Nitroacetamidation of Dienes by Indirect Electrochemical Nitration

A. Jon Bloom, Martin Fleischmann, and John M. Mellor*
Department of Chemistry, The University, Southampton SO9 5NH

Solutions of nitronium tetrafluoroborate in acetonitrile were obtained by anodic oxidation of N_2O_4. The electrogenerated NO_2BF_4 efficiently nitroacetamidates conjugated dienes. Buta-1,3-diene, isoprene, 2,3-dimethylbutadiene, *trans*-penta-1,3-diene and *trans-trans*-hexa-2,4-diene give mixtures of products by 1,2- and 1,4-addition. Structures of the 1,2- and the 1,4-nitroacetamides are assigned on the basis of spectroscopic analysis and conversion of 1,2-nitroacetamides into dihydroimidazoles. The observed selectivity of 1,2-addition relative to 1,4-addition, regioselectivity, and stereoselectivity are compared with related electrophilic additions to conjugated dienes.

We have recently described[1] the nitroacetamidation of alkenes by nitration in acetonitrile using commercially available nitronium tetrafluoroborate. We have also described[2] the electrogeneration of nitronium tetrafluoroborate by anodic oxidation of N_2O_4 in acetonitrile and given preliminary details of the use of this reagent in the nitration of aromatic compounds, silyl enol ethers, alkenes, and conjugated dienes. We now describe fully the preparation of 1,2-nitroacetamides and 1,4-nitroacetamides, a new type of nitro compound, by nitroacetamidation of conjugation dienes, a process previously unreported prior to our preliminary communication. Although there are some reports[3] in the earlier literature concerning the nitroacetamidation of alkenes, not only had the nitroacetamidation of conjugated dienes not been described but there was only an isolated report[4] of a procedure permitting the formation of two new carbon–nitrogen bonds in an addition to a conjugated diene.

The nitroacetamidation studies required a cheap, efficient method of generation of solutions of nitronium tetrafluoroborate in acetonitrile. We find that solutions of nitronium tetrafluoroborate are afforded by anodic oxidation of nitrogen dioxide (N_2O_4) in acetonitrile using a divided cell. With platinum mesh electrodes and lithium tetrafluoroborate (0.25M) as electrolyte it was possible to generate in an H-cell nitronium tetrafluoroborate (80% current efficiency and 80% yield) at constant current (50 mA cm^{-2}). The concentration of the electrogenerated nitronium tetrafluoroborate was established by withdrawal of aliquots of the anolyte, addition to benzene, and subsequent analysis by g.l.c. for nitrobenzene.

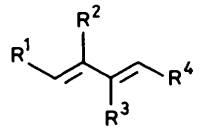
The result of nitration of a number of dienes in acetonitrile is shown in the Table. In each case reaction with the diene took place at *ca.* −70 °C and after a short reaction time formation of nitroacetamides was completed by addition of aqueous acetonitrile. Products were easily separated in most cases by chromatography over silica gel: the 1,2-nitroacetamides are substantially less polar than the 1,4-nitroacetamides.

Butadiene (**1**) reacts to give the 1,2-adduct (**6**) in 48% yield and the 1,4-adduct (**12**) in 51% yield. Distinction between the two structures is easily made by analysis of the ^1H and ^{13}C n.m.r. spectra. The expected regioselectivity of addition to give the 1,2-adduct (**6**) is confirmed by chemical shift data (CH_2NO_2 at δ 4.72 p.p.m.) and by the observed coupling between the methine proton and the NH proton. The *trans*-stereochemistry in the 1,4-adduct (**12**) is established by observation of the vicinal coupling constant (J_{trans} 15 Hz).

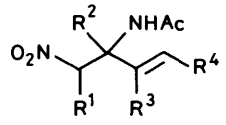
Isoprene (**2**) reacts to give the 1,2-adduct (**7**) in 39% yield and the 1,4-adduct (**13**) in 50% yield. Analysis of the ^1H- and ^{13}C-n.m.r. spectra established the regioselectivity of addition to the more substituted double bond to give the 1,2-adduct (**7**). A single 1,4-adduct (**13**) is obtained and the regioselectivity of this

Table. Reaction of electrogenerated nitronium tetrafluoroborate with dienes

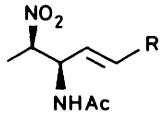
Diene	Products and yields (%) 1,2-Adducts	1,4-Adducts
(1)	(**6**) (48)	(**12**) (51)
(2)	(**7**) (39)	(**13**) (50)
(3)	(**8**) (35)	(**14**) (35)
(4)	(**10**; R=H) (26)	(**15**) (39)
		(**16**) (25)
(5)	(**10**; R = Me) and (**11**; R = Me) (6)	(**17**) and (**19**) (78)



