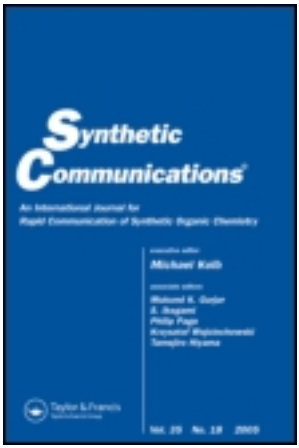

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Preparation of Alkyl Nitrates, Nitrites, and Thiocyanates from Alcohols Utilizing Trichloroisocyanuric Acid with Triphenylphosphine

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ABSTRACT

Alcohols in acetonitrile are converted into alkyl nitrates, nitrites, or thiocyanates by the action of triphenylphosphine and trichloroisocyanuric acid along with silver nitrate, silver nitrite, or sodium thiocyanate, respectively.

Key Words: Alcohols; Alkyl nitrates; Alkyl nitrites; Alkyl thiocyanates; Substitution; Preparation; Synthesis; Trichloroisocyanuric acid; Triphenylphosphine.

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INTRODUCTION

Recently we have shown that the combination of trichlorisocyanuric acid (**1**) [1,3,5-trichloro-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione; TCICA, $C_3Cl_3N_3O_3$] with triphenylphosphine will convert alcohols into alkyl chlorides and carboxylic acids to acid chlorides.[1,2] In these substitution reactions, it has been proposed that **1** and triphenylphosphine react to form a water sensitive species that is capable of reaction with an alcohol to make the oxygen a good leaving group. We report here a related procedure for the conversion of alcohols into alkyl nitrates, alkyl nitrites, and alkyl thiocyanates.

Nitrate esters were prepared by dissolving silver nitrate, triphenylphosphine, and an alcohol in anhydrous acetonitrile and then slowly adding **1**. The reaction was heated for 3 hr, and after filtration to remove the precipitate of cyanuric acid, water was added and the ester was extracted with pentane and purified by flash chromatography (Eq. 1). Using the same general procedure, nitrite esters were prepared from silver nitrite and thiocyanates were prepared from sodium thiocyanate. The results are shown in Table 1.

$$CH_3(CH_2)_7CH_2OH + AgNO_3 + (C_6H_5)_3P + C_3Cl_3N_3O_3 \longrightarrow CH_3(CH_2)_7CH_2ONO_2 \quad (1)$$

The order of addition is important. If the triphenylphosphine and **1** were first combined, as is done in the previously reported synthetic reactions, and then the silver nitrate followed by the alcohol were added, most of the alcohol was recovered unchanged. If the triphenylphosphine and **1** were combined and then the alcohol was added followed by the silver nitrate, the alkyl chloride was the major product along with some nitrate ester.

Conversion of cyclohexanol into the corresponding nitrate and nitrite esters gives low yields of products, but the two authentic standards were also formed in low yield.[3,4] Benzyl alcohol was converted into benzaldehyde instead of benzyl nitrite when using the procedure described here and also when using sodium nitrite, sulfuric acid, and benzyl alcohol in an attempt to prepare the authentic sample. Cyclohexyl thiocyanate was not formed from either the procedure described here or the literature procedure.

EXPERIMENTAL

All reagents were used as received unless otherwise stated. Anhydrous acetonitrile, 1-nonanol, 1-octanol, cyclohexanol, benzyl alcohol, 1-chlorononane, 1-chlorooctane, chlorocyclohexane, benzyl bromide, triphenylphosphine, sodium nitrite, and silver nitrite were obtained from Aldrich. **1** (99%)

Table 1. Conversion of alcohols into alkyl nitrates, nitrites, and thiocyanates.

