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SYNTHESIS OF 1-NITRO-1,3-DIENES VIA NITROTRIFLUOROACETOXYLATION OF 1,3-DIENES

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Abstract: Nitrotrifluoroacetate adducts, obtained from 1,3-dienes by reaction with ammonium nitrate in trifluoroacetic anhydride, readily eliminate to afford 1-nitro-1,3-dienes in high yield.

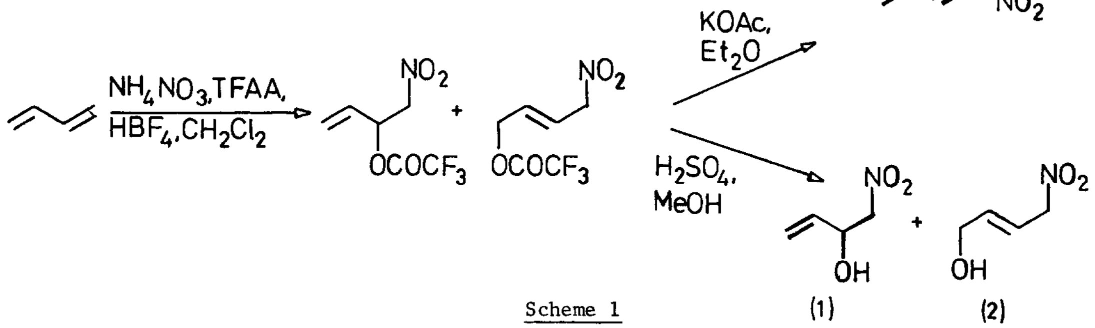
Recently the chemistry of 1-nitroalkenes has been extensively investigated and their synthetic utility is well established.[1] In contrast due to inefficient methods of preparation the chemistry and use as synthetic intermediates of 1-nitro-1,3-dienes has not been developed. The earlier Russian literature describes methods for preparation of 1-nitro-1,3-dienes by addition of N_2O_5[2], NO_2/I_2[3] of NO_2/O_2[3] to 1,3-dienes followed by elimination. However, these methods appear to be characterized by inefficient eliminations proceeding in low yields and giving products of unspecified stereochemistry. More recently a patent[4] discloses the addition of acetylnitrate to isoprene and subsequent elimination to give 2-methyl-1-nitro-1,3-butadiene. However, again this procedure is limited by the inefficient elimination reaction. No high yielding route for conversion of 1,3-dienes to 1-nitro-1,3-dienes has been described. The recent in situ preparation of trifluoroacetyl nitrate from ammonium nitrate and trifluoroacetic anhydride, a procedure used in the nitration of aromatics[5] and enol acetates,[6] and in the oxidation of hydrocarbons,[7] suggested a method to overcome the problem. It might be expected that following initial addition of trifluoroacetyl nitrate the intermediate nitrotrifluoroacetate adducts might undergo elimination under mild conditions. In this paper we describe a general procedure for the efficient synthesis of 1-nitro-1,3-dienes in two steps from 1,3-dienes based upon this strategy.

The general procedure involves the in situ preparation of trifluoroacetyl nitrate, which at 35°C readily adds to 1,3-dienes in dichloromethane to give mixtures of 1,2- and 1,4-nitrotrifluoroacetate adducts. A mixture of the adducts, purified by flash chromatography, on treatment with either potassium acetate in ether, or sodium hydride in tetrahydrofuran smoothly eliminates to afford the 1-nitro-1,3-dienes (see Table). The nitrodienes are very sensitive to both acids and bases but they may be purified either by flash chromatography on silica gel impregnated with sodium carbonate (5% by weight) or by distillation under reduced pressure. The pure dienes are stable at -20°C for weeks. Typically 1-nitro-1,3-butadiene is prepared in 89% overall yield by the following procedure:

> Ammonium nitrate (8g, 0.1 mole) was added portionwise to a solution of 1,3-butadiene (7g, 0.12 mole) in dichloromethane (100 ml) containing trifluoroacetic anhydride (20ml) and fluoroboric acid (0.5 ml, 40% aq. solution) at 35°C. The rate of addition was such that gentle reflux was maintained. After the addition was complete the solution was allowed to cool to room temperature and water (100 ml) was added. The organic phase was washed with brine (5 x 100 ml) and dried over magnesium sulphate. Removal of the solvent

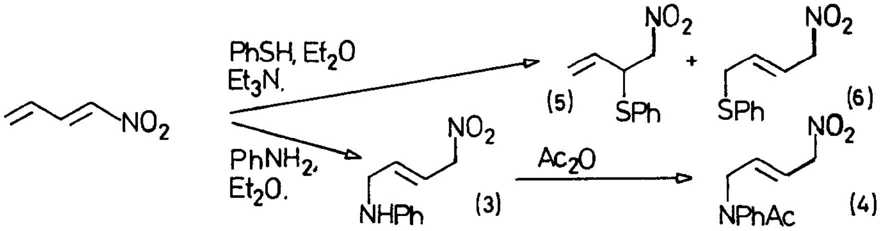
under reduced pressure afforded a crude residue purified by filtration chromatography (silica gel-dichloromethane). To a portion of the purified mixture of nitrotrifluoroacetates(2g) in ether (20 ml) anhydrous potassium acetate (1.9g, 2 mmole) was added and the mixture was stirred at room temperature for 18h. (t.l.c. analysis showed complete loss of nitrotrifluoroacetates). The ethereal solution was washed with brine, dried over magnesium sulphate, and the solvent removed to afford crude product, which was purified by distillation to give 1-nitro-1,3-butadiene (0.84g) (89% yield from 1,3-butadiene) b.p.$_{-1}$40°C (oven temperature) at 0.5mm, ν_{max} ($CHCl_3$) 1640, 1600, 1550 and 1350cm^{-1}; δH 5.86 (2H,m), 6.54 (1H,m), 7.20 (1H,d,J14Hz) and 7.60 (1H,dd,J14,11Hz).