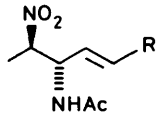
(1) $R^1 = R^2 = R^3 = R^4 = H$
(2) $R^1 = R^3 = R^4 = H$, $R^2 = Me$
(3) $R^1 = R^4 = H$, $R^2 = R^3 = Me$
(4) $R^1 = Me$, $R^2 = R^3 = R^4 = H$
(5) $R^1 = R^4 = Me$, $R^2 = R^3 = H$



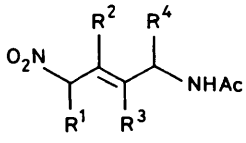
(6) $R^1 = R^2 = R^3 = R^4 = H$
(7) $R^1 = R^3 = R^4 = H$, $R^2 = Me$
(8) $R^1 = R^4 = H$, $R^2 = R^3 = Me$
(9) $R^1 = Me$, $R^2 = R^3 = R^4 = H$



(**10**)



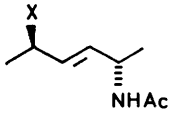
(**11**)



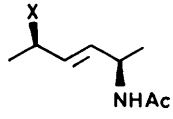
(12) $R^1 = R^2 = R^3 = R^4 = H$
(13) $R^1 = R^3 = R^4 = H$, $R^2 = Me$
(14) $R^1 = R^4 = H$, $R^2 = R^3 = Me$
(15) $R^1 = Me$, $R^2 = R^3 = R^4 = H$
(16) $R^1 = R^2 = R^3 = H$, $R^4 = Me$

addition is established by decoupling experiments. The assignment of stereochemistry about the double bond is based on the analogy of addition to butadiene (**1**), 2,3-dimethylbutadiene (**3**), and the related nitroacetoxylation[5] of isoprene (**2**).

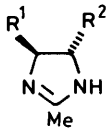
2,3-Dimethylbutadiene (**3**) gives a 1,2-adduct (**8**) in 35% yield and a 1,4-adduct (**14**) in 35% yield. Analysis of the ^1H and ^{13}C n.m.r. spectra of the adducts (**8**) and (**14**) readily permit structural assignments based on the comparison of the spectra of adducts obtained from butadiene (**1**) and isoprene (**2**). The *trans* stereochemistry of the double bond was established by n.O.e. difference experiments. *trans*-Penta-1,3-diene (**4**) gives three adducts of which the 1,2-adduct (**9**) is readily isolated by column chromatography. Formation of a 1,2-adduct is easily established by observation of three protons associated with the vinyl group. The regioselectivity of the addition is established by decoupling experiments. Discrimination between formation of the 1,2-adduct (**10**; R = H), a product of *cis*-addition, and the formation of the possible 1,2-adduct (**11**; R = H), a product of *trans*-addition, is made by conversion of the 1,2-adduct (**10**; R = H) into the dihydroimidazole (**21**). Reduction of the 1,2-adduct (**10**; R=H) by aluminium amalgam in moist ethyl acetate and then over platinum in the presence of hydrogen, followed by



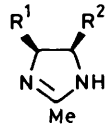
(**17**) X = NO_2
(**18**) X = NHAc



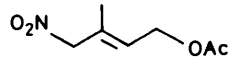
(**19**) X = NO_2
(**20**) X = NHAc



(**21**) R^1 = Me, R^2 = Et
(**22**) R^1 = Me, R^2 = Ph
(**23**) R^1 = Me, R^2 = Pr



(**24**) R^1 = Me, R^2 = Et
(**25**) R^1 = Me, R^2 = Ph
(**26**) R^1 = Me, R^2 = Pr



(**27**)

acid catalysed cyclisation, afforded a single dihydroimidazole. Distinction between the two possible structures (**21**) and (**24**) could be made by comparison of the observed n.m.r. spectrum with the spectra reported[1] for the diastereoisomeric dihydroimidazoles (**22**) and (**25**). In the dihydroimidazole having *trans* substituents, the vicinal coupling constant between the methine protons is 6 Hz but in the dihydroimidazole (**25**) having *cis* substituents the related coupling constant is only 4 Hz. Observation of a coupling constant of 7 Hz in our dihydroimidazole permits the unequivocal assignment of structure (**21**) to this adduct. Hence this result defines a *cis*-addition to pentadiene (**4**) to give the 1,2-adduct (**21**).

