

# AN ENVIRONMENTALLY-FRIENDLY ROUTE TO NITRAMINES AND NITRATE ESTERS VIA NITRODESILYLATION CHEMISTRY USING DINITROGEN PENTOXIDE

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## Abstract

Nitramines and nitrate esters are synthesised conventionally using strongly acidic nitration media such as sulphuric-nitric acid mixtures, and the resulting spent liquors from these nitrations are difficult to dispose of without damage to the environment. The novel method described here dispenses with the need for strong acids as the reaction medium and instead uses dinitrogen pentoxide ( $N_2O_5$ ) in an inert solvent as the nitrating agent. The  $N_2O_5$  cleaves heteroatom-silicon bonds, in silylamines and silyl ethers respectively, to yield the desired energetic groupings (nitramines or nitrate esters respectively) without liberation of acids which would occur with conventional substrates (amines or alcohols). These nitrodesilylation reactions proceed cleanly and in good yield, and furthermore the co-product, a silyl nitrate, can be used to effect further nitrations, hence eliminating the need for disposal.

The scope of the reaction will be illustrated by 25 examples, some of which produce high energy compounds, notably plasticisers and an energetic polymer precursor, whilst in others novel energetic functions such as N-nitroaziridines can be accessed directly for the first time. When taken in conjunction with the current advances in  $N_2O_5$  chemistry in other fields, which have made this reagent available on large scale at reasonable cost, the use of clean routes to energetic materials such as those described here constitutes a powerful reason for changing the methods of manufacture of energetic materials in the next century.

## Introduction

Nitramines and nitrate esters are classes of compounds which find widespread application in propellant and explosive technology<sup>1-3</sup>. Nitrate esters also find use in medicine as vasodilators<sup>4,5</sup>. The chemistry of each class of compound has been reviewed<sup>6,7</sup>, and their methods of preparation by traditional routes will first be considered before describing the chemistry involved in the novel desilylative routes. Finally the advantages in the novel chemistry will be assessed, particularly from the environmental point of view.

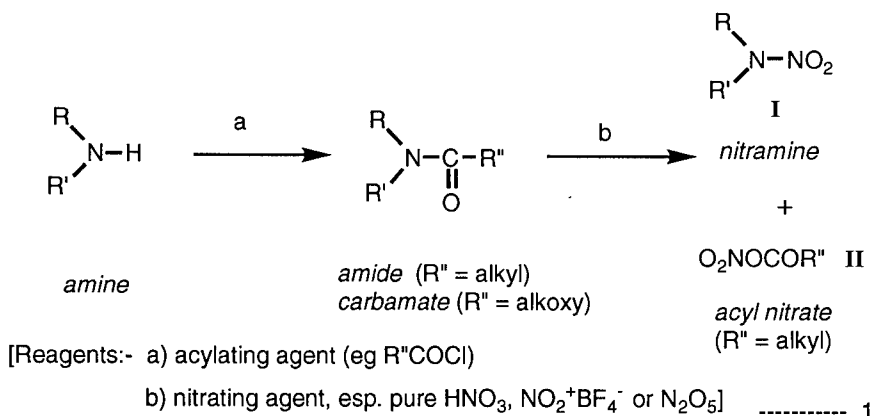
### *Nitramines*

Nitramines are commonly prepared by the reaction of secondary amides with nitric acid in dehydrating media such as acetic anhydride<sup>8</sup>, although other routes are possible, for instance by the addition of nitrate salts of secondary amines to acetic anhydride in the presence of a catalyst, e.g. chloride ion<sup>9</sup>, by direct interaction of an amine with dinitrogen pentoxide,  $N_2O_5$ <sup>10</sup>, or by nitrolysis of gem-diamines with nitric acid-acetic anhydride<sup>11,12</sup>. More recently developed methods include the reaction of N,N-dialkyl-amides with nitronium tetrafluoroborate<sup>13</sup>, the reaction of *tert.*-butylamines with nitric acid or  $N_2O_5$ <sup>14</sup>, and the action of nitric acid-acetic anhydride on *tert.* amines with *in situ* oxidation of the resulting

nitrosamines with peracetic acid<sup>15</sup>. (Routes involving oxidation of isolated nitrosamines have been disregarded owing to the high toxicity of these compounds.)

Many of these routes have disadvantages such as contamination of the product by nitrosamines which are awkward to remove<sup>16</sup>, the use of reagents which are not available cheaply on an industrial scale (e.g.  $\text{NO}_2\text{BF}_4$ ), or the production of co-products which are difficult to dispose of, notably acyl nitrates. Further problems may arise from inaccessibility of substrates, for instance in the direct nitration of amines<sup>10</sup>, certain categories of amine either do not form the nitramine (particularly highly basic amines), or may not be preparable in their unsubstituted form (e.g. hexahydropyrimidines - see later). Such shortcomings limit the scope and utility of existing routes for the synthesis of nitramines.

