



Scheme 2 Reagents: i, MCPBA (100%); ii, HClO₄ (85%)

GC/MS 5988A. The liquid products were monitored by GLC, performed on a Carlo Erba Fractovap 4160 using a capillary column of Duran glass (0.32 mm × 25 m), stationary phase OV1 (film thickness 0.4–0.45 nm). Elemental analyses were performed using an Analyzer Model 185 from Hewlett-Packard. (Z)-Dec-4-en-1-ol was purchased from Alfa products.

(Z)-1-Nitrodec-4-ene **1a**.—To a mechanically stirred solution of (Z)-dec-4-en-1-ol (10.92 g, 0.07 mol) and pyridine (2.66 cm³, 0.0282 mol), cooled in an ice–water-bath, was added, dropwise, phosphorus tribromide (1.8 cm³, 0.0234 mol) during 20 min. The mixture was stirred at room temperature for 2 h, water (25 cm³) was added and the product was extracted with diethyl ether (3 × 30 cm³). The organic layer was washed consecutively with HCl (2 mol dm⁻³; 15 cm³), sodium hydroxide (2 mol dm⁻³; 15 cm³), and finally with water (20 cm³). The ethered layer was dried (MgSO₄), then evaporated, and the residue was distilled under reduced pressure to give (Z)-1-bromodec-4-ene (10.57 g, 69%), b.p. 114 °C (0.6 mmHg).

The obtained bromide (4.8 g, 0.0219 mol) was added to a stirred solution of sodium nitrite (2.74 g, 0.0416 mol) in DMF (50 cm³). The solution was stirred for 6 h, then quenched with cold water (80 cm³), and the mixture was extracted with diethyl ether (3 × 30 cm³). The combined extract was dried (MgSO₄), filtered through a bed of Florisil and evaporated at reduced pressure, and the residue was purified by column chromatography with hexane–ethyl acetate (90:10 v/v) to give (Z)-1-nitrodec-4-ene **1a** (2.55 g, 63%), b.p. 140 °C (0.03 mmHg) (Kugelrohr) (Found: C, 65.0; H, 10.5; N, 7.3. C₁₀H₁₉NO₂ requires C, 64.83; H, 10.34; N, 7.56%); δ_H 0.88 (3 H, t, *J* 7.5), 1.18–1.41 (6 H, m), 1.93–2.22 (6 H, m), 4.37 (2 H, t, *J* 7.5), 5.23–5.38 (1 H, m) and 5.42–5.55 (1 H, m); ν_{max}(film)/cm⁻¹ 1555.

α-Nitro Ketones **3a, b**.—A 100 cm³, two-necked flask equipped with a mechanical stirrer was charged with a nitro compound **1** (0.01 mol) and cooled in an ice–water-bath. An aldehyde **2** (0.01 mol) was added and the mixture was stirred for 5 min. Amberlyst A-21 (3 g) was then added and the mixture was stirred for 7 h at room temperature before being extracted with dichloromethane (3 × 15 cm³). The filtered extract was poured into a 250 cm³, three-necked flask equipped with a mechanical stirrer. Tetrabutylammonium hydrogen sulphate (0.35 g, 0.001 mol) was added and the mixture was cooled to –10 °C. 30% Sulphuric acid (20 cm³) and potassium dichromate (3.9 g, 0.0132 mol) were added simultaneously and the mixture was stirred for 2 h at –10 °C. After this time 10% aq. iron(II) sulphate (20 cm³) was added and the layers were separated. The organic phase was dried (MgSO₄) and passed through a bed of Florisil. The solvent was removed under reduced pressure to afford the crude nitro ketone **3a** or **3b**, which was used without further purification.

(Z)-10-Nitroheicos-6-en-11-one **3a** (2.75 g, 78%); oil (Found: C, 71.6; H, 11.4; N, 4.1. C₂₁H₃₉NO₃ requires C, 71.34; H, 11.12; N, 3.96%); δ_H 0.82–0.92 (6 H, m), 1.18–1.65 (22 H, m), 1.9–2.19 (6 H, m), 2.42–2.65 (2 H, m), 5.1–5.18 (1 H, m), 5.21–

5.35 (1 H, m) and 5.40–5.57 (1 H, m); ν_{max}(film)/cm⁻¹ 1730 and 1552.