The two 1,4-adducts obtained from pentadiene (**4**) could not be readily separated by column chromatography. However, separation by h.p.l.c. permitted the isolation of the two rather unstable 1,4-adducts (**15**) and (**16**). The structure of the major 1,4-adduct (**15**) was established by observation of a coupling between a methylene group and the NH proton, and of a *trans* coupling constant (*J* 15 Hz) associated with a *trans* double bond. The structure of the major adduct (**15**) was confirmed by observation of coupling between a methyl group and the downfield resonance of a methine proton at δ 5.22 p.p.m. The structure of the minor 1,4-adduct (**16**) was similarly established by observation of a downfield methylene resonance (CH_2NO_2) at δ 5.12 p.p.m.; coupling of a methine proton at 4.60 p.p.m. with the NH proton, and of a *trans* coupling constant (*J* 15 Hz) associated with a *trans*-double bond.

trans–trans-Hexa-2,4-diene (**5**) gives a mixture of two 1,2-adducts (**10**; R = Me) and (**11**; R = Me) which could not be separated and a mixture of two 1,4-adducts (**17**) and (**19**) which again could not be separated. Column chromatography readily afforded the two respective mixtures. The ^1H n.m.r. spectrum of the mixture of 1,2-adducts (**10**; R = Me) and (**11**; R = Me) suggested formation of a single nitroamide. The presence of two compounds in this mixture was clearly indicated, however, both by extra peaks in the ^{13}C n.m.r. spectrum (see Experimental section) and by the observation of two components on h.p.l.c. analysis of the mixture. Comparison of the ^1H n.m.r. spectrum of the penta-1,3-diene adduct (**9**) with the spectra of the two 1,2-adducts (**10**; R = Me) and (**11**; R = Me) from *trans–trans*-hexa-2,4-diene permits a straightforward assignment of the regioselectivity in 1,2-addition to the hexadiene (**5**). The lack of stereoselectivity in this addition is confirmed by conversion as described above of the mixture of 1,2-adducts (**10**; R = Me) and (**11**; R = Me) into a mixture of dihydroimidazoles (**23**) and (**26**). Hence both *cis*- and *trans*-addition is observed in nitroacetamidation of *trans–trans*-hexa-2,4-diene (**5**).

The major products (78%) of nitroacetamidation of *trans–trans*-hexa-2,4-diene are the 1,4-adducts (**17**) and (**19**). Again the ^1H n.m.r. spectrum of the mixture (**17**) and (**19**) failed to show the presence of more than a single isomer. Observation of two doublet signals associated with the two methyl groups proves the formation of 1,4-adducts. Although h.p.l.c. analysis of the mixture of 1,4-adducts failed to establish the presence of two components (a single peak was observed on several columns), an extra peak in the ^{13}C n.m.r. spectrum (see Experimental section) suggests that nitroacetamidation of *trans–trans*-hexa-2,4-diene (**5**) gives a mixture rather than a single 1,4-adduct. This suggestion is confirmed by reduction of the mixture of nitroamides (**17**) and (**19**) and subsequent acetylation to give a mixture of the *meso*- and (±)-diamides (**18**) and (**20**) respectively. Use of a chiral solvating reagent shows that a mixture of amides, and not a single amide product, is obtained.

Nitroacetamidation of 1,4-diphenylbutadiene and cyclohexa-1,3-diene were briefly investigated. In the case of 1,4-diphenylbutadiene a complex mixture of products containing nitroamides only as minor components was obtained. With cyclohexa-1,3-diene a good yield of crude nitroacetamides was obtained but further analysis suggested the formation of a complex product mixture.

A number of points emerge from the above results. First both 1,2- and 1,4-nitroacetamides are readily available by use of electrogenerated nitronium tetrafluoroborate. Secondly, the observed regioselectivity accords well with analogous additions to dienes.[5–8] In the case of 1,4-addition to isoprene, formation of the single 1,4-adduct (**13**) compares with the reported[5] formation of the 1,4-adduct (**27**) by nitroacetoxylation. In both cases attack by NO_2^+ gives the more substituted allylic cation. In addition to *trans*-penta-1,3-diene two 1,4-adducts are obtained on nitroacetamidation; the major 1,4-adduct corresponds to electrophilic attack by NO_2^+ at the more substituted double bond. This selectivity has been previously reported[8] in other electrophilic additions to *trans*-penta-1,3-diene. The regioselectivity observed in 1,2-addition follows that reported above for 1,4-addition.