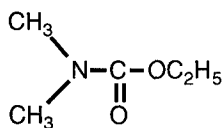
The problems outlined above are exemplified in one of the most commonly used routes for nitramine synthesis, namely the reaction of secondary amides with nitric acid under dehydrating conditions (eqn 1), where the cleavage of the N-acyl bond results in formation of the desired nitramine (I), but an acyl nitrate co-product (II) is also formed during the reaction (termed a nitrolysis<sup>8</sup>). The disposal of these acyl nitrates is awkward and also poses safety



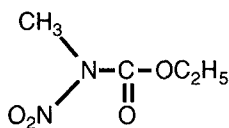
problems in certain circumstances, for instance in the synthesis of HMX from DADN<sup>17</sup>. A further drawback of the nitrolysis of acylamines is that cleavage of N-C bonds *other* than the acyl linkage may occur, resulting in competing reaction pathways and hence lower yields and product contamination, and in extreme cases little of the desired product may be formed (e.g. N,N-dimethylurethane (III) yields ethoxy N-methyl-N-nitrocarbamate (IV) instead of N,N-dimethylnitramine<sup>18</sup>). Finally, some acyl derivatives of polycyclic polyamines (e.g. the precursor of bicyclo-HMX, V) are completely inert to nitrolysis<sup>19</sup>.

#### Nitrate esters

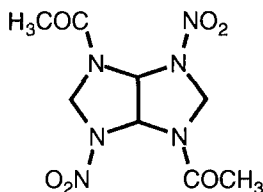
The majority of the methods reported for the synthesis of this class of compounds has relied on the use of mixed acids ( $\text{HNO}_3\text{-H}_2\text{SO}_4$ ) or pure nitric acid, both of which media



III



IV



V

suffer from disposal problems of spent liquors which are unfriendly to the environment. Some methods utilising transfer nitrating agents<sup>7b,7c</sup> would appear to offer an escape from these problems until it is realised that nitronium tetrafluoroborate ( $\text{NO}_2\text{BF}_4$ ), a chemical which requires aggressive reagents for its synthesis, is required for the preparation of these reactants, whilst more recent methods utilising either silver salts<sup>20</sup> or Lewis acids (e.g.  $\text{BF}_3$ )<sup>21</sup> can be ruled out on grounds of hazard and expense.

## Discussion

### Nitramines

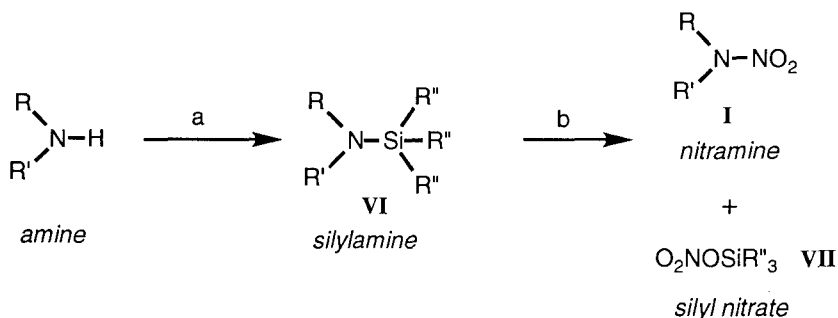
In an attempt to overcome the twin problems of controlling the direction of nitrolysis reactions and forming more easily handleable co-products, the replacement of acyl functions by other readily nitrolysable groups was considered. It was felt that these problems stemmed largely from the inertness of the nitrogen atom towards electrophilic attack as a result of the electron-withdrawing acyl function, and therefore employment of substituents with the opposite inductive effect, i.e. electron-donating substituents, would be beneficial. With this rationale in mind, obvious candidate elements for consideration would be the group IV metalloids, and it was already known that stannylamines could be nitrolysed to yield nitramines<sup>22</sup>. Furthermore, publications in the mid-1980s had indicated that C-silyl compounds could be cleaved by reagents such as nitronium tetrafluoroborate to yield C-nitro compounds<sup>23</sup>. However, as no reports were known of the nitrolysis of the corresponding N-silyl compounds, silylamines (VI), this therefore seemed an obvious class of compound to examine.

In the subsequent discussion, the N-silyl substrates are divided into two categories - i) dialkylsilylamines and ii) cycloalkyl silylamines, with thirteen examples in all. The nitrodesilylation reactions of twelve silyl ethers are described later.

