Pergamon

Tetrahedron Letters 40 (1999) 5279–5282

TETRAHEDRON
LETTERS

Cycloaddition reactions of sodium dinitroxytrioxide (Angeli's salt)

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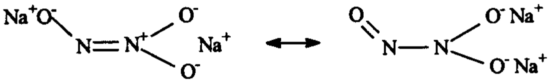
Received 7 April 1999; revised 10 May 1999; accepted 12 May 1999

Abstract

Angeli's salt undergoes a quantitative reaction with 1,3-diphenylisobenzofuran in a methanol/water solution at room temperature to give a product (**1**) explicable by an initial [4+2] cycloaddition reaction. Under the same conditions, Angeli's salt reacts with 1-naphthaldehyde to give 1-naphthoic acid in good yield. This reaction can also be explained by an initial [2+2] cycloaddition to give a hydroxamic acid, which is then hydrolyzed to the carboxylic acid. © 1999 Elsevier Science Ltd. All rights reserved.

The chemical reactivity of Angeli's salt[1] (sodium trioxodinitrate, $Na_2N_2O_3$; see structures in Scheme 1) is relatively unexplored. The most extensive study of its reactivity with organic molecules was reported by Smith and Hein[2] in which these workers revisited reported reactions of the salt with aldehydes and alkyl halides. The chemistry was found to be variable and dependent on the batch of Angeli's salt in hand.



Scheme 1.

Angeli's salt has become of more recent interest because it is a source of the nitroxyl anion (NO^-), also a relatively unexplored species that is isoelectronic with oxygen and can exist as both singlet and triplet states. The singlet and triplet species are reported to be formed when the salt is heated,[3] and photolyzed,[4] respectively, in basic media. With this in mind we have explored the reaction of Angeli's salt with 1,3-diphenylisobenzofuran (DPIBF), a known singlet oxygen trap,[5] with the hope of isolating a cycloaddition product.

1,3-Diphenylisobenzofuran (DPIBF) was added to a heterogeneous mixture of Angeli's salt in 10% aqueous methanol. Initially, the reaction mixture was heated at reflux, optimal conditions for generating the nitroxyl anion.[3] The nitroxyl anion is observed through the formation of $Ni(NO)(CN)_3^{2-}$ from $K_2Ni(CN)_4$, which occurs in a matter of minutes at high temperatures but only over several hours at

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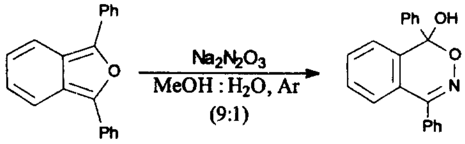
PII: S0040-4039(99)00962-4

room temperature.[6] It was ultimately determined that a reaction readily occurred at room temperature whereupon the characteristic yellow color of the solution became discharged in ca. 3 h (Eq. 1). When the reaction was carefully run under argon a single product was formed quantitatively. It was purified by chromatography under an inert atmosphere to give a white crystalline solid (1; mp 154–155°C). The mass spectrum confirmed that a net addition of HNO to DPIBF had occurred [EI (*m*/*z*): M$^+$=301, base peak=270; CI (*m*/*z*): (M+H)$^+$ base peak=302] while the infrared spectrum confirmed the presence of an OH or NH group (3203 cm^{-1}). The proton NMR spectrum indicated the presence of 14 aryl hydrogens (δ 6.60–7.70 ppm) plus the OH or NH proton as a broad peak at δ 4.65–4.75 ppm. The product was characterized by X-ray analysis (Fig. 1) and thereby identified as the alcohol depicted in Eq. 1. *o*-Dibenzoylbenzene, a known oxidation product of DPIBF,[7] was also isolated when oxygen was present during the reaction.



DPIBF 1

(1)

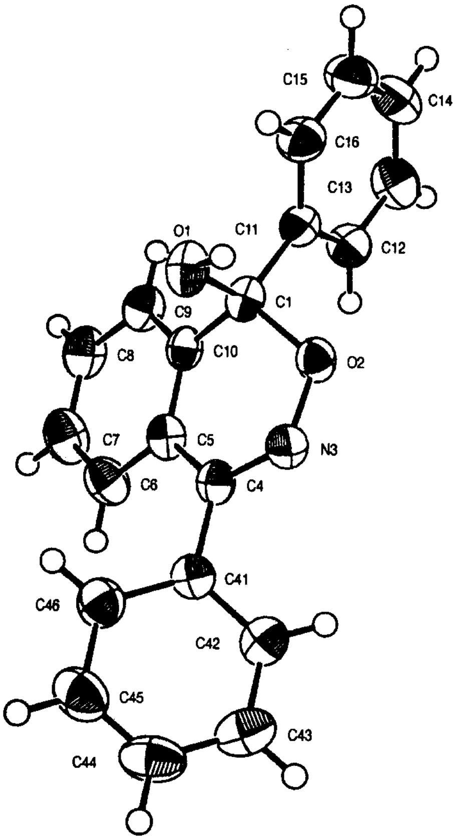
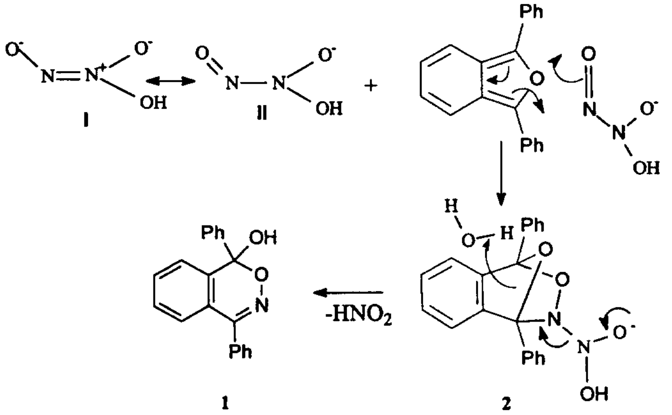