(Z)-3-Nitronon-6-en-2-one **3b** (1.3 g, 70%); b.p. 105 °C (0.5 mmHg) (Kugelrohr) (Found: C, 58.5; H, 8.3; N, 7.3. C₉H₁₅NO₃ requires C, 58.36; H, 8.16; N, 7.56%); δ_H 0.93 (3 H, t, *J* 7.3), 1.9–2.2 (6 H, m), 2.28 (3 H, s), 5.15 (1 H, m) and 5.18–5.60 (2 H, m); ν_{max}(film)/cm⁻¹ 1735 and 1550.

α-Nitro Ketone *p*-Tolylsulphonylhydrazones **4a, b**.—*p*-Tolylsulphonylhydrazine (1.4 g, 7.5 mmol) was added to a solution of an *α*-nitro ketone **3** (7-mmol) in methanol (6 cm³). The mixture was left for 12 h, then water was added to obtain, as a solid, the corresponding pure *p*-tolylsulphonylhydrazone **4**.

(Z)-10-Nitroheicos-6-en-11-one *p*-tolylsulphonylhydrazone **4a** (3.28 g, 90%); m.p. 58–60 °C (from aq. MeOH) (Found: C, 64.7; H, 9.2; N, 8.3; S, 6.0. C₂₈H₄₇N₃O₄S requires C, 64.46; H, 9.08; N, 8.06; S, 6.13%); δ_H 0.88 (6 H, t, *J* 7.5), 1.15–1.42 (24 H, m), 1.82–2.30 (8 H, m), 2.43 (3 H, s), 4.97–5.08 (1 H, m), 5.18–5.32 (1 H, m), 7.25 (s, 1 H) and 7.57 (4 H, AA'BB' pattern, *J* 8.0); ν_{max}(KBr)/cm⁻¹ 3220, 1610, 1555, 1335 and 1165.

(Z)-3-Nitronon-6-en-2-one *p*-tolylsulphonylhydrazone **4b** (2.32 g, 94%); m.p. 91–92 °C (from aq. MeOH) (Found: C, 54.55; H, 6.8; N, 12.0; S, 9.2. C₁₆H₂₃N₃O₄S requires C, 54.38; H, 6.56; N, 11.89; S, 9.05%); δ_H 0.95 (3 H, t, *J* 7.5), 1.83 (3 H, s), 1.86–2.3 (6 H, m), 2.42 (3 H, s), 4.98–5.08 (1 H, m), 5.12–5.5 (2 H, m), 7.25 (s, 1 H) and 7.57 (4 H, AA'BB' pattern, *J* 8.0); ν_{max}(KBr)/cm⁻¹ 3210, 1540, 1330 and 1165.

Denitration of *α*-Nitro Ketone *p*-Tolylsulphonylhydrazones to give Compounds **5a, b**.—A solution of a nitro compound **4** (5 mmol) in dry THF (30 cm³) was added dropwise to a cooled (0 °C) mixture of lithium aluminium hydride (0.57 g, 15 mmol) in dry THF (40 cm³) under nitrogen. The mixture was stirred for 1.5 h, treated carefully with cold water, acidified with HCl (2 mol dm⁻³), and extracted with Et₂O (3 × 30 cm³). The combined ethereal layers were dried (MgSO₄), passed through a bed of Florisil and evaporated under reduced pressure to afford the tosylhydrazone **5a** or **5b**, pure by analytical data.