#### i) Dialkylsilylamines

The silylamines (VI) were derived from the corresponding secondary amines, formed *in situ* where necessary (e.g. VII). Reaction with dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ) in halogenated solvents such as dichloromethane generated the nitramines (I) cleanly and in good to excellent yield (eqn. 2 and Table 1). The reaction was found to be general for a

range of alkyl substituents both on nitrogen (R & R') and silicon (R''), with the highest yields being obtained with trimethylsilyl derivatives (R = CH<sub>3</sub>, see Table 1). The reaction is



[Reagents:- a) silylating agent (R''<sub>3</sub>SiX where X is a leaving group such as halogen, dialkylamino etc)

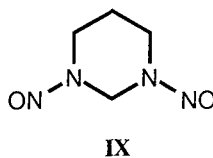
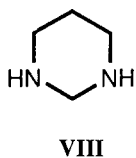
b) nitrating agent, esp. N<sub>2</sub>O<sub>5</sub>, also NO<sub>2</sub>BF<sub>4</sub>]

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applicable to cases which have proved troublesome in the past, for instance sterically hindered nitramines such as **If**, and yields were in many cases improved, sometimes markedly, upon those hitherto obtained.

#### ii) Disilylamines and Silylaziridines

Cyclic dinitramines (**II** & **Im**) were likewise preparable without difficulty from the corresponding disilyl precursors. It is notable that the precursor to **Im**, N,N'-bis-(trimethylsilyl)hexahydropyrimidine (**IIIm**, Table 1) is derived from an unstable diamine (hexahydropyrimidine, **VIII**) and highlights an intrinsic advantage of the novel nitration over other methods which require the use of the free amine, which may be unavailable. Furthermore, the dinitramine product (**Im**), which contains a geminal dinitramine moiety which is a substructural fragment found in the RDX and HMX molecules, is preparable in a

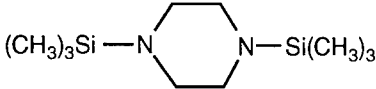
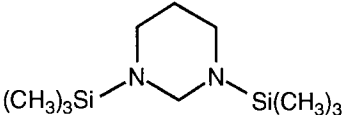


yield (69%) twice that reported in the hitherto best method (by nitro-denitrosation of the N,N'-dinitroso compound **IX**<sup>24</sup>). This hints at the potential of this reaction, and its viability is subject only to the availability of suitable silylated precursors; in this respect, few limitations have been encountered, one of the few groups which is incompatible with silylating agents being the nitrile group.

Table 1: Reactions of Silylamines with  $N_2O_5$ 

Silylamine		$R^1R^2N-Si(R^3)_2R^4$	$R^3$	$R^4$	$\frac{Rn.}{Time}$ (hr)	$\frac{Rn.}{Temp.}$ (°C)	$\frac{Yield\ of}{Nitramine}$ (%)
1. Monosilylamines							
No.	$R^1$ $R^2$						
VI	$\underbrace{\hspace{2cm}}$						
a	$-(CH_2)_2O(CH_2)_2-$	$CH_3$	$CH_3$	2	$0 \pm 2$	80	
b	$-(CH_2)_5-$	"	"	0.75	$-5 \pm 2$	81	
c	$-(CH_2)_4-$	"	"	0.5	-7 to -1	76	
d	$CH_3$ $CH_3$	"	"	0.75	$-5 \pm 2$	78	
e	$C_2H_5$ $C_2H_5$	"	"	0.75	$-5 \pm 2$	84	
f	$i-C_4H_9^\dagger$ $i-C_4H_9$	"	"	0.75	-5 to 0	87	
g	$-(CH_2)_2O(CH_2)_2-$	"	$t-C_4H_9$	$\left\{ \begin{array}{l} 2.25 \\ 6 \end{array} \right.$	0 to +5	37	
					+5 to +10	40*	
h	"	$n-C_4H_9$	$n-C_4H_9$	1.5	-5 to +5	39	
i	"	$C_2H_5$	$C_2H_5$	0.75	0 to +5	61*	
j	$i-C_4H_9^\dagger$ $i-C_4H_9$	"	"	1	0 to +5	70	
k	$-CH_2-CH(CH_3)-$	$CH_3$	$CH_3$	10 min.	$0 \pm 5$	‡	

## 2. Disilylamines

l		1	-8 to 0	91
m		1	-5 to +5	69**



i) *Acyclic silyl ethers*

These silyl ethers, which share the common feature that the silicon atom bears only one O-substituent, were prepared from the corresponding alcohols by literature methods<sup>30</sup>. In the case of trimethylsilyl ethers, hexamethyldisilazane was used (Eqn. 5) and this was applied to both monohydric (**a - c, f**) as well as dihydric (**d & e**) examples. Derivatives with longer alkyl chains were prepared from the corresponding silyl chlorides in the presence of an auxiliary base and a catalyst (4-(dimethylamino)pyridine, DMAP; Eqn. 6). Preparative

