Zwitterion-accelerated [3,3]-Sigmatropic Rearrangements and [2,3]-Sigmatropic Rearrangements of Sulphoxides and Amine Oxides

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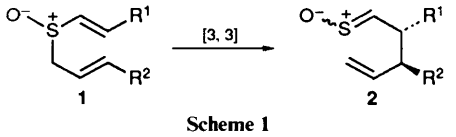
The effect of a zwitterionic moiety on [3,3]-sigmatropic rearrangements has been studied. The allyl vinyl sulphoxide **5** underwent a [3,3]-sigmatropic rearrangement at 23 °C under neutral conditions to give the thione *S*-oxide **6** (96%). This rearrangement (k_1 = 1.56 ± 0.04 × 10^{-1} h^{-1}) was 45 times faster than conversion of the corresponding sulphide **3** into the thione **4** (k_1 = 3.5 ± 0.1 × 10^{-3} h^{-1}). At 23 °C, the sulphoxide **7** also rearranged to give a mixture of (*E*)- and (*Z*)-thial *S*-oxide **8** (90%). These experiments showed that the accelerating effect of the charges in the sulphoxide, a zwitterionic moiety, did not cancel out. Instead, the sulphoxide moiety significantly facilitated the [3,3]-sigmatropic rearrangement.

In the thermolysis of hexa-1,5-dienes with a zwitterionic moiety attached to the C-3 position (*e.g.*, **9** and **24**), [2,3]-sigmatropic rearrangements occurred. The conversion of the allyl sulphoxide **21** into the corresponding sulphenate ester **22** by a [2,3] process was used as the key step in a total synthesis of yomogi alcohol **23**, a biologically active monoterpenoid.

The high temperatures at which [3,3]-sigmatropic rearrangements generally occur unless catalysts are used limits their application. Two methods are utilized to accelerate uncatalysed [3,3]-sigmatropic rearrangements: placement of an electron-donating or -withdrawing group in the substrate,[1-4] and introduction of a positive[5,6] or a negative[7-13] charge into the system. We herein provide evidence to show that acceleration can be obtained by placement of a zwitterionic moiety at an appropriate position in substrates.

The conversion of allyl vinyl sulphoxides into γ,δ-unsaturated sulphines belongs to a zwitterion-accelerated rearrangement,[14] —a specific class of charge-accelerated rearrangements.‡ In a zwitterion-accelerated [3,3]-sigmatropic rearrangement, the accelerating factor comes from a moiety that is either a betaine[15] or an ylide.[16] The conversion of allyl vinyl sulphoxides **1** into the sulphines **2** belongs to the latter category and could be synthetically useful (Scheme 1). A study of the



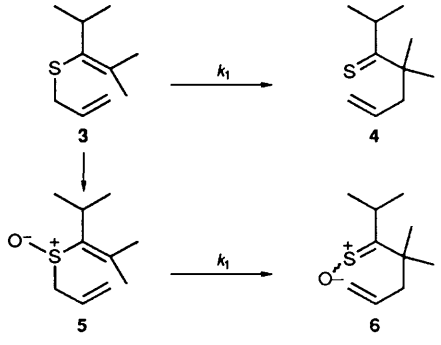
Scheme 1

kinetics of the reaction **1**→**2** may also provide valuable information about the effects of a zwitterionic moiety on the rearrangement rate.

We further investigated the influence of zwitterionic moieties, *e.g.* sulphoxide, amine oxide and nitro group, at the 3-position of hexa-1,5-dienes on their [3,3]-sigmatropic rearrangement. For the rearrangements involving sulphoxides or amine oxides, we explored whether the [3,3]- or the [2,3]-rearrangement prevails. Furthermore, we utilized the information obtained to synthesize yomogi alcohol, a monoterpenoid with biological activities.

Results

[3,3]-*Sigmatropic Rearrangements of Sulphoxides* **5** *and* **7**.— To determine the rate constants (k_1) of [3,3]-sigmatropic rearrangements of the sulphoxide **5** and the sulphide **3**, we monitored their concentrations in $CDCl_3$ as a function of reaction time by ^1H NMR spectroscopy. The sulphoxide **5** was prepared in 95% yield from the sulphide **3**[17] and 1.0 equiv. of *m*-chloroperoxybenzoic acid (*m*-CPBA). At 23 °C, k_1 was 1.56 ± 0.04 × 10^{-1} h^{-1} for the reaction **5**→**6** and 3.5 ± 0.1 × 10^{-3} h^{-1} for the reaction **3**→**4** (Scheme 2).



