



New methanetrisdiazeniumdiolates

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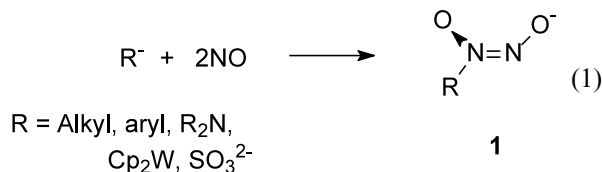
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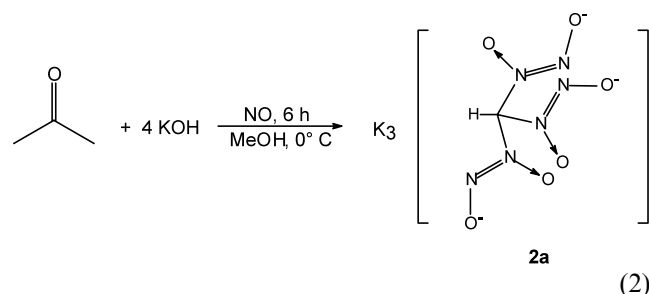
Abstract—Acetophenone and 1,3-biacetylbicyclo[1.1.1]pentane exhaustively condense all acidic α C–H with nitric oxide in basic methanol to give methanetrisdiazeniumdiolates, $\text{RC}(\text{O})\text{C}(\text{N}_2\text{O}_2\text{K})_3$ either as a trianionic salt in the case of acetophenone or as a hexanionic salt in the case of 1,3-biacetylbicyclo[1.1.1]pentane. © 2003 Elsevier Science Ltd. All rights reserved.

In a surprisingly general reaction, two nitric oxide molecules readily add to nucleophiles¹ to give diazeniumdiolates, RN_2O_2^- , **1** (Eq. (1)). A diverse array of R groups engage in this reactivity and include dialkylamines, carbanions, sulfites, and organometallic centers.² An equally remarkable range of naturally occurring diazeniumdiolates are now recognized, the most renowned of which is alanosine,³ l - $\text{HO}_2\text{CCH}(\text{NH}_2)(\text{CH}_2\text{N}_2\text{O}_2\text{H})$. Acidic hydrogens bound to carbon such as vicinal α -CH groups on ketones,⁴ nitriles,⁵ or carboxylates^{6,7} are excellent substrates for diazeniumdiolation, but a major complication of this reaction is competition of single diazeniumdiolation with either polydiazeniumdiolation or one electron transfer chemistry. An important consequence of this complicated reactivity pattern is that these reactions have been largely unexplored.



We have recently described a new variation of the polydiazeniumdiolation reaction, one where six nitric oxides readily add to a carbon-acid to give a trisdiazeniumdiolate, **2**.⁸ These relatively simple and moderately stable compounds were isolated as their potassium and sodium salts and characterized structurally, spectroscopically, and thermochemically. The combination

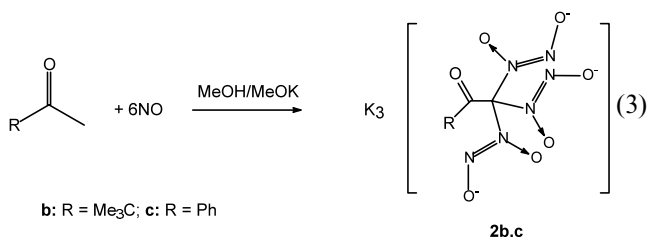
of their relatively high thermal stabilities and their ease of preparation and isolation make them ideal candidates for new high-energy density materials for solid rocket propellant applications. As single propellants however, these salts are low in carbon and hydrogen, and we sought ways to introduce substituents with higher endotherms of formation. The most logical of these components are those with strained rings, and we have identified the bicyclic bisacetyl derivative **3**,¹² as a suitable candidate for diazeniumdiolation. In this communication, we describe the synthesis and characterization of two new polydiazeniumdiolates, in particular one with 12 nitric oxides added to a single substrate, and which thus has a concomitant charge of -6 .



