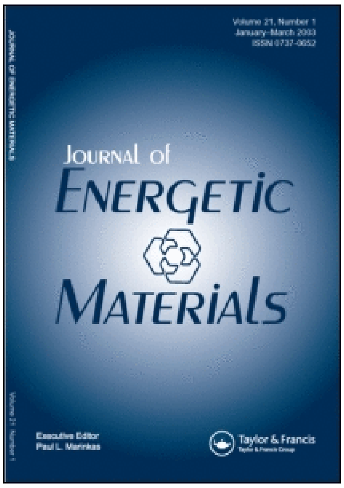

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A new synthetic route to nitrate esters

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A NEW SYNTHETIC ROUTE TO NITRATE ESTERS

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ABSTRACT

The synthesis of unsaturated nitrate esters and dinitrate esters in a single step is described. The use of NO_2BF_4 in diethyl ether -78°C has been found to be a nitration route relatively free from side reactions.

INTRODUCTION

We are engaged in a continuing study of the synthesis and characterization of new explosives involving nitrate esters stabilized by resonance and inductive effects.[1] Conventional methods of nitration of alcohols involve the use of mixed acid (a mixture of concentrated nitric and sulfuric acid) at 0°C or metathesis of the alkyl halide with $AgNO_3$ in acetonitrile.[2] However, with alcohols sensitive to facile oxidation or dehydration, the mixed acid is not suitable for the preparation of the nitrate ester; and the use of $AgNO_3$ for nitration, although fairly gentle in terms of oxidizing ability, is costly in addition to involving the extra synthetic step of converting the alcohol to the alkyl halide.

In our laboratory we have found that NO_2BF_4 is a safe, effective and specific nitrating agent suitable for the synthesis of nitrate esters containing acid sensitive and easily oxidizable functionalities. Olah has reviewed the synthetic utility of NO_2BF_4 in nitrating aromatics, amines, alkenes, carboxylic acids, alkanes, and alcohols.[3] We would like to add to that list unsaturated alcohols and diols and report that diethyl ether can be used successfully as a reaction medium at -78°C.

RESULTS AND DISCUSSION

Samples of 3-buten-1-nitrate and 1,4 butane dinitrate were needed to study the kinetics and products of thermolysis. On first attempt a classical approach was taken. To a 50:50 mixture of concentrated nitric and sulfuric acid (15 mL) maintained at 0°C, 3-buten-1-ol (6 g, 0.083 mol) was slowly added. Extensive decomposition occurred immediately. Evidently oxidation of the double bond is more facile than esterification.

To circumvent potential side reactions use of the potent nitrating reagent NO_2BF_4 was considered. Solvent selection is limited when nitronium salts are employed. Although nitronium salts are soluble in THF and acetonitrile and both are commonly used, in the presence of certain substituents side reactions can occur.[4] For example, addition of NO_2BF_4 to an olefin in CH_3CN may result in the Ritter reaction.[5] Nitronium salts are sometimes used in a CH_2Cl_2 slurry; however, when the nitration of 3-buten-1-ol was attempted in CH_2Cl_2, complete decomposition occurred in a few seconds both at ambient temperature and at 0^oC.

It was decided that very low temperatures were needed for successful nitration in the presence of a double bond. Diethyl ether, which at room temperature is an unsuitable solvent for NO_2BF_4 since the nitronium ion can be attacked by the ether oxygen, is unreactive at -78^oC and readily dissolves the salt. Nitration was attempted with allyl alcohol under these conditions with success. The NO_2BF_4, though not completely soluble at this temperature, gradually dissolved as the reaction proceeded. Gas chromatography-mass spectrometry and infrared spectroscopy confirmed the structure of the product and that the double bond had not reacted. It should be noted that the allyl nitrate is not stable at room temperature for extended periods. 3-Buten-1-nitrate and 1,4 butane dinitrate were prepared under similar conditions. These nitrate esters appear to be stable at room temperature.

