

Vanadium(v) oxytrinitrate, VO(NO₃)₃. A powerful reagent for the nitration of aromatic compounds at room temperature under non-acidic conditions

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Vanadium(v) oxytrinitrate is an easy to handle reagent which can be used to nitrate a range of substituted aromatic compounds in dichloromethane at room temperature, leading to >99% yields of nitration products in most cases.

The nitration of aromatic compounds is an immensely important industrial process, and a plethora of new methods and procedures have become available recently which address contemporary issues such as selectivity, safety, economy, waste and the environment.¹ Hitherto, traditional methods for the nitration of aromatic compounds have used mixtures of nitric acid and sulfuric acid which have not always been selective and lead to problems associated with waste disposal under environment friendly conditions. Low oxides of nitrogen in the presence of ozone (Kyodai nitration),² and dinitrogen pentoxide (prepared by the oxidation of N₂O₄ with O₃) in nitric acid³ or liquid sulfur dioxide⁴ show promise as pollution-free cocktails for aromatic nitrations, and the advantages of using solid supports,⁵ molecular sieves, zeolites, and recyclable Lewis acid catalysts, *eg.* lanthanide(III) triflates,⁶ have been emphasised by a number of researchers.

Inorganic metal nitrates in the presence of strong mineral acids have also been used to nitrate aromatic compounds,⁷ and in some cases organic acids have been included in the reaction media.⁸ In earlier work⁹ we have shown that vanadium(v) oxytrinitrate can be produced on a large scale by the reaction between vanadium pentoxide and dinitrogen pentoxide.¹⁰ The oxytrinitrate is a yellow liquid (mp 2 °C) which, although

it hydrolyses in moist air, can be handled as a solution in dichloromethane at room temperature. We now show how this oxytrinitrate can be used as a powerful reagent for the convenient nitration of aromatic compounds in high yields.

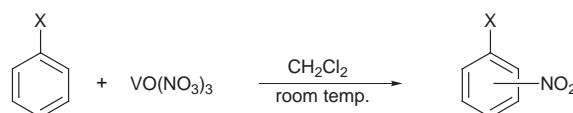
Thus, in our procedure, the aromatic compound was simply added rapidly to a preformed solution of VO(NO₃)₃ in dichloromethane (~12 wt%) at room temperature. An orange suspension was formed during the course of the reaction, and after an appropriate period of time (see Table 1), the mixture was quenched with water and the product was extracted with dichloromethane. The yields and ratios of the products were then determined by analysis of ¹H NMR spectra using 1,1,2,2-tetrachloroethane as an internal standard.

As can be seen from Table 1, the nitrations of most mono-substituted benzene derivatives with *one* equivalent of VO(NO₃)₃ are complete within 3–20 min at room temperature, and lead to quantitative yields of nitration products. Only strongly deactivated aromatic compounds such as nitrotoluene, methyl benzoate and benzoic acid required long periods of time for nitration, and benzonitrile failed to react at all.

The nitrations of anisole, phenol and acetanilide, in contrast to most other methods, led to excellent yields of nitration products (Table 1). In the cases of phenol and anisole trace amounts of 1,4-benzoquinone were produced concurrently, and the nitration of *ortho*-nitrotoluene with *one* equivalent of VO(NO₃)₃ led to a 3:1 mixture of 2,4- and 2,6-dinitrotoluenes in quantitative yield.

The product patterns obtained from the nitrations of toluene,

Table 1 Nitration of aromatic compounds with an equimolar ratio of VO(NO₃)₃



X	t/min ^a	<i>ortho</i> (%)	<i>meta</i> (%)	<i>para</i> (%)	2,4-disub. (%)	Yield (%)
H	10	>99; nitrobenzene				>99
CH ₃	6	35	2	41	19	>99 ^b
Bu ^t	3	11	6	77	6	>99
OH	0.5	32		9	51	93 ^c
OMe	15	23		38		61 ^d
Br	20	48		52		>99
Cl	20	43		57		>99
I	20	35		62		97
NHAc	15	37		48		85 ^e
CO ₂ H	5 d	15	37	2		54 ^f
CO ₂ Me	2 d	29	67	4		>99
CN	26 h					0 ^g

^a Minutes if not stated otherwise. ^b 2,6-Dinitrotoluene was formed in 3% yield. ^c 2,6-Dinitrophenol was formed in 1% yield and 1,4-benzoquinone was formed in 3% yield. ^d 1,4-Benzoquinone was formed in 5% yield. ^e 10% Recovered starting material. ^f 46% Recovered starting material. ^g >99% Recovered starting material.

Table 2 Nitration of aromatic compounds with $\frac{2}{3}$ equivalents of $\text{VO}(\text{NO}_3)_3$

X	t/min ^a	ortho (%)	meta (%)	para (%)	Yield (%)
CH ₃	3	50	3	47	>99 ^b
Bu'	3	14	6	80	>99
I	20	34		63	97
CO ₂ Me	4 d	27	67	4	98

^a Minutes if not stated otherwise. ^b Trace amounts of 2,4- and 2,6-disubstituted products were produced concurrently.

tert-butylbenzene and phenol with $\text{VO}(\text{NO}_3)_3$ all indicated that more than one of the nitro groups from the reagent was transferred during the reactions. Further investigations showed that two equivalents of $\text{VO}(\text{NO}_3)_3$ are sufficient to achieve quantitative nitration of three equivalents of the aromatic compound (Table 2); as expected this stoichiometry led exclusively to the mono-nitrated product.

We have demonstrated that $\text{VO}(\text{NO}_3)_3$ is an extremely powerful and efficient nitrating agent for aromatic compounds under simple conditions. Evidence suggests that oxides of nitrogen are liberated during the reaction cycles thereby leading to the possibility that the 'reagent' can be regenerated in the presence of these oxides, and act as a highly active catalyst. These and other developments of $\text{VO}(\text{NO}_3)_3$ in catalytic nitration processes are in progress.

Acknowledgements

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- 9 Vanadium(v) oxytrinitrate was produced from the reaction of vanadium pentoxide with dinitrogen pentoxide using a modification of the procedure described by Schmeisser: M. Schmeisser, *Angew. Chem.*, 1955, **67**, 493. The dinitrogen pentoxide was most conveniently prepared by the dehydration of white fuming nitric acid with phosphorus pentoxide at 50 °C in the presence of a slow stream of ozone, cf. N. S. Gruenhut, M. Goldfrank, M. L. Cushing and G. V. Caesar, *Inorg. Synth.*, 1950, **3**, 78.
- 10 (a) The vanadium(v) oxytrinitrate, like all other nitrates, is moisture sensitive and it was stored and handled in a dry nitrogen filled glovebox containing 3 Å molecular sieves or *in vacuo* on a standard vacuum manifold. The reagent can be stored at room temperature in a glovebox for long periods of time. Slow decomposition occurs at temperatures above 80 °C but beyond this we have no information regarding the thermal stability of $\text{VO}(\text{NO}_3)_3$. We therefore recommend **CAUTION** with respect to the use and storage of vanadium oxytrinitrate; (b) although CH_2Cl_2 was used as solvent in all the studies described, vanadium(v) oxytrinitrate is also soluble in CCl_4 , CH_3NO_2 , cyclohexane and CFCl_3 . With CH_3CN it forms a complex $\text{VO}(\text{NO}_3)_3\text{-CH}_3\text{CN}$ which has a low nitrating ability, and other coordinating solvents like ethers, aromatics and amines are not expected to be compatible with the reagent.

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