Before this research, two $\text{RC}(\text{N}_2\text{O}_2^-)_3$ species were known, R = H, pivaloyl, **2a,b**,⁸ (Eq. (2) and (3)), and we sought to generalize the trisdiazeniumdiolation reaction. For our initial substrate we chose acetophenone which, when treated with nitric oxide in MeOH/KOH, gives a copious white precipitate which corresponds to a 55% yield of the benzoyl-methanetrisdiazeniumdiolate, **2c** (Eq. (3)), which is isolated as an analytically pure tripotassium salt⁹ after filtration of the precipitate and washing with methanol, ethanol, and hexane. This

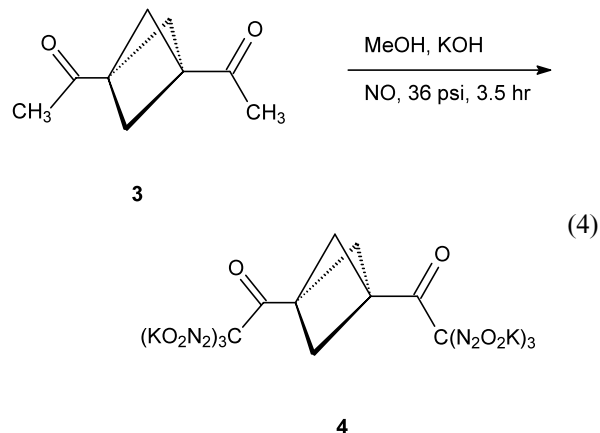
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salt decomposes exothermically at 171°C, with $\Delta H_{\text{dec}} = -284$ kcal/mol, and is readily water soluble. Aqueous solutions of **2c** are relatively stable under alkaline conditions and, although spectroscopic data can be readily obtained to confirm its identity,¹⁰ under these conditions its decomposition follows first order kinetics with $k_{\text{obs}} = 6.3(7) \times 10^{-4} \text{ s}^{-1}$ at 30°C and pH 9 as determined by UV–vis spectrophotometry, and following the loss of the absorbance at 264 nm. From ^1H and ^{13}C NMR spectroscopy benzoate is the sole carbon containing decomposition product. Taken together the solubility and stability of **2c** is similar to that of **2a**, but it is markedly less stable than **2b** in base. The origin of these relative stabilities is possibly due to the differing steric requirements of the R group for the trisdiazoniumdiolate. That is the stability of the pivaloyl is greater than the benzoyl derivative.



The same conditions used for the preparation of **2c** from acetophenone also lead to rapid nitric oxide addition to the biacetyl **3** (Eq. (4)). In this case the product, **4**, is also isolated as a white product in 51% yield, and corresponds to the addition of 12 nitric oxides to give a symmetric bis(methanetrissdiazoniumdiolate) of bicyclo[1.1.1]pentane. The product **4** is formulated as a bis(methanetrissdiazoniumdiolate) on the basis of elemental analysis, spectroscopy, and thermochemical characteristics.¹¹ Although the solubility of **4** is limited to water, its aqueous solutions are much more stable than for **2c** and there is no loss of A_{264} in 0.1 M KOH over 8 h at 30°C. Under differential scanning calorimetry conditions the hexakispotassium salt of **4** is thermally stable to 161.1°C but decomposes irreversibly and exothermally, $\Delta H_{\text{dec}} = -464$ kcal/mol. This exothermic decomposition is 65% greater than that found for **2b**. In addition to the strong IR bands typical of the six new diazeniumdiolate substituents in **4** at 1366.2, 1261.8, 1187.4, 1091.9, and 1015.5 cm^{-1} , the $\nu(\text{C}=\text{O})$ of the carbonyl groups are split by 14 cm^{-1} to 1718.8, and 1703.9 cm^{-1} as compared to 1708 cm^{-1} in **3**.¹² The origin of this small splitting may be either due to solid state effects or to cross ring vibrational coupling of the two carbonyls. A single bridging methylene resonance at 2.1 ppm is seen in the ^1H NMR spectrum of the product and at 51.9 ppm in the ^{13}C NMR spectrum. Thus, in both spectra the characteristic signals for the methyl groups have been lost and replaced by an easily saturated peak at 143.5 ppm in the ^{13}C NMR spectrum.

