

CLAY-SUPPORTED REAGENTS IV.¹

A NOVEL COUPLING OF THIOLS INTO DISULPHIDES, VIA THIONITRITE INTERMEDIATES
USING A CLAY-SUPPORTED NITROSATION REAGENT.

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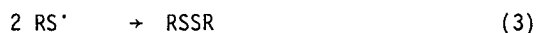
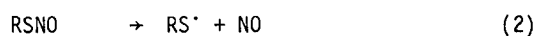
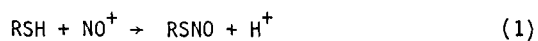
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Abstract : Thiols are converted into symmetrical disulphides, under very mild conditions, by bentonite-supported $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$.

THIONITRITES are becoming increasingly useful as sources of thiyl radicals², or as nitrosating reagents³. Hence, the search for a mild set of conditions to prepare them from thiols^{4,5,6,7}. We have recently reported the stereospecific conversion using "clayfen"¹, i.e. K-10 clay-supported ferric nitrate⁸, of various alcohols into nitrite esters, with retention of configuration. This strongly suggests potentialities of this reagent analogous to those of nitrosyl halides NOX , of salts of NO^+ nitrosonium ions, or of dinitrogen tetroxide N_2O_4 .

Because of all the potential advantages of what would be the first supported nitrosation reagent (mild conditions, ease of set-up and of work-up⁹), we have explored the method on the oxidative coupling of thiols into disulphides. This is a reaction likely to occur by a thionitrite pathway of the type⁴ :



We are pleased to report indeed, with the sole exception of the t-butylmercaptan, formation of the symmetrical RSSR disulphides with fair to excellent yields (Table 1). This method, as compared with nitric oxide or nitrogen dioxide oxidation⁴, has the advantage of not requiring gaseous nitrogen oxides as reagents; and it is a novel way of activating thiols into thionitrites⁷, using extremely mild reaction conditions, such as hydrocarbon solutions and ambient temperature.

Thiol	Isolated yield ^a (%)	Solvent	Observations
C ₆ H ₅ SH	97	hexane	b
4-NO ₂ -C ₆ H ₄ SH	58	toluene	c
2,4,5-Cl ₃ C ₆ H ₂ SH	80	toluene	c
C ₆ H ₅ CH ₂ SH	85	toluene	c
(C ₆ H ₅) ₃ CSH	65	benzene	c
<u>n</u> -C ₄ H ₉ SH	88	pentane	b
<u>i</u> -C ₃ H ₇ SH	39	pentane	b,d
<u>t</u> -C ₄ H ₉ SH	- ^e	pentane or hexane	

^a unoptimized, refers to pure compounds with satisfactory analyses and identification; is quite sensitive to dilution⁷. ^b 0.1 mole thiol in 250 ml of solvent, adding 50 g "clayfen". ^c 0.02 mole thiol in 100 ml of solvent, adding 10 g "clayfen". ^d slight heating needed to promote gaseous evolution; low yield results from extensive foaming during work up, which requires Kugelrohr vacuum evaporation, losses are due to the volatility of the disulphide. ^e even under reflux, discolouration is very slow, and reaction leads to a complex products mixture.

Table 1. Formation of disulphides from thiols.

When freshly prepared "clayfen" is added to an hydrocarbon solution of the thiol, one observes the gradual development of an intense colouration - bright red or dark green, depending on the substrate -, indicative of thionitrite formation⁷. This is followed by a sudden evolution of nitric oxide, with concomitant colour fading. Filtration affords an almost colourless solution from which the disulphide is isolated.

A control experiment, upon $n\text{-C}_4\text{H}_9\text{SH}$ in pentane, admixed with a pentane suspension of powdered $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$, in the absence of the clay, shows essentially no reaction. Similarly, no significant amount of disulphide was produced with the K-10 clay alone.

In order to show conclusively the intermediacy of a thionitrite (steps (1) and (2)), a reaction with triphenylmethanethiol as substrate was quenched (filtration and chilling before nitric oxide evolution). UV spectral analysis of the filtrate showed ca. 10 % conversion of thiol into triphenylmethylthionitrite ($\lambda_{\text{max}} (\text{C}_6\text{H}_6) \pm 2 \text{ nm} : 353, 602; A_{353}/A_{602} = 17; \text{litt}^{10} \lambda_{\text{max}} 353, 600; \epsilon_{353}/\epsilon_{600} = 16.4$). Moreover, an authentic sample of triphenylmethylthionitrite¹⁰, placed under the identical reaction conditions, readily affords the same disulphide as the original reaction. Hence, even though transition metals can induce such couplings¹¹, the main pathway here is via the thionitrite.

In summary, alcohols and thiols alike are converted by "clayfen", into the corresponding RONO or RSNO nitrites. The former can be used in the Barton reaction¹² or further oxidized into carbonyl compounds⁷; the latter can be transformed into disulphides, according to the sequence (2) + (3).

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