Table 2: Reactions of Silyl Ethers with  $N_2O_5$ 

<u>Entry</u>	<u>Silyl Ether</u>	<u><math>N_2O_5</math> used</u> (mol)	<u>Rn. Temp.</u> °C	<u>Rn. Time</u> h	<u>Nitrate</u> <u>Ester</u>	<u>Yield</u> %
i)	2-ethylhexanol TMS ( <b>XIIIa</b> )	1.1	-5 to +8	1.5	<b>XIVa</b>	92
ii)	n-decanol TMS ( <b>XIIIb</b> )	1.1	-5 to +8	1.5	<b>XIVb</b>	87*
iii)	2-octanol TMS ( <b>XIIIc</b> )	1.1	-5 to +15	5†	<b>XIVc</b>	88
iv)	hexane-1,6-diol bis-TMS ( <b>XIIIId</b> )	2.2	-5 to +3	0.75	<b>XIVd</b>	83
v)	2,2-(pentamethylene)-propane- 1,3-diol bis-TMS ( <b>XIIIe</b> )	5.5**	-20 to +10	1.5	<b>XIVe</b>	**
vi)	3,3-bis(TMSoxymethyl)oxetane ( <b>XIIIIf</b> )	2.2	-5	2.0	<b>XIVf</b>	35
vii)	2-aziridineethanol TMS ( <b>XIIIg</b> )	2.2	-10 to +5	1.5	<b>XVIII</b>	56††
viii)	2-ethylhexanol TBDMS ( <b>XIIIh</b> )	1.15	-5 to +5	18	<b>XIVa</b>	<5
viii)a	" " "	2.0	-5	18	"	35
ix)	2-ethylhexanol tri(n-butyl) ( <b>XIIIi</b> )	1.1	-5	18	<b>XIVa</b>	87
ix)a	" " "	2.0	-5	18	"	94
x)	2-ethylhexanol tri(isopropyl) ( <b>XIIIj</b> )	1.1	-5	18	<b>XIVa</b>	29
x)a	" " "	2.0	-5	18	"	53
xi)	2,2-dimethylpropane-1,3-diol cyclic DMS ( <b>XIX</b> )	2.2	-10 to +3	1.5	<b>XXII</b>	‡
xii)	butane-1,2-diol cyclic DMS ( <b>XX</b> )	5.0	-5	24	<b>XXIII</b>	66

Notes

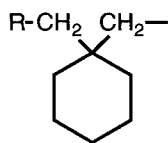
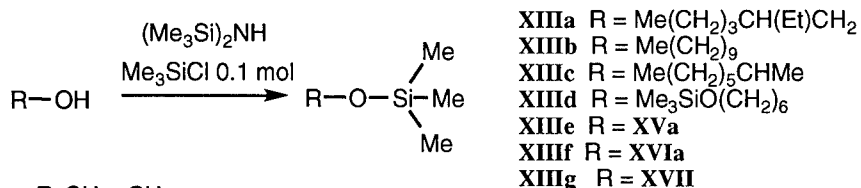
\* The organic extract floated on brine.

† Reaction was incomplete after 2.5 h (nmr).

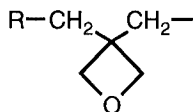
\*\* Impure product obtained, also with lower mol ratios of  $N_2O_5$ .

†† Nitramine-nitrate prepared, but impure.

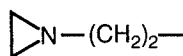
‡ Main product obtained is silyl nitrate (for structure see text)



**XVa** R = Me<sub>3</sub>SiO  
**XVb** R = O<sub>2</sub>NO

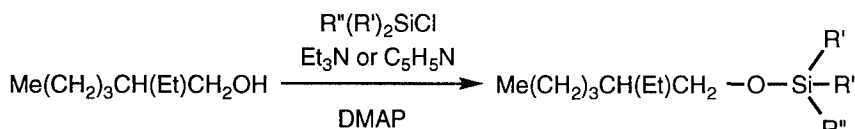


**XVIa** R = Me<sub>3</sub>SiO  
**XVIb** R = O<sub>2</sub>NO



**XVII**

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**XIIIh** R' = Me, R'' = Bu<sup>t</sup>

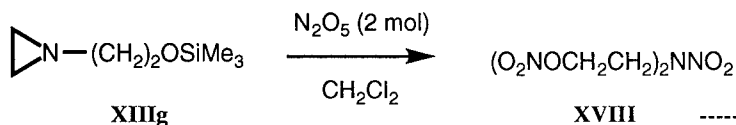
**XIIIi** R' = R'' = Bu<sup>n</sup>

**XIIIj** R' = R'' = Pr<sup>i</sup>

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yields were generally in the range 75 to 93%. In one case (**XIIIg**) a second functionality (an aziridine ring) was present in the molecule, offering the possibility of introducing further energetic moieties by ring-opening nitration<sup>31</sup>.

