334 m, 1321 m, 1278 s, 1267 s, 1255 s, 1235 s, 1200 s, 1181 s, 1125 m, 1115 m, 1078 w, 958 m, 943 m, 876 w, 846 s, 821 s, 755 w, 745 w, 640 w, 610 w, 575 w, 425 w. ^{1}H NMR: 2.56 (q, 2H, *J* = 7.3), 2.32 (s, 3H), 1.07 (t, 3H, 7.3). ^{13}C NMR: 202.8, 101.0, 29.2 (q, *J* = 130.3), 28.9 (t, *J* = 131.1), 11.0 (q, *J* = 130.3), λ_{max} (ϵ) in H_2O: 259 nm (11210 M^{-1}cm^{-1}); 235 (sh). The filtrate was rotary evaporated to near dryness and dissolved in hot water (5 mL), and treated with methanol until the solution became cloudy. The solution was cooled at 5 °C overnight. The colorless crystals of potassium propane-1,1-bis(diazeniumdiolate), **5b**, formed were filtered and dried. Yield: 2.2 g (18.3%) assuming 1 equiv of **5b** is formed from 1 equiv of the ketone. Anal. Calcd for $C_3H_6N_4O_4K_2$: C, 15.00; H, 2.52; N, 23.34. Found: C, 14.99; H, 2.54; N, 23.17. IR (cm^{-1}): 2975 m, 2934 w, 2879 w, 1462 w, 1392 m, 1376 m, 1340 m, 1324 m, 1283 s, 1263 m, 1219 s, 1199 s, 1119 m, 1082 m, 1037 w, 966 s, 945 s, 921 s, 835 m, 789 s, 694 s, 584 w, 556 w, 514 m. ^{1}H NMR: 5.95 (t, *J* = 7.5), 2.36 (q, *J* = 7.4), 0.93 (t, *J* = 7.4). ^{13}C

NMR: 92.5 (d, $J = 157.5$), 24.9 (t, $J = 132.5$), 11.4 (q, $J = 126.4$). λ_{max} in H_2O (ϵ): 255 (15860 M^{-1} cm^{-1}).

Reaction of 2-Pentanone with 5 equiv of Potassium Methoxide (Entry 4, Table 1). To a freshly prepared solution of K metal (5 g, 0.128 mol) in absolute methanol (100 mL) was added 2-pentanone (2.15 g, 0.025 mol). The clear solution was allowed to react with nitric oxide. The precipitate was filtered, dried (2.5 g), and recrystallized from water (10 mL). The crystals of **1b**·H_2O formed were filtered and dried. Yield: 0.8 g (10.3%). On complete evaporation of the filtrate, an off-white solid (0.9 g) was obtained. An ^{1}H NMR spectrum measured for the solid in D_2O indicated that the solid is predominantly potassium methane-1,1-bis(diazeniumdiolate), **6b**,[11] which corresponds to a yield of 17% assuming 1 equiv of the salt is formed from 1 equiv of the ketone.

The filtrate of the reaction mixture was rotary evaporated to ~10 mL and the oily residue dissolved in hot ethanol (100 mL). On cooling the solution to room temperature, crystals of potassium propane-1,1-bis(diazeniumdiolate), **5b**, formed. The crystals were filtered and dried. Yield: 4.2 g (71.2%).

