Preparation of 1-Nitro-1,3-dienes *via* Nitrotrifluoroacetoxylation of 1,3-Dienes

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1,3-Dienes react with trifluoroacetyl nitrate, generated *in situ* by reaction of ammonium nitrate with trifluoroacetic anhydride, to give mixtures of 1,2- and 1,4-nitrotrifluoroacetates. Subsequent reaction of these mixtures with a base, *e.g.* potassium acetate or sodium hydride, affords 1-nitro-1,3-dienes in good yield. Examples of the hydrolysis of the nitrotrifluoroacetates to afford 1,2- and 1,4-nitro alcohols, and of nucleophilic additions to the 1-nitro-1,3-dienes, are given.

The use of nitration procedures based on the *in situ* formation of trifluoroacetyl nitrate by reaction of ammonium nitrate with trifluoroacetic anhydride (TFAA), in order to nitrate a variety of organic substrates, has recently been described. In this paper we describe an extension to the nitration of 1,3-dienes which permits an efficient synthesis of 1-nitro-1,3-dienes *via* elimination of the intermediate 1,2- and 1,4-nitrotrifluoroacetates.

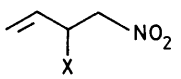
A solution of ammonium nitrate and TFAA in dichloromethane is considered to exist in equilibrium with trifluoroacetyl nitrate and ammonium trifluoroacetate. Establishment of this equilibrium permits the efficient nitration of aromatic substrates,[1,2] of enol acetates[3] to afford α-nitro ketones, and even of oxidation of saturated hydrocarbons.[4] In view of the analogous use of acetyl nitrate[5–7] to give nitro acetates with unsaturated hydrocarbons we decided to investigate the possible addition of trifluoroacetyl nitrate to such hydrocarbons in the belief that such addition might permit an improved route to nitroalkenes and nitrodienes.

Although there are now many efficient preparations of 1-nitroalkenes,[8] which have permitted their chemistry to be explored, in contrast the chemistry of 1-nitro-1,3-dienes has been little investigated because of the inefficiency of the described synthetic methods. From 1,3-dienes although the initial addition of NO_2X may be efficient the subsequent elimination step to afford the 1-nitro-1,3-diene is invariably unsatisfactory. For example, nitrodienes are obtained in 10—35% yield[9] by reaction of dienes with dinitrogen tetraoxide and iodine followed by elimination with lead acetate. Buta-1,3-diene and 2,3-dimethylbutadiene give a single nitrodiene of undetermined geometry, whereas isoprene and penta-1,3-diene both give mixtures of nitrodienes. Treatment[10] of the nitro acetates, obtained by reaction of isoprene with acetyl nitrate, with sodium hydroxide gives a mixture of nitrodienes in 39% yield. A mixture of the 1,2- and 1,4-nitro nitrates, available by reaction of buta-1,3-diene with dinitrogen pentaoxide, on treatment with triethylamine gives[11] a 1-nitrobuta-1,3-diene of undetermined stereochemistry in modest yield. An earlier claim[12] that 1-nitrobuta-1,3-diene can be prepared by direct reaction of butadiene with nitric acid has been questioned.[9] The more conjugated 1,4-diphenylbutadiene after nitration with dinitrogen tetraoxide and elimination with ammonia affords 1-nitro-1,4-diphenylbuta-1,3-diene[13] in better than 68% yield. Aside from the generation of nitrodienes by attack of nitrous acid on dienoate esters, exemplified[14] by preparation of mutagenic nitro derivatives of sorbic acid, a procedure of minor importance, the only other general route to nitrodienes is *via* condensation reactions. However, such condensations[15,16] with, for example, nitromethane are complicated by the competitive 1,4-addition alongside the desired condensation with the appropriate unsaturated aldehyde. Thus, until our recent report, in a preliminary form,[17] of the synthesis of 1-nitro-1,3-dienes *via* nitro trifluoroacetoxylation no generally satisfactory synthesis of 1-nitro-1,3-dienes was known.