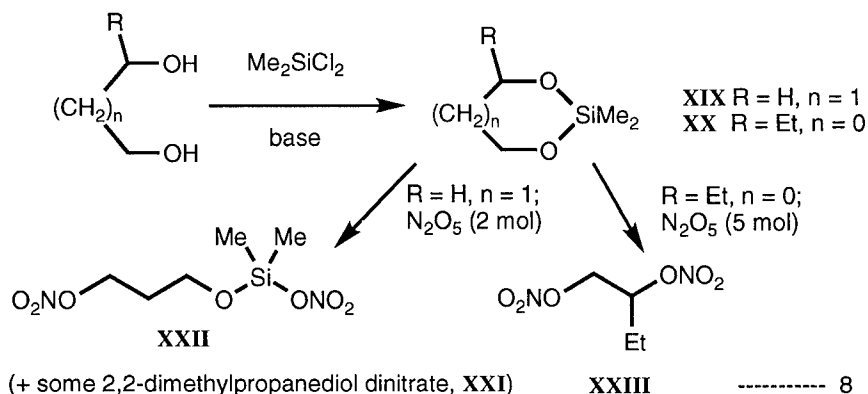
When the simple trimethylsilyl ethers **XIIIa-d** were treated with a small excess of N<sub>2</sub>O<sub>5</sub> in dichloromethane, the corresponding nitrate esters **XIVa-d** were obtained cleanly and in high (83-92%) yield (see Eqn. 4 and Table 2, entries i) - vi)). The secondary example (**XIIIc**) reacted more slowly but the ultimate yield of nitrate ester **XIVc** (after 5 h at near ambient temperature) was in line with the other examples. The difunctional trimethylsilyl ethers **XIIIe-f** gave much lower yields owing to the neopentyl situation of the silyl ether functions, which gives rise to much reduced reactivity because of steric hindrance. The remaining trimethylsilyl ether, **XIIIg**, was treated with 2 mol N<sub>2</sub>O<sub>5</sub> to enable reaction to occur on the aziridine function as well as the silyl ether, and a moderate (56%) yield of the known nitramine-nitrate (DINA, **XVIII**) was obtained (Eqn. 7).





The remaining acyclic silyl ethers **XIIIh-j** (Table 2, entries viii - x), which bore longer alkyl chains (up to C<sub>4</sub>) on the silicon atom (the alcohol chain, R, was in all cases 2-ethylhexyl), in general reacted more slowly with N<sub>2</sub>O<sub>5</sub>, mirroring the trends found in the silylamine reactions (see above). In particular, those with branched alkyl substituents were the least reactive, and with *tert.*-butyldimethyl substitution on Si a maximum yield of **XIVa** of only 35% was attained, even under forcing conditions (100 molar % excess of N<sub>2</sub>O<sub>5</sub> for 18 h). These findings indicate that if, for instance, it were necessary to use a *tert.*-butyldimethylsilyl ether in a synthetic strategy (e.g. as a blocking group) then the nitrate ester could not be generated efficiently by direct reaction with N<sub>2</sub>O<sub>5</sub>, and alternative strategies might have to be sought. Completing the reactivity comparison of compounds **XIIIh-j**, it is apparent that the tri(*n*-butyl) derivative is the most reactive towards N<sub>2</sub>O<sub>5</sub>, giving similar yields to the trimethylsilyl examples (although with substantially longer reaction times), whilst the tri-(isopropyl) derivative displays an intermediate reactivity, yielding up to 53% nitrate ester **XIVa**.

ii) Cyclic silyl ethers



Two compounds in this class were studied: **XIX** and **XX**. They were prepared (Eqn. 8) from the corresponding 1,2- or 1,3-diols by reaction with dichlorodimethylsilane according to the literature<sup>32</sup>. The products obtained upon treatment with N<sub>2</sub>O<sub>5</sub> were strongly dependent on the conditions. Thus with **XIX**, use of a small excess of N<sub>2</sub>O<sub>5</sub> and a short reaction time resulted in the isolation of very little of the desired dinitrate **XXI**, and the major product was the partially cleaved silyl nitrate **XXII**. This compound belongs to a class of compounds, the silyl nitrates, which have received scant attention in the literature<sup>33</sup>. It showed interesting spectral properties whereby unusual nitrate ester bands at 1263 (symm. NO<sub>2</sub> stretch) and 808 (ONO<sub>2</sub> group) cm<sup>-1</sup> were observed, which were at lower frequencies than those of C-nitrates by some 15 and 60 cm<sup>-1</sup> respectively, presumably on account of the attachment of the heavier silicon atom in place of carbon.

On the other hand, when silyl ether **XX** was treated with a large (150%) excess of  $N_2O_5$  and allowed to react for a protracted period, the dinitrate **XXIII** was obtained in useful (66%) yield (Eqn. 8). Presumably **XIX** would also give a substantial yield of **XXI** under similar conditions, but insufficient sample remained to test this hypothesis.