Reaction of Nitric Oxide with 3-Pentanone and 2 equiv of Potassium Methoxide (Entry 5, Table 1) Forming 7b. To a freshly prepared solution of K metal (5.0 g, 0.128 mol) in absolute methanol (100 mL) was added 3-pentanone (5.52 g, 0.064 mol). The clear solution was allowed to react with nitric oxide. The precipitate formed was filtered and dried. Attempts to recrystallize the precipitate from aq KOH were not successful as the solution continued to form bubbles for several days indicating slow decomposition of the product. The filtrate was rotary evaporated to ~50 mL and allowed to stand at room temperature overnight. The large colorless crystals of potassium 3-pentanone-2,2-bis(diazeniumdiolate), **7b**, formed were filtered and dried. Yield: 1.5 g (8.3%). Anal. Calcd for $C_5H_8N_4O_5K_2$: C, 21.28; H, 2.86; N, 19.86. Found: C, 21.34; H, 2.91; N, 19.69. IR (cm^{-1}): 2923 w, 2853 w, 1727 s, 1444 w, 1409 m, 1349 m, 1330 s, 1287 s, 1261 m, 1210 s, 1171 m, 1113 m, 1083 m, 1048 w, 1017 m, 970 m, 939 s, 921 s, 818 m, 797 w, 752 m, 723 m, 696 w, 599 m, 576 m, 553 w, 502 m, 470 w. ^{1}H NMR: 2.68 (q, 2H, $J = 7.2$), 2.12 (s, 1H), 1.10 (t, 3H, $J = 7.1$). ^{13}C NMR: 206.3, 98.7, 34.5 (t, $J = 128.1$), 21.4 (q, $J = 133.2$), 10.9 (q, $J = 128.7$). λ_{max} (ϵ) in H_2O: 258 nm (13040 M^{-1} cm^{-1}); 235 nm (sh).

Reaction of Nitric Oxide with 3-Pentanone and 4 equiv of Potassium Methoxide (Entry 6, Table 1) Forming 8b·H_2O and 9b·$^1/_2$EtOH. To a freshly prepared solution of K metal (5.0 g, 0.128 mol) in absolute methanol (100 mL) was added 3-pentanone (2.76 g, 0.032 mol). The clear solution was allowed to react with nitric oxide. The off-white precipitate formed was filtered, dried (3.5 g), and treated with boiling methanol (100 mL) for 0.5 h. The undissolved solid was filtered and dried (2.8 g). The solid was recrystallized from aq potassium hydroxide (0.1 N, 10 mL) by slow evaporation. The microcrystalline potassium propanoate-2,2-bis(diazeniumdiolate) hydrate, **8b**·H_2O, formed were washed with methanol and dried. Yield: 2.6 g (24.9%) based on the amount of base used and assuming 1 equiv of **8b** and **3b** are formed from 1 equiv of 3-pentanone and 5 equiv of the base. Anal. Calcd for $C_3H_5N_4O_7K_3$: C, 11.05; H, 1.55; N, 17.19. Found: C, 10.97; H, 1.61; N, 17.10. IR (cm^{-1}): 3426 b, 2968 w, 2950 w 1649 s, 1471 w, 1374 m, 1357 m, 1341 m, 1270 s, 1209 s, 1146 m, 1119 m, 1086 m, 1010 w, 943 s, 926 m, 890 m, 825 s, 763 s, 709 s, 603 m, 546 w, 397 w. ^{1}H NMR: 2.08 (s); ^{13}C NMR: 173.1, 98.0, 23.9 (q, $J = 132.4$). λ_{max} (ϵ) in 0.1 N aq KOH: 255 nm (17110 M^{-1} cm^{-1}).

The filtrate from the reaction mixture and the methanol washings of the precipitate were mixed and rotary evaporated to ~10 mL, treated with boiling ethanol (50 mL), and allowed to stand at 5 °C overnight. The crystals of **3b**·H_2O formed were filtered and dried. Yield: 2.8 g (57.4%). The filtrate was rotary evaporated to ~20 mL and the solution was allowed to stand at −20 °C for several days when potassium acetate-1-diazeniumdiolate crystallized out solvated with ethanol as **9b**·$^1/_2$EtOH. The crystals were filtered and dried. Yield: 0.64 g (8.6%) based on the amount of the base used and assuming 1 equiv of **9b** is formed from 1 equiv of 3-pentanone and 4 equiv of the base. Anal. Calcd for $C_4H_7N_2O_{4.5}K_2$: C, 20.60; H, 3.03; N, 12.02. Found: C, 20.63; H, 3.08; N, 11.96. IR (cm^{-1}): 3397 b, 2970 w, 2952 w, 1614 s, 1456 w, 1408 m, 1376 m, 1252 s, 1186 m, 1098 m, 1079 m, 1052 w, 1018 m, 939 s, 876 m, 714 m, 587 w, 490 w, 385 w. ^{1}H NMR: 4.82 (q, $J = 7.2$), 3.65 (q, $J = 7.1$, CH_3CH_2OH), 1.57 (d, $J = 7.2$), 1.18 (t, $J = 7.1$, CH_3CH_2OH). ^{13}C NMR: 184.3, 72.0 (d, $J = 140.7$), 60.2 (q, $J = 143.3$, CH_3CH_2OH), 19.6 (q, $J = 126.2$, CH_3CH_2OH), 18.0 (q, $J = 130.5$). λ_{max} (ϵ) in H_2O: 250 nm (8290 M^{-1} cm^{-1}).