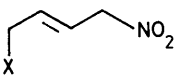
Our initial study centred on the development of efficient procedures for nitrotrifluoroacetoxylation of buta-1,3-diene. Slow addition of ammonium nitrate to a solution of 1,3-butadiene in dichloromethane containing TFAA proved to be satisfactory. The rate of addition was arranged in order to maintain a gentle reflux. The initial reaction could be initiated efficiently by prior addition of a few drops of fluoroboric acid. Although the reaction mixture became highly coloured, subsequent work-up and purification of the mixture of 1,2- and 1,4-nitrotrifluoroacetates by filtration chromatography afforded the pale yellow nitro esters in good yield. The 1,2- and 1,4-adducts could not be separated either by chromatography or by attempted distillation, which only resulted in extensive decomposition. Hydrolysis of the mixture of nitro esters in acidified methanol afforded the 1,2-nitro alcohol (**1**) and the 1,4-nitro alcohol (**4**), which were readily separated by flash chromatography. Treatment of the respective pure nitro alcohols with TFAA afforded the nitro esters (**2**) and (**5**). In nitrotrifluoroacetoxylation the nitro esters (**2**) and (**5**) are formed in the ratio 3:2.

The generation of 1-nitrobuta-1,3-diene (**10**) from the mixture of nitro esters (**2**) and (**5**) was examined using a number of bases. The simplest and most efficient procedure used potassium acetate or potassium propionate as base. Thus reaction of a mixture of the nitro esters (**2**) and (**5**) with fused potassium acetate in anhydrous ether affords the single nitrodiene (**10**) in 89% yield overall from buta-1,3-diene (**9**). The nitrodiene (**10**) could be purified further without difficulty by Kugelrohr distillation under reduced pressure. However, it is a sensitive compound which undergoes decomposition on being kept at room temperature. At −20 °C the nitrodiene (**10**) is stable for over a week. The formation of the single *E*-isomer (**10**) is based on g.l.c. analysis (1 peak) and observation, in the ^1H n.m.r. spectrum, of a coupling of $J_{1,2}$ 13 Hz, indicative of the *E*-geometry. No indication of a second isomer was observed in the ^{13}C n.m.r. spectrum of either the crude or purified nitrodiene (**10**).

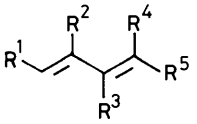
Attempted elimination by reaction of the 1,2- and 1,4-nitro esters from buta-1,3-diene (**9**) with triethylamine in ether at −40 °C proved to be less satisfactory. Although at this temperature reaction was rapid and the 1-nitrobuta-1,3-diene (**10**) could be isolated in low yield, extensive decomposition occurred. Elimination using sodium hydride as a base proved to be more satisfactory. A mixture of the nitroalkenyl trifluoroacetates (**2**) and (**5**) was added to a suspension of sodium hydride in tetrahydrofuran (THF) at −40 °C. The reaction mixture was allowed to warm to room temperature and subsequent work-up then permitted the isolation of the nitrodiene (**10**) in 80% yield. This elimination with sodium hydride has unusual features. The addition of the nitro esters to the suspension of sodium hydride at −40 °C is not accompanied by any effervescence. Instead dissolution of the sodium hydride leads to formation of a slight yellow suspension. On allowing



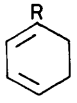
(1) X = OH
(2) X = $OCOCF_3$
(3) X = SPh



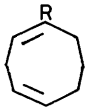
(4) X = OH
(5) X = $OCOCF_3$
(6) X = SPh
(7) X = NHPh
(8) X = NAcPh



(9) $R^1 = R^2 = R^3 = R^4 = R^5 = H$
(10) $R^1 = R^2 = R^3 = R^4 = H, R^5 = NO_2$
(11) $R^1 = R^2 = R^4 = R^5 = H, R^3 = Me$
(12) $R^1 = R^2 = R^4 = H, R^3 = Me, R^5 = NO_2$
(13) $R^1 = R^2 = R^5 = H, R^3 = Me, R^4 = NO_2$
(14) $R^1 = R^4 = R^5 = H, R^2 = R^3 = Me$
(15) $R^1 = R^4 = H, R^2 = R^3 = Me, R^5 = NO_2$
(16) $R^1 = R^5 = Me, R^2 = R^3 = R^4 = H$
(17) $R^1 = R^4 = Me, R^2 = R^3 = H, R^5 = NO_2$
(18) $R^1 = Me, R^2 = R^3 = R^4 = R^5 = H$
(19) $R^1 = Me, R^2 = R^3 = R^4 = H, R^5 = NO_2$
(20) $R^1 = R^2 = R^3 = H, R^4 = Me, R^5 = NO_2$
(21) $R^1 = EtO_2C, R^2 = R^3 = R^4 = R^5 = H$
(22) $R^1 = EtO_2C, R^2 = R^3 = R^4 = H, R^5 = NO_2$
(23) $R^1 = MeO_2C, R^2 = R^3 = R^4 = H, R^5 = Me$
(24) $R^1 = MeO_2C, R^2 = R^3 = H, R^4 = Me, R^5 = NO_2$