## Conclusions

Therefore nitrodesilylations of silylamines and silyl ethers by  $N_2O_5$  afford the corresponding nitro compounds, nitramines and nitrate esters respectively, generally in good to excellent yields. With the silylamines the reaction<sup>34</sup> is of wide applicability, and products bearing 1,3-bis-(N-nitro) functions are accessible such as **Im**. The success of the method in this case is significant and augurs well for the extension to polynitramines. The conditions necessary to effect the cleavage of the N-Si bond are much milder than, for instance, those required to cleave N-acyl substrates (i.e. amides) and suggest applications in those areas where cleavage of acetamides have failed to yield nitramine products, e.g. polycyclic nitramines such as bicyclo-HMX<sup>19</sup>.

The by-product from the nitration reaction, the volatile silyl nitrate  $(CH_3)_3SiONO_2$  (**VII**,  $R'' = CH_3$ , Eqn 2), is a nitrating agent in its own right<sup>35</sup> and could easily be collected by distillation and used profitably to carry out other nitrations, such as toluene to dinitrotoluene. The formation of silyl nitrates such as **VII** is also preferable to the acidic by-products (viz.  $BF_3$  or  $HBf_4$ ) which would arise from the corresponding reactions with  $NO_2BF_4$ . Another advantage is the non-acidic nature of the reaction medium which suggests applications involving acid-sensitive substrates hitherto precluded from study in conventional nitration media.

Likewise the reaction of silyl ethers with  $N_2O_5$  is a viable means of synthesising nitrate esters, particularly when the alkyl silicon substituents possess short or unbranched chains (particularly methyl), and yields in excess of 90% can be realised. When these substituents are branched chains the yields are lower, and with *tert.*-butyl derivatives the yield is only acceptable under forcing conditions. The short chain derivatives have the added advantage that the silyl nitrate by-product is more volatile, resulting in easier separation and purification of the nitrate ester product; hence the use of the longer chain derivatives should only be entertained if other considerations dictate that their usage is essential, e.g. protecting group strategies.

With cyclic silyl ethers, although only two cases were studied, it became apparent that more forcing conditions are necessary for the satisfactory preparation of dinitrates from these substrates. This may cause some problems if these functions are to be used in a protecting group capacity, since excesses of  $N_2O_5$  necessary for their complete removal may interfere with functional groups elsewhere in the molecule. In this respect the silyl ethers differ from the silylamines investigated earlier, where reactivities were in general higher, even on

electron-deficient functions such as amides. Such reactivity trends are to be expected owing to the well-established difference in basicity of these elements resulting from the relative availability of the electrons in their respective lone pairs to participate in bonding. Thus the nitrogen lone pair is loosely bound and hence can readily form a sigma bond on approach of an electrophile such as the nitronium ion (which exists in  $N_2O_5$  solutions under laboratory conditions<sup>36</sup>). On the other hand, the more tightly bound lone pairs on oxygen are more reluctant to do so, resulting in lower reactivities with this class of compound, in agreement with experimental observation.

Finally, it should be emphasised that this approach to nitramines and nitrate esters comprises a novel alternative to methods employing strong mineral acids, and will overcome many of the problems inherent in the latter concerning the disposal of waste acid liquors. These liquors are in some cases quite hazardous owing to the solubility of some nitrate esters in them (e.g. triethyleneglycol dinitrate shows *ca* 9% vol./vol. solubility in spent  $HNO_3$ - $H_2SO_4$ <sup>37</sup>), and care is required in their handling and disposal. Furthermore, the solubility of certain nitrate esters in water can be problematic (e.g. ethyleneglycol dinitrate shows *ca* 4% wt./vol. solubility in water<sup>38</sup>, a high figure for a covalent ester) and the necessity of water washing in conventional processes can be a distinct disadvantage. All of these factors must be taken into consideration when designing environmentally-friendly processes for the manufacture of energetic materials, such as will have to be employed next century in order to meet new legislation<sup>39</sup>. Nitrodesilylation methodologies such as those described here are well placed to meet such requirements, and offer the opportunity to solve many of the problems inherent in the clean manufacture of energetic ingredients for munitions applications.

### Acknowledgements

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### Experimental

#### *Silylamine Preparations and Their Reactions with $N_2O_5$ .*

Details have been presented elsewhere<sup>40</sup>.

