Reversible Oxidation of 1,3-Dithiolan-2-thione

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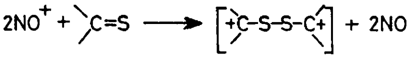
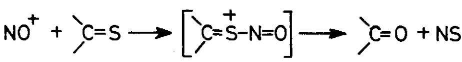
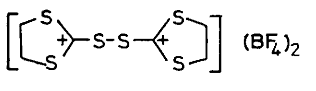
Summary Oxidation of 1,3-dithiolan-2-thione by nitrosonium tetrafluoroborate to 2,2′-dithio-*bis*-(1,3-dithiolanium) ditetrafluoroborate is reversible and is linked to nitrosative exchange of sulphur for oxygen.

CONSIDERABLE interest has recently been focused on the oxidation of thiocarbamates[1] and thioureas.[2,3] Nitrosonium salts or nitrous acid,[1a,2] like numerous other mild oxidizing agents,[3] are reported to convert dithiocarbamates and thioureas into stable dimeric dipositive ions that contain the disulphide linkage. Although the limitations of this process have not been reported, the known susceptibility of sulphur compounds to oxidation suggests that a similar oxidative transformation [equation (1)] is general for compounds that possess a carbon–sulphur double bond. However, by analogy with nitrosative exchange of nitrogen for oxygen in reactions of nitrosonium salts with imines,[4] nitrosative substitution of sulphur for oxygen in reactions of nitrosonium salts with thiocarbonyl compounds [equation (2)] is also possible. We have found that in reactions of nitrosonium tetrafluoroborate with 1,3-dithiolan-2-thione the oxidative process described by equation (1) is reversible and is linked to the nitrosative exchange reaction of equation (2).

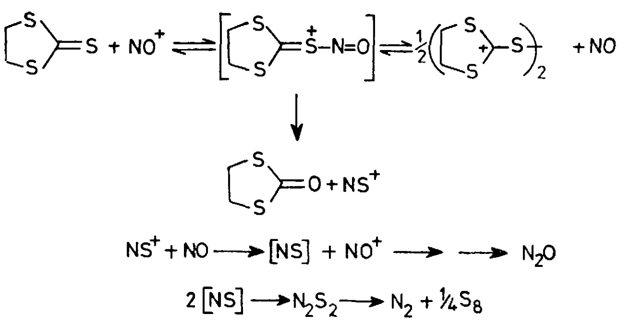

(1)


(2)

Addition of 1,3-dithiolan-2-thione to nitrosonium tetrafluoroborate (1 equiv.) in anhydrous acetonitrile resulted in the immediate evolution of gas (94% NO, 4% N_2, and 2% N_2O) and in the formation of 2,2′-dithio-*bis*(1,3-dithiolanium) ditetrafluoroborate (**1**). This salt was only moderately soluble in acetonitrile and precipitated as a white solid from the reaction solution as it was formed. Spectral measurements [^{1}H n.m.r. δ (MeCN) 4·47 (s); i.r. (Nujol) 1200—800 cm^{-1} $\bar{\nu}(BF_4^-)$; u.v. (MeCN) transparent above 250 nm] were consistent with the proposed structure for (**1**). Elemental analyses obtained for this air- and water-sensitive compound agreed with the formula $C_6H_8B_2F_8S_6$.


(1)

In addition to (**1**), however, reactions of 1,3-dithiolan-2-thione with nitrosonium tetrafluoroborate at 25 °C consistently produced 1,3-dithiolan-2-one[5] in 12 ± 2% yield. Since these reactions were performed under an inert atmosphere of nitrogen or argon and all reagents and acetonitrile were rigorously dried, it appeared unlikely that the formation of 1,3-dithiolan-2-one was due to water contamination. Furthermore, the gaseous products resulting from the reaction of 1,3-dithiolan-2-thione with nitrosonium tetrafluoroborate included nitrogen and nitrous oxide, products that are consistent with the formation of thiazyl compounds and their subsequent reactions with nitrosyl compounds.[6] These results suggested that 1,3-dithiolan-2-one was formed by nitrosative exchange of sulphur for oxygen and that the processes represented by equations (1) and (2) are competing reactions linked through an *S*-nitrosated thiocarbonate intermediate. To test this hypothesis, 1,3-dithiolan-2-thione was added to $NO^+BF_4^-$ (1 equiv.) in acetonitrile that was saturated with nitric oxide. As expected, there was a substantial increase in the yield of 1,3-dithiolan-2-one relative to (**1**) (35% 1,3-dithiolan-2-one at 25 °C, 54% at 0 °C); elemental sulphur was also produced in amounts that were commensurate with the yield of 1,3-dithiolan-2-one. 1,3-Dithiolan-2-thione was unreactive towards nitric oxide.


SCHEME

Treatment of (**1**) with nitric oxide in acetonitrile also yielded 1,3-dithiolan-2-one. For example, treatment of (**1**) with a saturated solution of nitric oxide for 3 h at 25 °C gave a mixture of 34% 1,3-dithiolan-2-one and 66% (**1**). The reversible chemical oxidation of 1,3-dithiolan-2-thione is apparent in this observation; the reversible electrochemical generation of dications from tetrathioethylenes has recently been reported.[7]

These results are consistent with the process represented in the Scheme and suggest a more complex behaviour of thiocarbonyl compounds in oxidation reactions than has been previously reported.

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