(25) R = H
(26) R = NO_2



(27) R = H
(28) R = NO_2

the temperature to rise to room temperature the apparent amount of suspended matter increases and the solution becomes dark red. Addition of aqueous acid at room temperature causes dissolution of the suspended solid, loss of the red colour, and a small amount of effervescence. Work-up then affords the nitrodiene (**10**). If the aqueous acid is added at the lower temperature then subsequent work-up affords only the nitro alcohols (**1**) and (**4**). Furthermore, if the nitro esters are added to the suspension of sodium hydride at a higher temperature, for example −20 °C, then a rapid reaction occurs with much effervescence but the yield of the nitrodiene (**10**) is reduced. Our explanation of these observations is that initial reaction with sodium hydride at −40 °C is reduction of the ester. Proton abstraction then permits formation of the coloured nitronate anion, which then slowly undergoes elimination to afford the nitrodiene (**10**). At higher temperatures sodium hydride reacts competitively as a base. These results suggest the formation of trifluoroacetaldehyde as a product.

The general method of nitrotrifluoroacetoxylation followed by elimination with potassium acetate in ether was used for preparation of a number of nitrodienes (see Table). In the case of isoprene (**11**) elimination using triethylamine or potassium acetate gave a mixture of two nitrodienes (*e.g.* 42% yield using triethylamine: ratio 1:1 from g.l.c. and ^1H n.m.r. analysis). However, nitrotrifluoroacetoxylation of isoprene followed by elimination using sodium hydride afforded a single nitrodiene (**12**) in 55% yield. The assignment of structure to this single nitrodiene (**12**) is made by analogy to spectral features of the related nitrodiene (**10**). The second nitrodiene isolated from use of triethylamine or potassium acetate is tentatively assigned the structure (**13**) on the basis of chemical-shift data. 2,3-Dimethylbuta-1,3-diene (**14**) on nitrotrifluoroacetoxylation and subsequent elimination with potassium propionate in ether afforded the *E*-nitrodiene (**15**) in 75% yield. Similarly nitrotrifluoroacetoxylation of *E,E*-hexa-2,4-diene (**16**) and elimination using potassium acetate in ether afforded the *E,E*-nitrodiene (**17**) in 84% yield. In contrast nitrotrifluoroacetoxylation of *E*-penta-1,3-diene (**18**) followed by elimination with potassium acetate gave an inseparable mixture of nitrodienes (**19**) and (**20**) (84% yield: ratio 1:1). The cyclic dienes, cyclohexa-1,3-diene (**25**) and cyclo-octa-1,3-diene (**27**), gave the corresponding nitrodienes (**26**) and (**28**) respectively. 1-Nitrocyclohexa-1,3-diene (**26**), obtained in 70% yield, could be purified either by chromatography on deactivated silica gel, or by distillation. On exposure to air it is rapidly converted into nitrobenzene. 1-Nitrocyclo-octa-1,3-diene (**28**), also obtained in 70% yield, was slightly contaminated by a minor impurity which could not be removed. In contrast to these successful reactions attempted nitrotrifluoroacetoxylation of cyclopentadiene only gave black tars.

Ethyl (*E*)-penta-2,4-dienoate (**21**) on nitrotrifluoroacetoxylation and subsequent elimination with potassium acetate gave the nitro ester (**22**) in 35% yield. The structure of this known[16] ester was confirmed by the ^1H and ^{13}C n.m.r. spectra. Similarly nitrotrifluoroacetoxylation of methyl (*E,E*)- hexa-2,4-dienoate (**23**) and subsequent elimination using potassium acetate afforded the nitro ester (**24**) in 94% yield.

The above procedures for synthesis of 1-nitrobuta-1,3-dienes have a number of common features. Use of a mild base, potassium acetate, permits the elimination of trifluoroacetic acid to take place to afford the nitrodienes in good yield. Typically a single diene is obtained. Amine bases are less effective. Although the nitrodienes are rather unstable the mild conditions under which they are formed and isolated has permitted preliminary investigation of aspects of the chemistry of the nitrodienes.