#### *Silyl Ethers*

The following trimethylsilyl ethers were prepared<sup>30</sup> by treatment of the corresponding alcohol with hexamethyldisilazane [HMDS] with a trace of chlorotrimethylsilane [CTMS] as follows:-

2-Ethylhexanol, n-decanol and 2-octanol: A mixture of the alcohol (0.2 mol) and HMDS (0.11 mol), to which a few drops of CTMS had been added, was heated with stirring in an oil bath in a RB flask equipped with an air condenser, initially at 60 to 65°C. The temperature was raised progressively to 150°C over 2-3 h (evolution of ammonia noted - moist indicator

paper check) and the reaction was held at this temperature overnight, or until no further ammonia could be detected. The product was then distilled, either bulb-to-bulb on a Büchi Kugelrohr GKR 50 (#) or by fractionation (Fisher Spaltrohr HMS 300 (§) or 10 cm Vigreux column (¶)), to give the pure silyl ether. Thus prepared were: i) 2-ethylhexanol trimethylsilyl ether (**XIIIa**), b.pt.(¶) 88-89°C/ 20 mm (85%); <sup>1</sup>H nmr, δ: 0.20(s,9); 1.00(t,6); 1.35(m,8); 3.5(m,2);  $v_{\max}$  (liq. film): 2959(s), 2930(s), 2867(s), 1462(m), 1382(m), 1251(s), 1092(s), 878(s), 841(s), 746(m) cm<sup>-1</sup>; ii) n-decanol trimethylsilyl ether (**XIIIb**), b.pt. (#) 164°C/ 90 mm (75%); <sup>1</sup>H nmr, δ: 0.20(s,9); 0.95(t,3); 1.32(brs,16); 3.60(t,2);  $v_{\max}$  (liq. film): 2956(s), 2926(s), 2855(s), 1467(m), 1384(m), 1250(s), 1100(s), 841(s), 746(m) cm<sup>-1</sup>; iii) 2-octanol trimethylsilyl ether (**XIIIc**), b.pt. (¶) 95-99°C/ 30 mm (74%); <sup>1</sup>H nmr, δ: 0.15(s,9); 0.85(m,3); 1.00(d,3); 1.2(m,10); 3.65(m,1);  $v_{\max}$  (liq. film): 2958(s), 2928(s), 2859(s), 1459(m), 1374(m), 1250(s), 1084(m), 841(s), 747(m) cm<sup>-1</sup>. Hexane-1,6-diol, 2,2-(pentamethylene)propane-1,3-diol<sup>41</sup> and 3,3-bis(hydroxymethyl)oxetane<sup>42</sup> were treated as above, but using 0.10 mol diol and 0.11 mol HMDS (with CTMS). Thus prepared were iv) hexane-1,6-diol bis(trimethylsilyl) ether (**XIII d**), b.pt. (#) 165-170°C/ 15 mm (93%); <sup>1</sup>H nmr, δ: 0.15(s,18); 1.45(m,8); 3.60(t,4);  $v_{\max}$  (liq. film): 2938(s), 2861(s), 1385(m), 1251(s), 1096(s), 1036(m), 873(s), 841(s), 747(m) cm<sup>-1</sup>; v) 2,2-(pentamethylene)propane-1,3-diol bis(trimethylsilyl) ether (**XIII e**), b.pt. (§) 103.5-104°C/ 4.5 mm (85%); purity (by <sup>1</sup>H nmr) ca 90%; <sup>1</sup>H nmr, δ: 0.0(s,18); 1.3(brs,10); 3.30(s,4);  $v_{\max}$  (liq. film): 2955(s), 2930(s), 2859(s), 1460(m), 1250(s), 1086(s), 885(s), 841(s), 747(m) cm<sup>-1</sup>; and vi) 3,3-bis(trimethylsilyloxy-methyl)oxetane (**XIII f**), b.pt. (#) 135-150°C/ 10 mm (60%); <sup>1</sup>H nmr, δ: 0.30(s,18); 3.85(s,4); 4.50(s,4);  $v_{\max}$  (liq. film): 1252(s), 1085(s), 870(s), 841(s) cm<sup>-1</sup>.

Long-chain silyl ethers<sup>30</sup>: 2-ethylhexanol *tert*-butyldimethylsilyl ether (**XIIIh**), b.pt. (#) 120°C/ 8mm (89%); <sup>1</sup>H nmr, δ: -0.05(s,6); 0.75(brs,5); 0.80(s,9); 1.2(brs, 10); 3.40(brs,2);  $v_{\max}$  (liq. film): 2958(s), 2929(s), 2858(s), 1472(m), 1463(m), 1384(m), 1255(s), 1095(s), 850(s), 836(s), 774(s) cm<sup>-1</sup>; 2-ethylhexanol tri-(*n*-butyl)silyl ether (**XIII i**): b.pt. (#) 160-180°C/ 0.5 mm; <sup>1</sup>H nmr, δ: 0.5-1.6(m,42); 3.5(br.s,2);  $v_{\max}$  (liq. film): 1092 cm<sup>-1</sup>; 2-ethylhexanol tri-(isopropyl)silyl ether (**XIII j**): b.pt. (#) 160-180°C/ 0.5 mm; <sup>1</sup>H nmr, δ: 1.0-1.7(m,36); 3.5(br.s,2).