Alcohol	Product	Yield[a] (%)	GC purity (%)
1-Nonanol	1-Nonyl nitrate	75[b]	99.6
1-Octanol	1-Octyl nitrate	63	99.7
2-Octanol	2-Octyl nitrate	72	95.8
Cyclohexanol	Cyclohexyl nitrate	27	99.2
Benzyl alcohol	Benzyl nitrate	46	96.2
1-Nonanol	1-Nonyl nitrite	65	97.8
1-Octanol	1-Octyl nitrite	60	95.9
2-Octanol	2-Octyl nitrite	39	96.6
Cyclohexanol	Cyclohexyl nitrite	9	96.5
Benzyl alcohol	Benzaldehyde	23	96.2
1-Nonanol	1-Nonyl thiocyanate	75	95.9
1-Octanol	1-Octyl thiocyanate	71	99.1
2-Octanol	2-Octyl thiocyanate	76	81.4[c]
Cyclohexanol	No thiocyanate formed		
Benzyl alcohol	Benzyl thiocyanate	62	94.7

[a]Purified by flash chromatography.
[b]Purified by distillation.
[c]Contains 17.5% of an unknown component which may be 2-octyl isothiocyanate based on the FT-IR spectrum: 2152 cm^{-1} (RSCN) and 2102 cm^{-1} (RNCS).[5]

was obtained from Chem Lab Products and OMNI. Silver nitrate and sodium thiocyanate were obtained from Baker. 2-Octanol and potassium thiocyanate were obtained from Fisher Scientific. 2-Chlorooctane was prepared from 2-octanol.[2] Pentane was distilled prior to using. Silver nitrate, silver nitrite, and sodium thiocyanate were dried under full pump vacuum for 24 hr before use.

All products were compared with authentic samples by means of ^{1}H NMR and FT-IR spectra and GC retention time. Alkyl nitrate samples were prepared from the alkyl halides and silver nitrate.[3] Alkyl nitrite samples were prepared from the alcohols, sodium nitrite, and sulfuric acid.[4] Alkyl thiocyanate samples were prepared from the alkyl nitrates and potassium thiocyanate.[3] All authentic samples were purified by flash chromatography.

^{1}H NMR spectra were recorded in $CDCl_3$ using an Anasazi-modified Varian EFT 90 MHz spectrometer. FT-IR spectra were recorded using a Perkin Elmer 1650 spectrometer. GC analyses were carried out with a Hewlett-Packard 5890 Series II on a 6 ft × 1/8 in. 10% Carbowax 20M column. The procedure below for preparation of 1-nonyl nitrate was also used for preparation alkyl nitrites and thiocyanates but silver nitrite and sodium

thiocyanate, respectively, were used in place of silver nitrate. All products and authentic samples, except for 1-nonyl nitrate, were prepared using about half a gram of alcohol or starting compound.

Conversion of 1-Nonanol into 1-Nonyl Nitrate

To an oven-dried, nitrogen-flushed, 500-mL three-neck round bottom flask fitted with a condenser, a nitrogen inlet, and two glass stoppers were added a magnet, vacuum dried silver nitrate, 8.943 g (52.6 mmol), and 200 mL anhydrous acetonitrile (via syringe). After 15 min stirring, 5.408 g (37.5 mmol) 1-nonanol and 13.973 g (53.3 mmol) triphenylphosphine were added. After 15 min of stirring, 4.299 g (18.5 mmol, 55.5 meq) of **1** was added over 1 min, and the flask was placed in an 82°C oil bath for 3 hr. The reaction mixture was vacuum filtered to remove the cyanuric acid and the solid washed with pentane. Water, 100 mL, was added to the filtrate which was then extracted with pentane (4 × 75 mL). The combined pentane extract was washed with water (100 mL) and saturated NaCl solution (75 mL). After drying over $MgSO_4$ and filtering, the pentane was removed with a rotary evaporator and the residue vacuum distilled through a concentric tube column to give 5.317 g. [75%, bp 77.5–80.3°C (27.5 torr)] of 1-nonyl nitrate. Analysis by GC showed a purity of 99.6%, and the retention time was identical to that of an authentic sample. The FT-IR and ^1H NMR spectra were identical to those of an authentic sample.

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