1-Nitrobuta-1,3-diene (**10**) with thiophenol in ether containing triethylamine at −40 °C afforded the 1,2-nitro sulphide (**3**) as the major product with some formation of the 1,4-nitro sulphide (**6**). A Russian study reports[18] that ethanethiol adds to 1-nitrobuta-1,3-diene (**10**) to give the 1,2-product. In contrast we find that aniline only gives the product (**7**) by 1,4-addition. The amine (**7**) obtained in 57% yield was characterised as the amide (**8**).

Table. Preparation of nitrodienes by nitration of 1,3-dienes and subsequent elimination

Diene	Base	Products and yields (%)
(**9**)	KOAc	(**10**) (89)
(**11**)	NaH	(**12**) (55)
(**11**)	Et_3N	(**12**) and (**13**) (42)
(**14**)	$KO_2CC_2H_5$	(**15**) (75)
(**16**)	KOAc	(**17**) (84)
(**18**)	KOAc	(**19**) and (**20**) (84)
(**21**)	KOAc	(**22**) (35)
(**23**)	KOAc	(**24**) (94)
(**25**)	KOAc	(**26**) (70)
(**27**)	KOAc	(**28**) (70)

In view of reports[11] in the earlier Russian literature, and in a patent,[10] of the addition of carbon nucleophiles to nitrodienes it is clear that a more profound study is merited of those factors, currently not understood, which control the outcome of addition of nucleophiles to nitrodienes. The present description of a general synthesis of 1-nitrobuta-1,3-dienes facilitates such a study.

Experimental

General experimental details have been described earlier.[19] N.m.r. spectra were recorded using a Bruker AM 360 spectrometer. Unless otherwise stated all products were homogeneous (t.l.c.).

General Procedure for Nitrotrifluoroacetoxylation.—Ammonium nitrate (1.6 g) was added portionwise to a solution of the diene (0.022 mol) in dichloromethane containing TFAA (5 ml) and fluoroboric acid (0.1 ml of a 40% aqueous solution) at 35 °C. The addition brought the solution to gentle reflux which was maintained through the addition. After the addition the solution was allowed to cool to room temperature. Water (100 ml) was carefully added to hydrolyse excess of anhydride. The aqueous layer was removed and the organic phase was washed with saturated brine until the washings were neutral, and was then dried over magnesium sulphate. Removal of the solvent under reduced pressure afforded a dark coloured residue, which was purified by filtration through a short column of silica gel (eluant dichloromethane) to afford mixtures of nitroalkenyl trifluoroacetates, $\nu_{max.}$($CHCl_3$) 1 800—1 780, 1 570—1 550, and 1 365 cm^{-1}, which were used directly.

1-*Nitrobut*-3-*en*-2-*ol* (**1**) *and* 4-*Nitrobut*-2-*en*-1-*ol* (**4**).—The mixture of adducts obtained from the nitrotrifluoroacetoxylation of buta-1,3-diene (**9**) (0.51 g) were dissolved in methanol (20 ml) containing conc. sulphuric acid (1 ml). After 1 h at room temperature the solution was neutralised by the addition of sodium hydrogen carbonate solution, then water, and extracted with ether. The combined extracts were dried ($MgSO_4$) and evaporated to give a brown oil. Separation by flash chromatography [eluant ethyl acetate–hexane(1 : 1)] gave as the less polar fraction 1-nitrobut-3-en-2-ol (**1**) (0.16 g, 57%), b.p. 78 °C (oven temperature) at 0.9 Torr; *m/z* (c.i. with NH_3) 118 (2%) and 43 (100); $\nu_{max.}$($CHCl_3$) 3 600, 1 550, and 1 370 cm^{-1}; δ_H 3.42 (1 H, s, OH), 4.46 (2 H, m, CH_2NO_2), 4.88 (1 H, m, C*H*OH), 5.42 (2 H, m, CH_2=C), and 5.95 (1 H, m, CH=C); δ_C 69.74 (CHOH), 79.34 (CH_2NO_2), 118.50 (vinyl), and 134.66 (vinyl); and as the more polar fraction (E)-4-*nitrobut*-2-*en*-1-*ol* (**4**) (0.10 g, 36% yield) (Found: M^+, 117.0452. $C_4H_7NO_3$ requires *M*, 117.0426); $\nu_{max.}$($CHCl_3$) 3 620, 1 550, and 1 370 cm^{-1}; δ_H 2.26 (1 H, br, OH), 4.28 (2 H, m, CH_2OH), 4.98 (2 H, m, CH_2NO_2), and 6.06 (2 H, m, vinyl); δ_C 61.84 (CH_2OH), 76.99 (CH_2NO_2), 118.79 (vinyl), and 139.54 (vinyl).