Finally, the question of stereoselectivity arises in the 1,2-addition to *trans*-penta-1,3-diene and to hexadiene (**5**). *cis*-Addition to pentadiene (**2**) and a lack of selectivity with both 1,2- and 1,4-addition to hexadiene (**5**) are observed. These observations accord with the view[9] that in addition by electrophilic nitration a *trans* product is formed *via* a carbocation intermediate.

Experimental

General experimental details have been described earlier.[1] Unless otherwise stated, mass spectra were recorded with a Kratos MS 30 spectrometer using chemical ionisation (c.i.) (NH_3).

Electrogeneration of Nitronium Tetrafluoroborate.—In a two-compartment cell with a glass frit separator, anode and cathode compartments of equal volume (50 ml), and with platinum mesh electrodes (area 6 cm^2), nitronium tetrafluoroborate was electrogenerated at the anode. The cell was maintained by external cooling at 0 °C. The anolyte was a solution of $LiBF_4$ (0.25M) in acetonitrile containing N_2O_4 (0.76 ml, 12.5 mmol). After passage of 0.9 'F mol^{-1} with a current of 250 mA the concentration of NO_2BF_4 was assayed by withdrawal of an aliquot (100 μl) of the anolyte and addition to benzene, and nitrobenzene was estimated by g.l.c. (Carbowax 20 M column at 130 °C). Typically the final concentration of NO_2BF_4 after electrolysis was 0.22M (88% current efficiency). The anolyte solution was used to nitrate dienes as described below.

Nitration of Dienes by Nitronium Tetrafluoroborate in Acetonitrile.—Typically the diene (*ca.* 10 mmol) in dichloromethane (10 ml) was added to a solution of the anolyte (50 ml) (see above) and dichloromethane (50 ml) at −70 °C (bath temperature). After 1 min, aqueous acetonitrile (1:1, 5 ml) was added and the mixture allowed to warm to room temperature. Evaporation of the solvents under reduced pressure afforded a residue to which saturated aqueous sodium hydrogen carbonate (10 ml) was added. Extraction with dichloromethane (3 × 20 ml) and work-up afforded the organic products. Products were isolated pure following chromatography [ethyl acetate–methanol (20:1)] and crystallisation.

Buta-1,3-diene (**1**) gave the following. N-(1-*Nitrobut*-3-*en*-2-*yl*)*acetamide* (**6**) (48%), m.p. 38—40 °C (ether) (Found: C, 45.4; H, 6.3; N, 18.0. $C_6H_{10}N_2O_3$ requires C, 45.6; H, 6.3; N, 17.7%); $\nu_{max.}$($CHCl_3$) 3 420m, 3 310w, 1 670s, 1 645sh, 1 560s, 1 500s, 1 370s, and 935m; δ_H[$(CD_3)_2CO$] 1.96 (3 H, s, MeCO), 4.72 (2 H, m, CH_2NO_2), 5.18 (1 H, m, C*H*NH), 5.20—5.44 (2 H, m, vinyl), 5.96 (1 H, m, vinyl), and 7.6 (1 H, br, NH); δ_C[$(CD_3)_2CO$] 170.48 (CO), 134.45 (vinyl), 117.81 (vinyl), 78.19 ($CHNO_2$), 50.65 (CHNH), and 22.81 (*Me*CO); *m/z* 159 (100, *M* + 1).

(E)-N-(4-*Nitrobut*-2-*enyl*)*acetamide* (**12**) (51%), as an unstable yellow oil. $\nu_{max.}$($CHCl_3$) 3 450m, 3 320w, 1 670s, 1 555s, 1 515s, and 1 375s; δ_H[$(CD_3)_2CO$] 1.95 (3 H, s, MeCO), 3.90 (2 H, m, CH_2NH), 5.12 (2 H, d, *J* 6 Hz, CH_2NO_2), and 5.98 (2 H, m, $J_{obs.}$ 15 Hz, vinyl); δ_C[$(CD_3)_2CO$] 170.26 (CO), 137.51 (vinyl), 120.67 (vinyl), 77.38 (CH_2NO_2), 40.70 (CH_2NH), and 22.72 (*Me*CO); *m/z* 159.0860 (86.5%); $C_6H_{11}N_2O_3$ requires (*M* + 1) 159.0770.