(Z)-Heneicos-6-en-11-one *p*-tolylsulphonylhydrazone **5a** (2.14 g, 90%); oil (Found: C, 70.3; H, 10.0; N, 5.6; S, 6.5. C₂₈H₄₈N₂O₂S requires C, 70.55; H, 10.15; N, 5.88; S, 6.71%); δ_H 0.89 (6 H, t, *J* 7.0), 1.09–2.2 (32 H, m), 2.42 (3 H, s), 5.2–5.5 (2 H, m), 7.25 (s, 1 H) and 7.57 (4 H, AA'BB' pattern, *J* 8.0); ν_{max}(KBr)/cm⁻¹ 3210, 1600, 1335 and 1165.

(Z)-Non-6-en-2-one *p*-tolylsulphonylhydrazone **5b** (1.34 g, 86%); m.p. 70–71 °C (from aq. MeOH) (Found: C, 62.6; H, 8.0; N, 8.9; S, 10.15. C₁₆H₂₄N₂O₂S requires C, 62.31; H, 7.85; N, 9.09; S, 10.37%); δ_H 0.93 (3 H, t, *J* 7.5), 1.4–2.21 (8 H, m), 1.75 (3 H, s), 2.4 (3 H, s), 5.18–5.48 (2 H, m), 7.25 (s, 1 H) and 7.57 (4 H, AA'BB' pattern, *J* 8.0); ν_{max}(KBr)/cm⁻¹ 3215, 1163 and 1135.

Regeneration of Carbonyl Compounds **6a, b** from Tosylhydrazones **5a, b**.—A 100 cm³ flask, equipped with reflux condenser and magnetic stirrer, was charged with a tosylhydrazone **5** (2.5 mmol), acetone–water (10:1; 20 cm³) and Amberlyst A-15 (1 g). The mixture was stirred at 80 °C for 5 h. The acetone was removed by distillation. Extraction with pentane (3 × 10 cm³), filtration and distillation gave the pure ketone **6**.

(Z)-Heneicos-6-en-11-one **6a** (0.731 g, 95%); b.p. 240 °C (0.7 mmHg) (Kugelrohr) [lit.,²⁰ 161–162 °C (0.05 mmHg)] (Found: C, 81.9; H, 13.3. Calc. for C₂₁H₄₀O: C, 81.75; H, 13.07%); δ_H 0.88 (6 H, t, *J* 7.5), 1.1–1.45 (22 H, m), 1.5–1.68 (2 H, m, *J* 7.2), 1.91–2.11 (4 H, m), 2.32–2.47 (4 H, m) and 5.25–5.48 (2 H, m); δ_C 14.081, 14.120, 22.588, 22.69, 23.751, 23.902, 26.579, 27.214, 29.293, 29.322, 29.437, 29.494, 29.58, 31.527, 31.903, 42.091, 42.89, 128.64, 130.99 and 211.17; *m/z* 380 (M⁺, 2%), 251 (7), 237

(12), 167 (16), 169 (44), 124 (85), 82 (100) and 55 (61); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1710.

(*Z*)-Non-6-en-2-one **6b** (0.325 g, 93%); b.p. 150 °C (45 mmHg) (Kugelrohr) [lit., ^{14c} 94–96 °C (20 mmHg)] (Found: C, 77.3; H, 11.3. Calc. for C₉H₁₆O: C, 77.09; H, 11.50%); δ_{H} 0.95 (3 H, t, *J* 7.4), 1.55–1.70 (2 H, m), 1.92–2.08 (4 H, m), 2.12 (3 H, s), 2.37–2.45 (2 H, m) and 5.2–5.5 (2 H, m); δ_{C} 23.578, 31.8455, 42.962, 128.11 and 209.169; *m/z* 140 (M⁺, 31%), 125 (37), 111 (57), 97 (43), 85 (34), 83 (43), 82 (93), 81 (56), 71 (50), 68 (35), 67 (100), 58 (37) and 55 (52); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1708.

(±)-*exo*-Brevicomine **8**.—(±)-*exo*-Brevicomine **8** was obtained in 85% yield from compound **6b** via its epoxidation with *m*-chloroperbenzoic acid to give **7**, then subsequent cyclization using perchloric acid, by the known method.¹⁰ B.p. 110 °C (20 mmHg) (Kugelrohr) [lit., ^{14c} 86–88 °C (50 mmHg)].

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