The nitro alcohols (**1**) and (**4**) were separately converted into their respective trifluoroacetate derivatives (**2**) and (**5**) by treatment with TFAA in ether followed by removal of excess of reagent and solvent under reduced pressure. 1-Nitrobut-3-en-2-ol (**1**) gave 1-nitrobut-3-en-2-yl trifluoroacetate (**2**), *m/z* (c.i. with NH_3) 218 (100%); $\nu_{max.}$($CHCl_3$) 1 800, 1 570, and 1 375 cm^{-1}; δ_H 4.68 (2 H, m, CH_2NO_2), 5.65 (2 H, m, vinyl), 5.95 (1 H, m, vinyl), and 6.08 (1 H m, $CHOCOCF_3$); δ_C 74.26 and 75.81 (CH_2NO_2 and $CHOCOCF_3$), 114.61 (CF_3), and 122.97 and 128.72 (vinyl).

4-Nitrobut-2-en-1-ol (**4**) gave (*E*)-4-nitrobut-2-en-1-yl trifluoroacetate (**5**) *m/z* 213 (0.6%) and 69 (100); $\nu_{max.}$($CHCl_3$) 1 790, 1 560, and 1 350 cm^{-1}; δ_H 4.96 (4 H, complex, CH_2NO_2 and CH_2OCOCF_3) and 6.12 (2 H, complex, vinyl); δ_C 66.60 (CH_2OCOCF_3), 76.31 (CH_2NO_2), and 124.61 and 131.20 (vinyl).

Preparation of Nitrodienes from Nitroalkenyl Trifluoroacetates—Method A. Anhydrous potassium acetate (*ca.* 20 mmol) was added to a solution of the crude nitroalkenyl trifluoroacetate (10 mmol) in dry ether (20 ml). The mixture was stirred at room temperature until all the nitroalkenyl trifluoroacetate was observed (t.l.c.) to have reacted (typically 18 h). The ether solution was then washed with brine (3 × 20 ml) and dried over magnesium sulphate. Evaporation afforded a crude product, which was purified by distillation (Kugelrohr) or by flash chromatography over neutral silica gel, and/or crystallisation. Potassium acetate could be replaced by potassium propionate.

Method B. Sodium hydride (12 mmol) (55% dispersion in mineral oil) was washed with pentane (5 × 10 ml) and then covered by dry THF (20 ml). A solution of the crude nitroalkenyl trifluoroacetate (10 mmol) in THF (5 ml) was added dropwise to the suspension at −40 °C. The addition gave rise to a fine pale yellow suspension but was not accompanied by an observed gas evolution. The mixture was allowed to warm to room temperature during 30 min, and the red mixture was poured into saturated aqueous ammonium chloride (50 ml). The solution was extracted with ether (3 × 50 ml). The combined extracts were dried over magnesium sulphate and evaporated under reduced pressure to afford the crude nitrodienes. The crude products were purified first by extraction of the residue with hexane (3 × 10 ml), evaporation of the solvent from the combined extracts, and then by distillation under reduced pressure.

Method C. A solution of triethylamine (*ca.* 10 mmol) in ether (20 ml) was added dropwise to a solution of the crude nitroalkenyl trifluoroacetate (10 mmol) in ether (30 ml) at −60 °C. After 10 min the ether solution was decanted from precipitated ammonium salts and was then washed successively with dil. hydrochloric acid (50 ml) and brine (2 × 50 ml). The organic phase was dried over magnesium sulphate and evaporated under reduced pressure to afford the crude nitrodienes. The crude products were purified first by extraction of the residue with hexane (3 × 10 ml), evaporation of the solvent from the combined extracts, and then by distillation under reduced pressure. The following nitrodienes were thus obtained.