Isoprene (**2**) gave the following. N-(2-*Methyl*-1-*nitrobut*-3-*en*-2-*yl*)*acetamide* (**7**), (39%), m.p. 81—82 °C (ether) (Found: C, 49.0; H, 7.0; N, 16.5. $C_7H_{12}N_2O_3$ requires C, 48.8; H, 7.0; N, 16.3%). $\nu_{max.}$($CHCl_3$) 3 440m, 3 340w, 1 685s, 1 550s, 1 500s, 1 365m, and 935w; δ_H[$(CD_3)_2CO$] 1.54 (3 H, s, Me), 2.02 (3 H, s, MeCO), 4.80 (1 H, d, *J* 10 Hz) and 5.08 (1 H, d, *J* 10 Hz) (CH_2NO_2), 5.26 (2 H, m, vinyl), 6.06 (1 H, dd, *J* 18, 10 Hz, vinyl), and 6.26 (1 H, br, NH); δ_C[$(CD_3)_2CO$] 171.22 (CO), 140.52 (vinyl), 115.30 (vinyl), 80.45 ($CHNO_2$), 57.24 (CHNH), 24.50 (Me), and 23.90 (Me); *m/z* 173 (69.2) (*M* + 1) and 82 (100).

N-(3-*Methyl*-4-*nitrobut*-2-*enyl*)*acetamide* (**13**), (50%), m.p. 43—44 °C (ethyl acetate); $\nu_{max.}$($CHCl_3$) 3 450m, 3 320w, 1 670s, 1 550vs, 1 510s, and 1 375s; δ_H[$(CD_3)_2CO$] 1.82 (3 H, s, Me), 1.91 (3 H, s, MeCO), 3.90 (2 H, dd, *J* 5, 6 Hz, CH_2NH), 5.06 (2 H, s, CH_2NO_2), 5.72 (1 H, m, vinyl), and 7.54 (1 H, br, NH); δ_C[$(CD_3)_2CO$] 170.78 (CO), 133.22 (vinyl), 128.83 (vinyl), 83.85 (CH_2NO_2), 37.58 (CHNH), 22.73 (*Me*CO), and 14.82 (Me); *m/z* 173.0692 (6.6) [$C_7H_{13}N_2O_3$ (*M* + 1) requires 173.0926].

2,3-Dimethylbutadiene (**3**) gave the following. N-(2,3-*Dimethyl*-1-*nitrobut*-3-*en*-2-*yl*)*acetamide* (**8**) (35%), m.p. 94—95 °C (from ether) (Found: C, 51.5; H, 7.6; N, 15.2. $C_8H_{14}N_2O_3$ requires C, 51.6; H, 7.5; N, 15.2%); $\nu_{max.}$($CHCl_3$) 3 440m, 3 320w, 1 685s, 1 550vs, 1 500s, 1 375s, and 910m; δ_H[$(CD_3)_2CO$] 1.51 (3 H, s, *Me*CN), 1.81 (3 H, s, Me), 2.01 (3 H, s, *Me*CO), 4.70—5.36 (2 H, ab, *J* 10 Hz, CH_2NO_2), 4.81 (1 H, s, vinyl), 4.99 (1 H, s, vinyl), and 6.33 (1 H, s, *NH*); δ_C[$(CD_3)_2CO$] 170.48 (CO), 147.49 (vinyl), 111.08 (vinyl), 79.95 (CH_2NO_2), 58.49 (CNH), 24.64 (Me), 23.31 (MeCO), and 19.33 (Me); *m/z* 187 (28.5) (*M* + 1) and 84 (100).

N-(2,3-*Dimethyl*-4-*nitrobut*-2-*enyl*)*acetamide* (**14**) (35%), m.p. 81—82 °C (ether) (Found: C, 51.4; H, 7.6; N, 15.2. $C_8H_{14}N_2O_3$ requires C, 51.6; H, 7.5; N, 15.1); $\nu_{max.}$($CHCl_3$) 3 450m, 3 320w, 1 670s, 1 550s, 1 515s, and 1 375s; δ_H($CDCl_3$) 1.84 (3 H, s, Me), 1.90 (3 H, s, Me), 2.02 (3 H, s, *Me*CO), 3.96 (2 H, s, *J* 6 Hz, CH_2NH), 5.00 (2 H, s, CH_2NO_2), and 6.3 (1 H, br, NH); δ_C[$(CD_3)_2CO$] 170.21 (CO), 138.20 (vinyl), 122.64 (vinyl), 79.53 (CH_2NO_2), 42.08 (CH_2NH), 22.70 (*Me*CO), 17.43 (Me), and 16.97 (Me); *m/z* 187 (7.6) (*M* + 1) and 98 (100).