The facile complete diazeniumdiolation of the acetyl groups in acetophenone and **3** under these conditions suggest that many such acetyl and polyacetyl species are substrates for the reaction in Eq. (4). Clearly further



research is required to elucidate the origin of the surprisingly variable stability of the resulting polydiazoniumdiolates as well as their decomposition pathways.

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References

- Hrabie, J. A.; Keefer, L. K. *Chem. Rev.* **2002**, *102*, 1135–1154.
- Keefer, L. K.; Flippen-Anderson, J. L.; George, C.; Shanklin, A. P.; Dunams, T. M.; Christodoulou, D.; Saavedra, J. E.; Sagan, E. S.; Bohle, D. S. *Nitric Oxide* **2001**, *5*, 377–394.
- Tyagi, A. K.; Cooney, D. A. *Adv. Pharmacol. Chemother.* **1984**, *20*, 69–121.
- Woodward, R. B.; Wintner, C. *Tetrahedron Lett.* **1969**, *10*, 2689–2692.
- Arnold, E. V.; Citro, M. L.; Keefer, L. K.; Hrabie, J. A. *Org. Lett.* **2002**, *4*, 1323–1325.
- Traube, W. *Ber. Dtsch. Chem. Ges.* **1895**, *28*, 1785–1797.
- Arulsamy, N.; Bohle, D. S. *Angew. Chem. Int. Ed.* **2002**, *41*, 2089–2091.
- Arulsamy, N.; Bohle, D. S. *J. Am. Chem. Soc.* **2001**, *123*, 10860–10869.
- Similar methods were used in the preparations of **2c** and **4**. Specific details for the preparation of **4** from **3** are as follows: 1,3-biacetylbicyclo[1.1.1]pentane, 0.081 g (0.53 mmol) was dissolved in 30 mL of MeOH containing 0.23 (4.11 mmol) of potassium hydroxide in a Fisher Porter thick-glass walled medium pressure flask. The flask and solvent were purged with a stream of nitrogen for 20 min, and the container was then pressurized with NO to 36 psi and held at this pressure for 3.5 h at which time the reaction was stopped. The solution changed from clear and colorless to a copious milky white suspension. The precipitate was suction filtered and washed with 20 mL each of methanol, ethanol, and hexane before being dried

overnight in a vacuum oven at room temperature. The white solid, 0.20 g, corresponds to 51% yield. Anal. calcd for $C_9H_6K_6N_{12}O_{14}$: C, 14.59; H, 0.82; N, 22.69. Found: C, 14.31; H, 1.04; N, 22.49%.

10. *Characteristic data for 2c*: NMR (0.1 M, NaOD): 1H NMR: 7.81 (d, $^3J_{HH}=7.41$ Hz, 2H), 7.60 (t, $^3J_{HH}=7.40$ Hz, 1H), 7.47 (t, $^3J_{HH}=7.4$ Hz, 2H); ^{13}C NMR: 208.64, 136.01, 134.08, 131.56, 131.41, 131.11 ppm. IR (KBr, strong bands only): $\nu(C=O)$ 1699.2; N_2O_2 : 1360.2, 1304.4, 1259.4, 1182.7 cm^{-1} . UV-vis (0.1 M, NaOH) 264 nm. Anal.

calcd for $C_8H_5K_3N_6O_7$: C, 23.18; H, 1.22. Found: C, 23.84, H, 1.68%. DSC: 170.9°C, irreversible, $\Delta H_{dec}=-284$ kcal/mol.

11. *Characteristic data for 4*: NMR (0.1 M, NaOD): 1H NMR: 2.1 (s, CH_2); ^{13}C NMR: 207.0, 49.6, 51.9, 143.5 ppm. IR (KBr, strong bands only): $\nu(C=O)$ 1703.92, 1718.81; N_2O_2 : 1366.2, 1261.8, 1187.4, 1150.4, 1091.9 and 1015.5 cm^{-1} . UV-vis (0.1 M, NaOH): 264 nm. DSC: 161.1°C, irreversible, $\Delta H_{dec}=-464$ kcal/mol.
12. Kaszynski, P.; Michl, J. *J. Org. Chem.* **1988**, 53, 4593–4594.