1-*Nitrobuta*-1,3-*diene* (**10**).—Buta-1,3-diene (**9**) by nitrotrifluoroacetoxylation and elimination by method A afforded (*E*)-1-nitrobuta-1,3-diene (**10**) (89% yield), b.p. 40 °C (oven temperature) at 0.5 Torr (lit.,[9] 56—57 °C at 10 Torr); $\nu_{max.}$ ($CHCl_3$) 1 640, 1 600, 1 550, and 1 350 cm^{-1}; δ_H 5.86 (2 H, m, CH_2), 6.54 (1 H, m, C*H*=CH_2), 7.20 (1 H, d, *J* 13 Hz, $CHNO_2$), and 7.60 (1 H, dd, *J* 14 and 11 Hz, C*H*=$CHNO_2$); δ_C 129.77, 131.18, 136.68, and 149.95; *m/z* 99 (M^+, 27%) and 82 (100).

2-*Methyl*-1-*nitrobuta*-1,3-*diene* (**12**). Isoprene (**11**) by nitrotrifluoroacetoxylation and elimination by method B afforded (*E*)-2-methyl-1-nitrobuta-1,3-diene (**12**) (55% yield), b.p. 50 °C (oven temperature) at 0.5 Torr (lit.,[9] 55—56 °C at 5 Torr); $\nu_{max.}$($CHCl_3$) 1 600, 1 515, and 1 350 cm^{-1}; δ_H 2.36 (3 H, d, *J* 2 Hz, Me), 5.82 (2 H, m, CH_2), 6.42 (1 H, dd, *J* 18 and 10 Hz, C*H*=CH_2), and 7.12 (1 H, br s, $CHNO_2$).

2-*Methyl*-1-*nitrobuta*-1,3-*dienes* (**12**) and (**13**). Isoprene (**11**) by nitrotrifluoroacetoxylation and elimination by method C afforded a mixture of (*E*)- (**12**) and (*Z*)-2-methyl-1-nitrobuta-1,3-diene (**13**) (42% yield); $\nu_{max.}$($CHCl_3$) 1 600, 1 590, 1 515, and 1 350 cm^{-1}; δ_H 2.06 [d, *J* 2 Hz, Me (**13**)], 2.36 [d, *J* 2 Hz, Me (**12**)], 5.3—6.1 (complex), 6.42 [dd, *J* 18 and 10 Hz, C*H*=CH_2 (**12**)], 6.98 [br, $CHNO_2$ (**13**)], 7.12 [br, $CHNO_2$ (**12**)], and 7.60 [dd, *J* 18 and 10 Hz, C*H*=CH_2 (**13**)].

(Z)-2,3-*Dimethyl*-1-*nitrobuta*-1,3-*diene* (**15**). 2,3-Dimethylbuta-1,3-diene (**14**) by nitrotrifluoroacetoxylation and elimination by method A using potassium propionate afforded (*E*)-2,3-dimethyl-1-nitrobuta-1,3-diene (**15**) (75% yield), b.p. 50 °C (oven temperature) at 0.5 Torr (lit.,[9] 63 °C at 5 Torr); $\nu_{max.}$($CHCl_3$) 1 600, 1 510, and 1 330 cm^{-1}; δ_H 2.00 (3 H, d, *J* 2 Hz, Me), 2.38 (3 H, d, *J* 2 Hz, Me), 5.42 (1 H, br s) and 5.60 (1 H, s) (CH_2), and 7.16 (1 H, br, $CHNO_2$).

2-*Nitrohexa*-2,4-*diene* (**17**). (*E,E*)-Hexa-2,4-diene (**16**) by nitrotrifluoroacetoxylation and elimination by method A afforded (*E,E*)-2-*nitrohexa*-2,4-*diene* (**17**) (84% yield), b.p. 60 °C (oven temperature) at 0.5 Torr [Found: M^+, (4%) 127.0589. $C_6H_9NO_2$ requires *M*, 127.0633]; $\nu_{max.}$($CHCl_3$) 1 650, 1 510, and 1 330 cm^{-1}; δ_H 1.94 (3 H, d, *J* 5 Hz, Me), 2.26 (3 H, 5, Me), 6.30 (2 H, m, CH), and 7.56 (1 H, br d, *J* 10 Hz, $CH{=}CNO_2$); δ_C 12.64 (Me), 19.22 (Me), 125.35, 133.64, and 143.62 (vinylic CH), and 144.99 (CNO_2).