Pentadiene (**4**) gave the following threo-N-(4-*Nitropent*-1-*en*-3-*yl*)*acetamide* (**10**; R = H) (26%), m.p. 88—90 °C (ether) (Found: C, 48.9; H, 7.1; N, 16.4. $C_7H_{12}N_2O_3$ requires C, 48.8; H, 7.0; N, 16.3%); $\nu_{max.}$($CHCl_3$) 3 340s, 3 320m, 1 680s, 1 640sh, 1 550s, 1 500s, and 940m; δ_H[$(CD_3)_2CO$] 1.60 (3 H, d, *J* 8 Hz, Me), 1.96 (3 H, s, *Me*CO), 4.8—5.1 (2 H, m, C*H*NO_2, C*H*NH), 5.16—5.46 (2 H, m, vinyl), 4.90 (1 H, m, vinyl), and 7.48 (1 H, br, N*H*); δ_C[$(CD_3)_2CO$] 170.23 (CO), 134.06 (vinyl), 118.78 (vinyl), 85.70 ($CHNO_2$), 55.26 (CHNH), 22.86 (*Me*CO), and 15.99 (*Me*); *m/z* 173 (4.9%) (*M* + 1) and 56 (100).

A mixture of the acetamides (**15**) *and* (**16**) (64%) which were separated in analytical amounts by h.p.l.c. (Zorbax-sil, eluant ethyl acetate; refractive index detection) (E)-N-(4-*Nitropent*-2-*enyl*)*acetamide* (**15**) an unstable oil, $\nu_{max.}$($CHCl_3$) 3 440m, 3 320w, 1 665s, 1 550s, 1 510s, 1 360m, and 970m; δ_H[$(CD_3)_2CO$] 1.61 (3 H, d, *J* 6 Hz, Me), 1.92 (3 H, s, *Me*CO), 3.86 (2 H, dd, *J* 6, 2 Hz, CH_2NH), 5.22 (1 H, m, C*H*NO_2), 5.92 (2 H, ab, $J_{obs.}$ 15 Hz, vinyl), and 7.3 (1 H, br, NH); δ_C[$(CD_3)_2CO$] 170.42 (CO), 134.74 (vinyl), 127.04 (vinyl), 84.73 ($CHNO_3$), 40.65 (CH_2NH), 22.76 (*Me*CO), and 19.44 (Me); *m/z* 173.0991 (6.4%) [$C_7H_{13}N_2O_3$ (*M* + 1) requires 173.0926]. (E)-N-(5-*Nitropent*-3-*en*-2-*yl*)*acetamide* (**16**) a low m.p. solid; $\nu_{max.}$($CHCl_3$) 3 440m, 3 320w, 1 670s, 1 555s, 1 510m, 1 370m, and 970m; δ_H[$(CD_3)_2CO$] 1.24 (3 H, d, *J* 6 Hz, Me), 1.94 (3 H, s, MeCO), 4.60 (1 H, m, C*H*NH), 5.12 (2 H, d, *J* 6 Hz, CH_2NO_2), 5.98 (2 H, ab, $J_{obs.}$ 15 Hz, vinyl), and 7.4 (1 H, br, NH); δ_C[$(CD_3)CO$] 169.54 (CO), 142.45 (vinyl), 119.24 (vinyl), 77.54 (CH_2NO_2), 46.21 (CHNH), 22.91 (MeCO), and 20.32 (Me); *m/z* 173.0970 (3.5%); $C_7H_{13}N_2O_3$ (*M* + 1) requires 173.0926.

Hexadiene (**5**) gave the following. threo-(**10**; R=Me) *and* erythro-(E)-N-(2-*Nitrohex*-4-*en*-3-*yl*)*acetamide* (**11**; R = Me) (6%), m.p. 118—120 °C (ether) (Found: C, 51.3; H, 7.6; N, 15.2. $C_8H_{14}N_2O_3$ requires C. 51.6; H, 7.5; N, 15.1%); $\nu_{max.}$($CHCl_3$) 3 340m, 3 320w, 1 680s, 1 670s, 1 550s, 1 500s, 1 370m, 1 360m, and 970m; δ_H[$(CD_3)_2CO$] 1.46 (3 H, d, *J* 6 Hz, *Me*NO_2), 1.68 (3 H, d, *J* 5 Hz, *Me*), 1.94 (3 H, s, *Me*CO), 4.84 (2 H, m, C*H*NO_2, C*H*NH), 5.30—5.98 (2 H, m, $J_{obs.}$ 15 Hz, vinyl), and 7.45 (1 H, br, NH); δ_C[$(CD_3)_2CO$] 170.13 (CO), 130.82 (vinyl), 126.74 and