### Nitrolyses

The silyl ether (20 mmol) dissolved in dry dichloromethane (*ca* 10 ml) was added dropwise over 10-15 min. to a solution of N<sub>2</sub>O<sub>5</sub><sup>43</sup> in the same solvent (20-25 ml). Quantities of N<sub>2</sub>O<sub>5</sub> used, and temperatures and times of reactions are shown in Table 1. After the appropriate reaction time, the mixture was worked up by washing with saturated sodium hydrogen carbonate solution (*ca* 50 ml), with addition of further solid sodium hydrogen carbonate if necessary, followed by washing with saturated brine. The organic extract (washed out with further dichloromethane (15-20 ml)) was then dried over anhydrous magnesium sulphate, and finally the solvent was removed on a Rotavapor to yield the nitrate ester product, which was characterised spectroscopically and, in some cases, by HPLC.

The HPLC analyses employed an internal standard method based on the response of the nitrate ester vs di-(*n*-pentyl)phthalate. A calibration curve was produced from three different concentrations of an authentic sample of the nitrate ester, and using quadratic curve fitting it was possible to calculate sample purities and hence percentage yields based on the HPLC analyses.

Thus prepared were: 2-ethylhexanol nitrate (**XIVa**); <sup>1</sup>H nmr, δ: 0.90(t,6); 1.3(m,8); 4.30(d,2);  $v_{\max}$  (liq. film) 1632(NO<sub>2</sub> as.), 1279(NO<sub>2</sub> s.), 867 (ONO<sub>2</sub> gp.) cm<sup>-1</sup>; n-decanol nitrate (**XIVb**); <sup>1</sup>H nmr, δ: 0.90(t,3); 1.3(brs,16); 4.45(t,2);  $v_{\max}$  (liq. film) 1632(NO<sub>2</sub> as.),

1280(NO<sub>2</sub> s.), 864 (ONO<sub>2</sub> gp.) cm<sup>-1</sup>; 2-octanol nitrate (XIVc); <sup>1</sup>H nmr, δ: 0.80(m,3); 1.35(m,13); 5.05(qr,1); ν<sub>max</sub> (liq. film) 1625(NO<sub>2</sub> as.), 1279(NO<sub>2</sub> s.), 876(ONO<sub>2</sub> gp.) cm<sup>-1</sup>; hexane-1,6-diol dinitrate (XIVd); <sup>1</sup>H nmr, δ: 0.15(s,18); 1.45(m,8); 3.60(t,4); ν<sub>max</sub> (liq. film) 1632(NO<sub>2</sub> as.), 1280(NO<sub>2</sub> s.), 872 (ONO<sub>2</sub> gp.) cm<sup>-1</sup>; 2,2-(pentamethylene)propane-1,3-diol dinitrate (XIVe); <sup>1</sup>H nmr, δ: 1.53(br.s,10); 4.43(s,4); ν<sub>max</sub> (liq. film) 1638(NO<sub>2</sub> as.), 1277 (NO<sub>2</sub> s.), 867(ONO<sub>2</sub> gp.) cm<sup>-1</sup>; 3,3-bis(nitratomethyl)oxetane (XIVf); <sup>1</sup>H nmr, δ: 4.65(s,4); 4.85(s,4); ν<sub>max</sub> (liq. film) 1644, 1278, 867 cm<sup>-1</sup>; DINA (XVIII); <sup>1</sup>H nmr, δ: 4.13(t,4); 4.76(t,4); ν<sub>max</sub> (mull) 1638(NO<sub>2</sub> as., n.ester), 1523(NO<sub>2</sub> as., nitramine), 1283(NO<sub>2</sub> s.) cm<sup>-1</sup>; 2,2-dimethylpropane-1,3-diol dinitrate (XXI); <sup>1</sup>H nmr, δ: 1.10(s,6); 4.28(s,4); ν<sub>max</sub> (liq. film) 1636(NO<sub>2</sub> as.), 1278(NO<sub>2</sub> s.), 866(ONO<sub>2</sub> gp.) cm<sup>-1</sup>; (XXII); <sup>1</sup>H nmr, δ: 0.05(s,6); 0.95(s,6); 3.40(d,2); 4.28(d,2); ν<sub>max</sub> (liq. film) 1632(NO<sub>2</sub> as.), 1279(NO<sub>2</sub> s.); 1263(NO<sub>2</sub> s.), 872, 808 (ONO<sub>2</sub> gp.) cm<sup>-1</sup>; butane-1,2-diol dinitrate (XXIII); <sup>1</sup>H nmr, δ: 0.5-0.8(m,2); 1.0(m,3); 4.3(m,2); 4.5(m,1); ν<sub>max</sub> (liq. film) 1640(NO<sub>2</sub> as.), 1270(NO<sub>2</sub> s.) cm<sup>-1</sup>.

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