Reaction of Nitric Oxide 3-Methyl-2-butanone and 1 equiv of Potassium Methoxide (Entry 7, Table 1) Forming 10b. To a freshly prepared solution of K (3.9 g, 0.1 mol) in absolute methanol (100 mL) was added 3-methyl-2-butanone (8.61 g, 0.1 mol). The solution was allowed to react with nitric oxide. There was no precipitate formed in this reaction. The reaction mixture was rotary evaporated to ~5 mL, the glassy solid was dissolved in absolute ethanol (10 mL), and the clear solution was treated with acetonitrile (100 mL). The cloudy solution was allowed to stand for several days in a closed container. The large plates crystallized out were separated by filtration and washed with acetonitrile. The filtrate was rotary evaporated to ~5 mL and the glassy solid treated as above, and a second crop of crystals of potassium 3-methyl-2-butanone-3-diazeniumdiolate (**10b**) was obtained and then combined and dried. Yield: 12.9 g (70.1%). Anal. Calcd for $C_5H_9N_2O_3K$: C, 32.60; H, 4.93; N, 15.22. Found: C, 32.52; H, 4.97; N, 15.16. IR (cm^{-1}): 3003 w, 2981 w, 2928 w, 1724 s, 1712 s, 1474 w, 1448 w, 1426 w, 1379 w, 1367 m, 1356 m, 1341 s, 1253 s, 1233 s, 1169 s, 1143 m, 1124 s, 1033 w, 1002 w, 980 w, 961 w, 938 s, 906 s, 893 m, 758 m, 645 w, 632 w, 612 w, 593 w, 550 m, 504 w, 480 w, 383 w, 367 m. ^{1}H NMR: 1.62 (s, 3H), 2.20 (s, 6H). ^{13}C NMR: 212.4, 80.3, 26.7 (q, $J = 129.2$), 24.7 (q, $J = 130.3$). λ_{max} in H_2O (ϵ): 251 nm (8950 M^{-1} cm^{-1}).

Reaction of Nitric Oxide with 3-Methyl-2-pentanone and 1 equiv of Potassium Methoxide (Entry 7, Table 1) Forming 11b. To a freshly prepared solution of K (3.9 g, 0.1 mol) in absolute methanol (100 mL) was added 3-methyl-2-pentanone (10.0 g, 0.1 mol), and the clear solution was pressurized with nitric oxide. Though absorption of the gas was observed, the reaction did not form any precipitate. The reaction mixture was rotary evaporated, and the glassy residue was dissolved in hot absolute ethanol and quickly filtered. The filtrate was allowed to stand at −10 °C for 1 week to form fluffy crystals of potassium 3-methyl-2-pentanone-3-diazeniumdiolate (**11b**). Yield: 12.1 g (61.1%). Anal. Calcd for $C_6H_{11}N_2O_3K$: C, 36.36; H, 5.60; N, 14.14. Found: C, 36.28; H, 5.67; N, 14.08. IR (cm^{-1}): 2979 w, 2853 w, 1718 s, 1576 w, 1454 w, 1380 m, 1357 m, 1331m, 1237 s, 1167 m, 1140 m, 1111 m, 1054 w, 1026 w, 1010 w, 973 m, 926 w, 868 m, 814 m, 807 w, 768 w, 648 w, 591 m, 528 w, 478 w. ^{1}H NMR: 2.18 (s, 3H); 2.17 (m, 1H); 1.94 (m, 1H), 1.58 (s, 3H); 0.80 (t, 3H, $J = 7.5$). ^{13}C NMR: 212.4, 83.7, 29.2 (t, $J = 131.1$); 27.1 (q, $J = 129.0$ Hz), 21.5 (q, $J = 130.1$); 9.8 (q, $J = 126.8$). λ_{max} in H_2O (ϵ): 251 nm (8862 M^{-1} cm^{-1}).