1-*Nitropenta*-1,3-*diene* (**19**) *and* 4-*nitropenta*-1,3-*diene* (**20**). Penta-1,3-diene (**18**) by nitrotrifluoroacetoxylation and elimination by method A afforded a mixture of (*E,E*)-1-nitropenta-1,3-diene (**19**) and (*E*)-4-nitropenta-1,3-diene (**20**) (84% yield 1:1); $\nu_{max.}$($CHCl_3$) 1 640, 1 610, 1 560, 1 510, 1 345, 1 330, and 1 315 cm^{-1}; δ_H 1.95 [d, *J* 6 Hz, Me (**19**)], 2.38 [s, Me (**20**)], 5.5—6.8 (complex), 7.08 [d, *J* 12 Hz, $CHNO_2$ (**19**)], 7.66 (d, *J* 12 Hz, $CH{=}CNO_2$ (**20**)], and 7.70 [m, $CH{=}CNO_2$ (**19**)].

1-*Nitrocyclohexa*-1,3-*diene* (**26**). Cyclohexa-1,3-diene (**25**) by nitrotrifluoroacetoxylation and elimination by method A afforded 1-*nitrocyclohexa*-1,3-*diene* (**26**) (70% yield), b.p. 70 °C (oven temperature) at 0.5 Torr [Found: M^+ (1%), 125.0547. $C_6H_7NO_2$ requires *M*, 125.0477]; $\nu_{max.}$($CHCl_3$) 1 575, 1 505, and 1 330 cm^{-1}; δ_H 2.2—2.7 (2 H, m, CH_2), 2.7—3.1 (2 H, m, CH_2), 6.0—6.5 (2 H, m, CH), and 7.36 (1 H, d, *J* 6 Hz, $CH{=}CNO_2$); δ_C 20.72 (CH_2), 23.93 (CH_2), 122.00, 127.86, and 136.23 (CH), and 146.53 (CNO_2).

1-*Nitrocyclo-octa*-1,3-*diene* (**27**). Cyclo-octa-1, 3-diene (**27**) by nitrotrifluoroacetoxylation and elimination by method A afforded 1-*nitrocyclo-octa*-1,3-*diene* (**28**) (70% yield), b.p. 70 °C (oven temperature) at 0.5 Torr [Found: M^+ (2.5%), 153.0824. $C_8H_{11}NO_2$ requires *M*, 153.0790]; $\nu_{max.}$($CHCl_3$) 1 520 and 1 335 cm^{-1}; δ_H 1.66 (4 H, complex, CH_2), 2.25 (2 H, m, CH_2), 2.79 (2 H, m, CH_2), 6.01 (2 H, m, CH), and 7.53 (1 H, d, *J* 4 Hz, $CH{=}CNO_2$); δ_C 21.91, 22.30, 26.23, and 29.11 (CH_2), 121.90, 130.25, and 138.50 (CH), and 150.29 (CNO_2).

Ethyl 5-*nitropenta*-2,4-*dienoate* (**22**). Ethyl (*E*)-penta-2,4-dienoate (**21**) by nitrotrifluoroacetoxylation and elimination by method A afforded ethyl (*E,E*)-5-nitropenta-2,4-dienoate (**22**) (35% yield), m.p. 105—106 °C (from ether) (lit.,[16] 101—102 °C); *m/z* (c.i. with CH_4) 172 ($M + 1^+$, 48%) and 79 (100); $\nu_{max.}$($CHCl_3$) 1 720, 1 610, 1 525, and 1 325 cm^{-1}; δ_H 1.34 (3 H, t, *J* 7 Hz, Me), 4.29 (2 H, q, *J* 7 Hz, CH_2), 6.48 (1 H, d, *J* 15.5 Hz, $CHCO_2Et$), 7.36 (2 H, m, $CH{=}CHCO_2Et$ and $CHNO_2$), and 7.64 (1 H, t, *J* 12.5 Hz, $CH{=}CHNO_2$); δ_C 14.0 (Me), 61.2 (CH_2), 133.2, 135.0, and 135.2 (CH), 144.4 (CNO_2), and 165.0 (CO).