EXPERIMENTAL SECTION

All reagents were purchased from Aldrich Chemical Co. and were used without further purification. ^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded in $CDCl_3$ at 90 MHz (^{1}H) on a JEOL FX-90Q spectrometer. Chemical shifts are reported relative to TMS or to residual chloroform (7.24 ppm) for ^{1}H and ^{13}C. Chemical shifts for ^{15}N are reported relative to CH_3NO_2. Infrared spectra were recorded on a Perkin-Elmer 1700 Fourier Transform Infrared (FTIR) spectrophotometer. Samples were analyzed as vapors if possible or as carbon tetrachloride solutions in sodium chloride cells. Gas chromatography-mass spectrometry (GC-MS) were carried out on a Hewlett-Packard 5970 series MS detector coupled with a Hewlett-Packard 5890 gas chromatograph using a SPB-5 methyl silicone glass capillary column (0.2 mm i.d. x 30 m).

Synthesis of $CH_2=CHCH_2ONO_2$

Nitronium tetrafluoroborate (1.5 g, 0.011 mol) was stirred in 15 mL of ether at -78^{o}C in a dry-ice-acetone bath. Slowly, 0.66g (0.011 mol) of allyl alcohol was added. The mixture was stirred for 2.5 h at -78°C at which time the NO_2BF_4 had completely disappeared. The mixture was allowed to warm to room temperature and extracted with water to remove HBF_4. The ethereal layer was dried over $MgSO_4$, filtered, and evaporated. A light yellow oil was isolated in approximately 75% yield (0.88g). Without further purification, it was determined to be about 99% pure by GC-MS, and its boiling point was 104°C (uncorrected) (lit. b.p. 106°C).[6] IR (cm^{-1}): 3085 (olefinic C-H stretch); 2901 (C-H stretch); 1638 (nitrate ester); 1273 (nitrate ester); 851 (nitrate ester). MS (EI), m/z: 27 ($C_2H_3^+$); 30 (NO^+); 41 ($C_3H_5^+$); 46 (NO_2^+); 76 ($CH_2{=}ONO_2^+$); 102 (P^+-H).

<u>Synthesis of $CH_2{=}CHCH_2CH_2ONO_2$</u>

Diethyl ether (20 mL) was cooled to -78°C and NO_2BF_4 (2.75g, 0.0207 mol) was added with vigorous stirring. To the slurry, 1.5 g (0.0207 mol) of 3-buten-1-ol was added slowly, and the mixture was stirred at -78°C until the undissolved NO_2BF_4 disappeared (about 2 h). The solution was then allowed to warm to room temperature and quenched with H_2O. The product was isolated from the ether layer in the usual manner, as a light-yellow acrid liquid in 66% yield

(1.6g) and determined by GC-MS to be about 90% pure. B.P.(uncorrected): 118^{o}C. ^{1}H NMR ($CDCl_3$), δ: 2.5 (skew quart, 2H); 4.5 (quart, 2H); 5.2 (m, 2H); 5.7 (m, 1H). MS(EI), m/z: 30 (NO^+); 39 ($C_3H_3^+$); 41($C_3H_5^+$); 46(NO_2^+); 76 ($CH_2{=}ONO_2^+$). IR (cm^{-1}): 3092 (olefinic C-H stretch); 2979 (C-H stretch); 1663 (nitrate ester); 1287 (nitrate ester); 851 (nitrate ester).

Synthesis of $O_2NO(CH_2)_4ONO_2$

Nitronium tetrafluoroborate (2.0 g, 0.015 mol) was added to 20 mL of diethyl ether at -78°C in a dry-ice acetone bath. To the slurry was added slowly 1,4-butane-diol (0.67g, 0.0074 mol) with rapid stirring. The mixture was stirred for 2 h at which time all the NO_2BF_4 has reacted. The reaction mixture was quenched with H_2O and worked up in the previously described manner yielding 1.18g (88%) of the desired product as a colorless viscous liquid. This proved identical spectrally with a sample of 1,4-butane dinitrate prepared from mixed acid.[7,8] ^{1}H NMR ($CDCl_3$), δ: 1.9 (s, br, 4H); 4.5 (s, br, 4H). ^{13}C NMR ($CDCl_3$), coupled, ppm: 23.4 (t, 2C); 72.1 (t, 2C). ^{15}N NMR ($CDCl_3$), ppm: -38.1 (s, 2N). MS (EI), m/z: 30 (NO^+); 46 (NO_2^+); 76 ($CH_2{=}ONO_2^+$). IR (cm^{-1}): 2964 (C-H stretch); 1659 (nitrate ester); 1276 (nitrate ester); 840 (nitrate ester).

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