Reaction of Nitric Oxide with 3-Methyl-2-butanone and 4 equiv of Potassium Methoxide (Entry 8, Table 1) Forming 12b·$^1/_2H_2O$. To a freshly prepared solution of K (7.8 g, 0.2 mol) in absolute methanol (150 mL) was added 3-methyl-2-butanone (4.3 g, 0.05 mol). The clear solution was allowed to react with nitric oxide. The white precipitate formed was filtered and dried (5.2 g). A ^{1}H NMR spectrum measured for the precipitate in D_2O immediately after dissolution indicated that it contained the previously reported potassium methanetris(diazeniumdiolate)[11] and potassium methanebis(diazeniumdiolate)[11] in a ca. 8:1 ratio. The filtrate was rotary evaporated to a syrupy solid, and the solid was dissolved in water (2 mL). The solution was treated with ethanol (50 mL) and cooled at 5 °C for several days. The large platelets of hydrated potassium isobutanoate-2-diazeniumdioate, **12b**·$^1/_2H_2O$, formed were filtered and dried at room temperature. Yield: 7.4 (63.5%). Anal. Calcd for $C_4H_7N_2O_{4.5}K_2$: C, 20.60; H, 3.03; N, 12.02. Found: C, 20.62; H, 3.08; N, 11.92. IR (cm^{-1}): 3445 b, 3356 b, 2995 m, 2941 m, 1605 s, 1596 s, 1474 m, 1440 w, 1399 s, 1368 m, 1359 s, 1341 s, 1248 s, 1200 m, 1171 s, 1131 s, 1009 w, 956 m, 919 s, 848 m, 793 w, 697 s, 629 w, 557 m, 507 w, 453 w. ^{1}H NMR: 1.62 (s). ^{13}C NMR: 181.3, 78.2, 27.0 (q, J = 129.7). λ_{max} in H_2O (ϵ): 246 nm (7750 M^{-1} cm^{-1}).

Reaction of Nitric Oxide 3-Methyl-2-pentanone with 4 equiv of Potassium Methoxide (Entry 8, Table 1). To a freshly prepared solution of K (5 g, 0.128 mol) in methanol (100 mL) was added 3-methyl-2-pentanone (2.57 g, 0.026 mol). The clear solution was allowed to react with nitric oxide. The white precipitate formed was filtered and dried (3.2 g). As in the previous reaction, the precipitate contained $CH(N_2O_2K)_3$ and $CH_2(N_2O_2K)_2$ in ca. 8:1 ratio. The filtrate was treated as in the above reaction, and the crystals of hydrated potassium 2-methylbutanoate-2-diazeniumdiolate (**13b**·1$^1/_2$$H_2O$) formed after several days were filtered and dried. Yield: 3.94 g (57.2%). Anal. Calcd for $C_5H_{11}N_2O_{5.5}K_2$: C, 22.64; H, 4.18; 10.57. Found: C, 22.56; H, 4.14; N, 10.60. IR (cm^{-1}): 3533 s, 3368 s, 3229 b, 2986 m, 2968 m, 2944 m, 2883 w, 1607 s, 1459 w, 1395 s, 1363 m, 1344 m, 1284 m, 1225 s, 1173 w, 1159 m, 1131 m, 1053 w, 1003 w, 942 s, 906 m, 860 m, 788 w, 732 m, 628 w, 593 w, 502 w, 458 w. ^{1}H NMR: 2.18 (m, 1H), 1.93 (m, 1H), 1.57 (s, 3H), 0.79 (t, 3H, J = 7.2). ^{13}C NMR: 181.0, 81.9, 31.8 (d, J = 130.2), 23.5 (q, J = 129.6) 10.5 (q, J = 126.6 Hz). λ_{max} in H_2O (ϵ): 246 nm (7670 M^{-1} cm^{-1}).