126.56 (vinyl), 85.96 ($CHNO_2$), 55.10 (CHNH), 22.87 (*Me*CO), 17.85 (Me), and 15.90 and 15.40 (Me); *m/z* 187 (0.4) (*M* + 1) and 70 (100); (E)-N-(*5-Nitrohex-3-en-2-yl)acetamides* (**17**) and (**19**) (78%), m.p. 45—47 °C (ether) $\nu_{max.}$($CHCl_3$) 3 440m, 3 320w, 1 670s, 1 555s, 1 510s, 1 370m, 1 360m, and 970m; δ_C[$(CD_3)_2CO$] 1.22 (3 H, d, *J* 6 Hz, Me), 1.61 (3 H, d, *J* 6 Hz, Me), 1.90 (3 H, s, MeCO), 4.36 (1 H, m, C*H*NH), 5.20 (1 H, m, C*H*NO_2), 5.90 (2 H, ab, $J_{obs.}$ 15 Hz, vinyl), and 7.2 (1 H, br, NH); δ_C[$(CD_3)_2CO$] 169.77 (CO), 139.45 (vinyl), 125.41 (vinyl), 84.71 ($CHNO_2$), 46.06 (CHNH), 22.89 (MeCO), 20.36 and 20.27 (Me), and 19.49 (Me); *m/z* 187.1039 (0.4) [$C_8H_{15}N_2O_3$ (*M* + 1) requires 187.1083].

trans-5-*Ethyl*-2,4-*dimethyl*-4,5-*dihydro*-1H-*imidazole* (**21**).—*threo-N*-(4-Nitropent-1-en-3-yl)acetamide (**10**; R = H) (0.24 g, 1.4 mmol) in ethyl acetate (5 ml) was added to a suspension of aluminium amalgam (2.5 g) in ethyl acetate (100 ml) containing sulphuric acid (0.01 M; 1 ml). The mixture was stirred for 2 h. The combined ethyl acetate solutions were concentrated (to 20 ml) by evaporation under reduced pressure. Platinum dioxide (10 mg) was added and the solution stirred under H_2 overnight. The catalyst was filtered off and the solvent removed under reduced pressure to afford a residue which was taken up in xylene (20 ml). After addition of toluene-*p*-sulphonic acid (2 mg) the solution was heated under reflux for 8 h and then cooled. Organic bases were removed by washing with dilute hydrochloric acid (3 × 20 ml). The combined aqueous solutions were washed with hexane (3 × 20 ml) and then neutralised with aqueous potassium hydroxide and further extracted with dichloromethane (3 × 20 ml). The combined dichloromethane solution was washed with water, dried ($MgSO_4$), and evaporated to afford an oily residue. Distillation (50 °C/0.1 Torr) gave as a colourless oil *trans*-5-ethyl-2,4-dimethyl-4,5-dihydro-1*H*-imidazole (**21**) (100 mg, 57%) $\nu_{max.}$($CHCl_3$) 3 430m and 1 630s; δ_H (360 MHz, $CDCl_3$) 0.94 (3 H, t, *J* 8 Hz, Me), 1.29 (3 H, d, *J* 6 Hz, Me), 1.45 (2 H, m, CH_2), 1.92 (3 H, s, MeC=N), 3.24 (1 H, q, *J* 7 Hz, CHEt), 3.52 (1 H, m, CHMe), 4.4 (1 H, br, NH); *m/z* (e.i.) 126.1168 (31.7); $C_7H_{14}N_2$ requires 126.1157.

cis- and trans-2,4*Dimethyl*-5-*propyl*-4,5-*dihydro*-1H-*imidazole* (**26**) *and* (**23**).—Following the above procedure, a mixture of the *threo*- and *erythro* acetamide (**10**; R = Me) and (**11**; R = Me) respectively were convened into a mixture of *cis*- and *trans*-2,4-dimethyl-5-propyl-4,5-dihydro-1*H*-imidazole (**26**) and (**23**) in 90% yield; $\nu_{max.}$($CHCl_3$) 3 440w and 1 630 cm^{-1}; δ_H (360 MHz, $CDCl_3$) 0.9—1.5 (complex), 1.94 (s, Me C=N), 3.32 (qm, *J* 7 Hz, CHPr, major isomer), 3.52 (q, *J* 7 Hz, CHMe, major isomer), 3.73 (m, CHPr, minor isomer), and 3.91 (m, CHMe, minor isomer). Integration indicated an isomer ratio *trans*:*cis* = 3:2; *m/z* (e.i.) 140.1335 (8.5%); $C_8H_6N_2$ requires 140.1313.