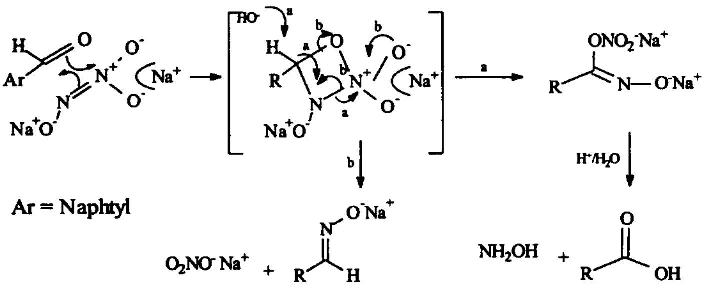
Figure 1. X-Ray structure of the cycloadduct 1

Because the reaction occurs at a temperature below that needed to generate the nitroxyl anion in substantial quantity, and because one observes the Angeli's salt dissolving as the reaction proceeds, we ascribe the chemistry being observed to a direct reaction between the Angeli's salt, i.e. its monobasic anion, and the DPIBF. A reasonable reaction pathway would be that in which the N=O double bond present in one resonance form of the reactant undergoes a [4+2] cycloaddition to the DPIBF to give the initial adduct **2** (see Scheme 2). Loss of HNO_2 and opening of the furan bridge leads directly to the product.



Scheme 2.

The observation of this reaction has led us to revisit the reaction of Angeli's salt with aldehydes which is reported to give hydroxamic acids. The Angeli's salt chemistry was discussed as likely to be analogous to that involved in a classic test for aldehydes using 'Piloty's acid' ($PhSO_2NHOH$) termed the Angeli–Rimini reaction.[8] We have carried out the reaction of Angeli's salt with 1-naphthaldehyde under conditions similar to those used with DPIBF (i.e. methanol:water, 9:1). At the end of 1 h, there was a 25% loss of the aldehyde, with 90% of this accounted for as 1-naphthoic acid. At reflux, the naphthaldehyde oxime joins the acid as a major product; for example, with a 3:1 excess of Angeli's salt and a 30 min reaction time, GC analysis shows an 80% loss of starting material with 42 and 33% conversions to the acid and the oxime, respectively.[9] The acid is a logical consequence of the hydrolysis of hydroxamic acid. This, in turn, has been rationalized as forming through the nucleophilic addition of Angeli's salt on the aldehyde. An alternative mechanism, suggested by the [4+2] chemistry outlined above, is shown in Scheme 3. Here a [2+2] cycloaddition of Angeli's salt with the aldehyde is invoked. The transient intermediate can decompose by two different pathways — path 'a' to a precursor of the hydroxamic acid (and ultimately the acid), and path 'b' which leads directly to the oxime. Clearly, since hydroxylamine is a by-product of the hydrolysis of the hydroxamic acid, its direct condensation with the aldehyde may also be a source of oxime.



Scheme 3.

Acknowledgements

We are grateful to Dr. Phil Fanwick for providing the X-ray structure of compound **1**.

References

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2. Smith, P. A. S.; Hein, G. H. *J. Am. Chem. Soc.* **1960**, *82*, 5731.
3. As evidenced by reaction with potassium tetracyanonickel(II) to give $K_2NiNO(CN)_3$; cf. Veprek-Siska, J.; Simirous, F.; Pliska, V. *Collect. Czech. Chem. Commun.* **1959**, *24*, 1175.
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7. Akasaka, T.; Nakagawa, M.; Ando, W. *J. Org. Chem.* **1986**, *51*, 4477. We find the formation of this product to be markedly accelerated by light. It would appear that the reaction involves the DPIBF photosensitized formation of singlet oxygen and the subsequent reaction of the DPIBF ground state with this species.
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9. The alcohol reduction product is observed at longer reaction times. This is the apparent co-product (with the carboxylic acid) of a Cannizaro reaction; control studies show the Cannizaro to be minor side-reaction at both room and reflux temperatures during the typical (<2 h) reaction times.