Reaction of Nitric Oxide with 2,6-Dimethylcyclohexanone and 2 equiv of Potassium Methoxide (Entry 9, Table 1) Forming 14b. To a freshly prepared solution of K (2.44 g, 0.06 mol) in methanol (100 mL) was added 2,6-dimethylcyclohexanone (3.78 g, 0.03 mol, mixture of cis and trans isomers, ∼20:80). The clear solution was allowed to react with nitric oxide. The precipitate formed was filtered and recrystallized from water (10 mL) as colorless crystals (0.75 g). The crystals were characterized as potassium *cis*-2,6-dimethylcyclohexanone-2,6-bis(diazeniumdiolate) from single-crystal X-ray diffraction data. The filtrate was rotary evaporated to a glassy solid. The gummy solid was dissolved in hot ethanol (20 mL), filtered to remove any insoluble solid, and treated with acetonitrile (30 mL). The solution was cooled at 5 °C for 2 days and a small amount of crystals of cis-**14b** (characterized by a comparison of its ^{1}H NMR spectrum with that of the above crystals) formed were filtered and dried (0.5 g). Combined yield of *cis*-**14b**: 1.25 g (12.9%). Anal. Calcd for $C_8H_{12}N_4O_5K_2$: C, 29.81; H, 3.75; N, 17.39. Found: C, 29.74; H, 3.84; N, 17.42. IR (cm^{-1}): 3020 w, 2988 w, 2954 m, 2934 m, 2904 m, 1732 s, 1710 m, 1459 m, 1372 m, 1355 m, 1334 s, 1302 w, 1280 m, 1246 s, 1206 m, 1185 s, 1127 m, 1063 m, 1022 w, 994 m, 976 w, 934 s, 908 s, 872 m, 844 m, 763 m, 710 w, 675 w, 617 w, 513 m, 479 m, 453 w. ^{1}H NMR: 2.84 (m, 2H), 2.06 (m, 4H), 1.76 (s, 6H). ^{13}C NMR: 208.0, 81.1, 37.2 (t, J = 130.0), 26.0 (q, J = 132.1), 19.7 (t, J = 129.2). λ_{max} (ϵ) in H_2O: 249 nm (13725 M^{-1} cm^{-1}).

The filtrate was rotary evaporated to a colorless glassy solid and the solid was dried in a vacuum oven at 60 °C overnight. The resultant highly hygroscopic colorless solid was characterized as *trans*-**14b**. Yield of *trans*-**14b**: 6.5 g (57.6%). Anal. Calcd for $C_8H_{18}N_4O_8K_2$: C, 25.53; H, 4.82; N, 14.89. Found: C, 25.71; H, 4.27; N, 14.62. IR (cm^{-1}): 3420−3280 b, 2941 m, 2879 w, 1720 s, 1663 m, 1610m, 1583 m, 1449 m, 1379 m, 1339 s, 1334 s, 1231 m, 1190 s, 1147 m, 1121 m, 1056 w, 991 w, 974 w, 937 s, 907 s, 859 m, 743 w, 694 w, 667 w, 520 m, 476 w. ^{1}H NMR: 2.62 (td, 2H, J = 14.9, 5.4), 1.93 (m, 4H, J = 14.8, 7.8), 1.76−1.68 (2H, m), 1.56 (s, 6H). ^{13}C NMR: 206.0, 79.3, 34.4 (t, J = 131.3), 25.0 (q, J = 130.6), 18.2 (t, J = 127.3). λ_{max} (ϵ) in H_2O: 241 nm (12020 M^{-1} cm^{-1}).

Crystallographic Data. X-ray diffraction data for **14b** were collected on a Bruker P4 diffractometer equipped with a molybdenum tube and a graphite monochromator at −100 °C. Unit cell dimensions were determined from several accurately centered reflections in high 2θ angles using XSCANS program.[29] Three standard reflections measured after every 97 reflections exhibited no significant loss of intensity. The structure was solved by direct methods and refined by least-squares techniques on F^2 using SHELXTL program.[30] Compound **14b** crystallizes in the monoclinic space group $P2_1/c$ with four molecular formula units. The ions are well ordered, and are located on general positions. All non-hydrogen atoms were located in the difference maps during successive cycles of least-squares, and were refined anisotropically. All H atoms were located and refined isotropically.

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Supporting Information Available: Crystallographic data (CIF files, Tables S1−S5) for **14b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[29] XSCANS V. 2.31, Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 1993.

[30] SHELXTL Crystallographic System 5.10 ed.; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 1997.