N-(4-N′-*Acetamido*-1-*methylpent*-2-*yl)acetamide* (**18**) *and* (**20**).—*N*-(1-Methyl-2-nitropent-2-yl)acetamide was reduced using the above conditions described for reduction of the nitroamide (**10**; R = H). The crude product from this reaction (0.17 g) was acetylated in acetic anhydride (2 ml) and acetic acid (1 ml). Work-up by evaporation and chromatography on silica gel (eluant 1:1 ethyl acetate–ethanol) gave *N*-(4-*N*′-acetamido-1-methylpent-2-enyl)acetamide (**18**) and (**20**) (0.2 g, 98%) as a white crystalline solid, m.p. 177—181 °C; *m/z* 184.1314 (0.1%); $C_{10}H_{18}N_2O_2$ requires 184.1338; $\nu_{max.}$ 3 440m, 3 310w, 1 665s, and 970m; δ_H($CDCl_3$) 1.22 (3 H, d, *J* 7 Hz, Me), 2.00 (3 H, s, MeCO), 4.54 (1 H, m, C*H*NH), 5.57 (1 H, m, vinyl H), and 5.9 (1 H, br, NH). In the presence of the chiral solvating agent (−)-9-(2,2,2-trifluoro-1-hydroxyethyl)anthracene the signal at *ca.* 2.0 p.p.m. was resolved into four signals of similar intensity. Similarly the doublet at 1.22 p.p.m. split to give seven observable signals.

Acknowledgements

We thank Dr. J. A. Organ and Mrs J. Street for recording mass spectra and n.m.r. spectra, respectively. This work has been carried out with support from Procurement Executive, Ministry of Defence.

References

1 A. J. Bloom, M. Fleischmann, and J. M. Mellor, *J. Chem. Soc., Perkin Trans. 1*, 1984, 2357.
2 A. J. Bloom, M. Fleischmann, and J. M. Mellor, *Tetrahedron Lett.*, 1984, **25**, 4971.
3 M. L. Scheinbaum and M. Dines, *J. Org. Chem.*, 1971, **36**, 3641; R. D. Bach, J. W. Holubka, R. C. Badger, and S. J. Rajan, *J. Am. Chem. Soc.*, 1979, **101**, 4416; V. M. Shitkin, T. N. Druzhkova, S. G. Zlotin, M. M. Krayushkin, and V. V. Sevost'yanova, *Bull. Acad. Sci. USSR Div. Chem. Sci.*, 1979, 1183.
4 K. B. Sharpless and S. P. Singer, *J. Org. Chem.*, 1976, **41**, 2506; H. Natsagari, R. R. Whittle, and S. M. Weinreb, *J. Am. Chem. Soc.*, 1984, **106**, 7867.
5 P. A. Wehrli and B. Schaer, *J. Org. Chem.*, 1977, **42**, 2939.
6 V. L. Heasley, G. E. Heasley, S. K. Taylor, and C. L. Frye, *J. Org. Chem.*, 1970, **35**, 2967; G. E. Heasley, V. L. Heasley, S. L. Manatt, H. A. Day, R. V. Hodges, P. A. Kroon, D. A. Redfield, T. L. Rold, and D. E. Williamson, *ibid.*, **38**, 4109.
7 G. E. Heasley, D. C. Hayse, G. R. McClung, D. K. Strickland, V. L. Heasley, P. D. Davis, D. M. Ingle, K. D. Rold, and T. S. Ungermann, *J. Org. Chem.*, 1976, **41**, 334.
8 G. H. Schmid, S. Yeroushalmi, and D. G. Garratt, *J. Org. Chem.*, 1980, **45**, 910.
9 F. G. Bordwell and E. W. Garbisch, *J. Org. Chem.*, 1962, **27**, 2322 and 3049; F. G. Bordwell and E. W. Garbisch, *ibid.*, **28**, 1765; F. G. Bordwell and J. B. Biranowski, *ibid.*, **32**, 629.

Received 22nd April 1985; *Paper* 5/654