Although the intermediate 1,2- and 1,4-nitrotrifluoroacetates cannot be separated easily, hydrolysis (see Scheme 1) affords the readily separable 1,2- and 1,4-nitroalcohols. In the case of 1,3-butadiene a 1:1 mixture of the two alcohols (1)^{8} and (2)^{9} is obtained. This lack of selectivity in the addition step is typical of the entries in the Table. In contrast the elimination step proceeded with high selectivity. In all cases other than isoprene (where exceptionally a second isomer is observed) elimination with potassium acetate in ether affords only a single nitrodiene.



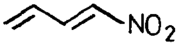
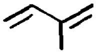
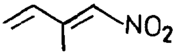
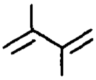
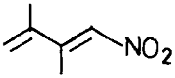
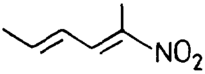
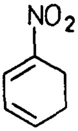
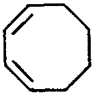
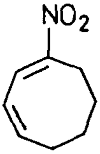
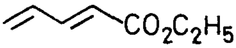
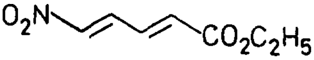
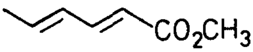
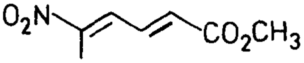
Scheme 1

The lack of regioselectivity in the electrophilic nitration leading to the mixtures of 1,2- and 1,4-nitrotrifluoroacetates contrasts with our initial results on nucleophilic addition to 1-nitro-1,3-butadiene. As shown in Scheme 2, the nitrodienes behave as powerful electrophiles and undergo both 1,2- and 1,4-addition with nucleophiles. However, the regioselectivity in such additions is markedly dependent on the nature of the nucleophile. Aniline gives in 57% yield only the adduct (3), characterized as the amide (4),^{10} but thiophenol gives mainly (54% yield) the 1,2-adduct (5)^{11} with the minor 1,4-adduct (6)^{12} formed in 13% yield. The synthetic potential of these selective additions and the understanding of their course are the subject of further study.



Scheme 2

TABLE 1 Synthesis of nitro dienes

Starting Diene	Time, temp	Nitro diene[a]	% yield from diene[b]
	15h, 20°C[c]		89
	1h, -40°C[c]		55[d]
	15h, 20°C[c]		75
	15h, 20°C[e]		84
	15h, 20°C[e]		70
	15h, 20°C[e]		70
	4h, 20°C[f]		35
	15h, 20°C[f]		94

a. All products have been characterised by spectroscopy (ir, ^{1}H and ^{13}C nmr) and gave satisfactory mass spectra or microanalytical data.

b. Isolated yields after purification.

c. Purified by distillation.

d. Elimination with KOAc gave a mixture of products; this elimination with NaH.

e. Purified by chromatography.

f. Purified by recrystallisation.

Acknowledgement

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8. Spectral data for (1): ν_{max} (CHCl$_3$) 3600, 1550 and 1370 cm^{-1}; δ_H (CDCl$_3$) 3.42 (1H,s), 4.46 (2H,m), 4.88 (1H,m), 5.42 (1H,m), and 5.74 - 6.20 (2H,m); δ_C (CDCl$_3$) 69.74, 79.34, 118.50 and 134.66.
9. Spectral data for (2): ν_{max} (CHCl$_3$) 3620, 1550, 1375 cm^{-1}; δ_H (CDCl$_3$) 2.26 (1H,br), 4.28 (2H,m), 4.98 (2H,m) and 6.06 (2H,m); δ_C (CHCl$_3$) 61.84, 76.99, 118.79 and 139.54.
10. Spectral data for (4): ν_{max} (CHCl$_3$) 3440 and 3320 cm^{-1}; δ_H (CDCl$_3$) 2.90 (3H,s), 4.38 (2H,d *J*5Hz), 4.91 (2H,d *J*6Hz), 6.94 (2H,m) and 7.1 - 7.6 (5H,m).
11. Spectral data for (5): ν_{max} (CHCl$_3$) 1555 and 1375 cm^{-1}; δ_H (CDCl$_3$) 4.32 (1H,m), 4.54 (2H,m), 5.26 (2H,m), 5.80 (1H,m) and 7.40 (5H,m); δ_C (CDCl$_3$) 48.14, 77.62, 119.03, 128.83, 129.00, 129.15, 131.24, 133.09 and 134.30.
12. Spectral data for (6): ν_{max} (CHCl$_3$) 1550 and 1370 cm^{-1}; δ_H (CDCl$_3$) 3.56 (2H,d *J*5Hz), 4.82 (2H, d *J*5Hz), 4.82 (2H, d *J*6Hz), 5.84 (2H,m) and 7.32 (5H,m); δ_C (CDCl$_3$) 36.03, 76.81, 121.42, 127.08, 129.12, 131.01 and 135.89.

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