Methyl 5-*nitrohexa*-2,4-*dienoate* (**24**). Methyl (*E,E*)-hexa-2,4-dienoate (**23**) by nitrotrifluoroacetoxylation and elimination by method A afforded methyl (*E,E*)-5-nitrohexa-2,4-dienoate (**24**) (94% yield), m.p. 123—124 °C (from ether); *m/z* (c.i. with CH_4) 172 ($M + 1^+$, 41%), 171 (M^+, 97), and 93 (100); $\nu_{max.}$($CHCl_3$) 1 720, 1 620, 1 525, and 1 310 cm^{-1}; δ_H 2.40 (3 H, s, Me), 4.84 (3 H, s, OMe), 6.38 (1 H, d, *J* 15 Hz, $CHCO_2Me$), 7.43 (1 H, dd, *J* 15 and 12 Hz, $CH{=}CHCO_2Me$), and 7.58 (1 H, d, *J* 12 Hz, $CH{=}CNO_2$); δ_C 13.25 (Me), 52.09 (OMe), 129.11, 130.77, and 136.01 (CH), 152.46 (CNO_2), and 165.78 (CO).

Addition of Thiophenol to 1-*Nitrobuta*-1,3-*diene* (**10**).—To a solution of thiophenol (0.17 g) and triethylamine (0.16 g) in ether (20 ml) at −40 °C was added dropwise a solution of 1-nitrobuta-1,3-diene (**10**) (0.16 g) and 3,5-di-t-butyl-4-cresol (1 mg) in ether (20 ml). The solution was allowed to warm to room temperature and after 1 h at that temperature was washed successively with dil. sulphuric acid (50 ml) and then with brine (2 × 50 ml). The organic phase was dried over magnesium sulphate and evaporated under reduced pressure to give a mixture of products, which was separated by flash chromatography (eluant hexane–ether (5:1)]. The less polar product was further purified by distillation to afford 4-*nitro*-3-(*phenylthio*)*but*-1-*ene* (**3**) (0.18 g, 54% yield), b.p. 80 °C (oven temperature) at 0.5 Torr (Found: M^+, 209.0491. $C_{10}H_{11}N_2O_3S$ requires *M*, 209.0510); *m/z* (c.i. with NH_3) 209 (39%); $\nu_{max.}$($CHCl_3$) 1 555 and 1 375 cm^{-1}; δ_H 4.32 (1 H, m, CHS), 4.54 (2 H, m, CH_2NO_2), 5.26 (2 H, m, $CH_2{=}CH$), 5.80 (1 H, m, $CH{=}CH_2$), and 7.40 (5 H, m, Ph); δ_C 48.14 (CHS), 77.62 (CH_2NO_2), 119.03, 128.83, 129.00, 129.15, 129.25, 131.24, 133.09, and 134.30. The more polar product was further purified by distillation to afford (E)-1-*nitro*-4-(*phenylthio*)*but*-2-*ene* (**6**) (43 mg, 13% yield), b.p. 90 °C (oven temperature) at 0.5 Torr (Found: M^+, 209.0480); *m/z* 209 (26%); $\nu_{max.}$($CHCl_3$) 1 550 and 1 370 cm^{-1}; δ_H 3.56 (2 H, d, *J* 6 Hz, CH_2S), 4.82 (2 H, d, *J* 6 Hz, CH_2NO_2), 5.84 (2 H, m, vinyl), and 7.32 (5 H, m, Ph); δ_C 36.03 (CH_2S), 76.81 (CH_2NO_2), 121.42, 127.08, 129.12, 131.01, and 135.89.

Addition of Aniline to 1-*Nitrobuta*-1,3-*diene* (**10**).—To a solution of (*E*)-1-nitrobuta-1,3-diene (**10**) (0.2 g) in ether (20 ml) was added aniline (0.38 g). After 10 h the solution was washed with brine (20 ml), dried over anhydrous magnesium sulphate, and evaporated under reduced pressure to give a mixture of products, which were separated by flash chromatography (eluant dichloromethane). The isolated (*E*)-1-anilino-4-nitrobut-2-ene (**7**) (0.22 g, 57%) was characterised as its low melting acetyl derivative by acetylation with acetic anhydride and purification by flash chromatography to give N-[(E)-4-*nitrobut*-2-*enyl*]-N-*phenylacetamide* (**8**) (Found: M^+, 234.0996. $C_{12}H_{15}N_2O_3$ requires *M* 234.1004); $\nu_{max.}$($CHCl_3$) 3 440, 3 320, 1 650, 1 595, 1 555, and 1 375 cm^{-1}; δ_H 1.89 (3 H, s, Me), 4.46 (2 H, d, *J* 6 Hz, CH_2N), 4.91 (2 H, d, *J* 6 Hz, CH_2NO_2), 5.9 (2 H, m, vinyl), and 7.1—7.6 (5 H, m, Ph).

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