Scheme 2

For the reaction **5**→**6**, we plotted ln[**5**] *versus* reaction time to give a straight line (see Fig. 1). Thus, this rearrangement was first-order and irreversible.[18a] The slope of the line is equal to the rate constant (k_1).[18a] For the reaction **3**→**4**, a plot of ln([**3**] − [$\mathbf{3}_{eq}$]) *versus* reaction time gave a straight line (Fig. 2). This indicates that the rearrangement was first-order and reversible.[18b] The slope is equal to the observed rate constant (k_{obsd}), which is the sum of the forward (k_1) and the reverse rate constants (k_{-1}).[18b] The K_{eq} for the reaction **3**→**4** is equal to $[\mathbf{4}]_{eq}/[\mathbf{3}]_{eq}$, where $[\mathbf{3}]_{eq}$ and $[\mathbf{4}]_{eq}$ represent the concentrations of **3** and **4**, respectively, remaining at equilibrium.[18b] Consequently, we were able to obtain the forward rate constant (k_1) of the reaction **3**→**4** by using the equations $k_{obs} = k_1 + k_{-1}$ and $K_{eq} = k_1/k_{-1}$.[18b]

We found that sulphoxide **5** completely rearranged to the sulphine **6** over a wide range of temperatures (8, 23, 50, 80 and

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‡ For the definition of the charge-accelerated rearrangement, see ref. 6, p. 658.

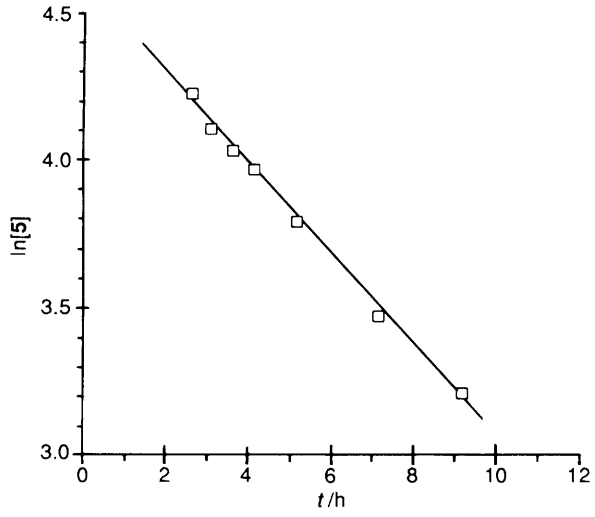


Fig. 1 Plot of ln[**5**] *versus* reaction time under neutral conditions, where [**5**] = concentration of starting material **5** remaining at time *t*

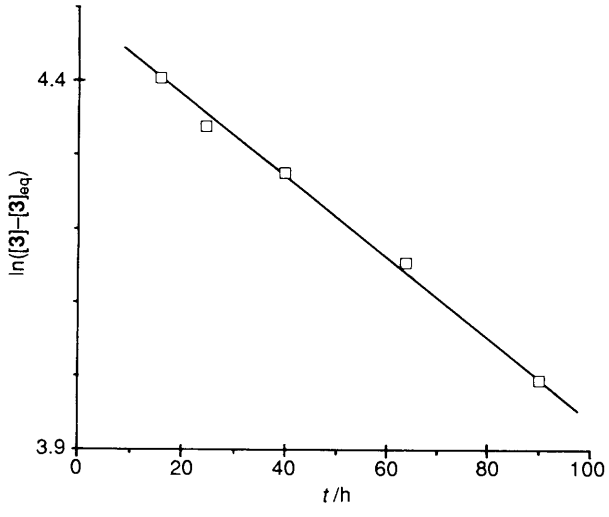
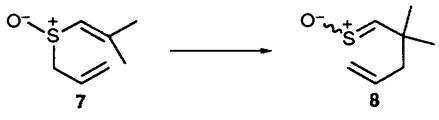


Fig. 2 Plot of $\ln([\mathbf{3}] - [\mathbf{3}]_{eq})$ *versus* reaction time, where [**3**] = concentration of starting material **3** remaining at time *t*, and $[\mathbf{3}]_{eq}$ = concentration of starting material remaining at equilibrium

101 °C). The corresponding sulphide **3**, however, reached equilibrium with **4** at 23 °C with the composition of 1:6.7 = **3**/**4**. At room temperature, the reaction **5**→**6** was complete in 30 h, while the reaction **3**→**4** required 34 days to equilibrate.

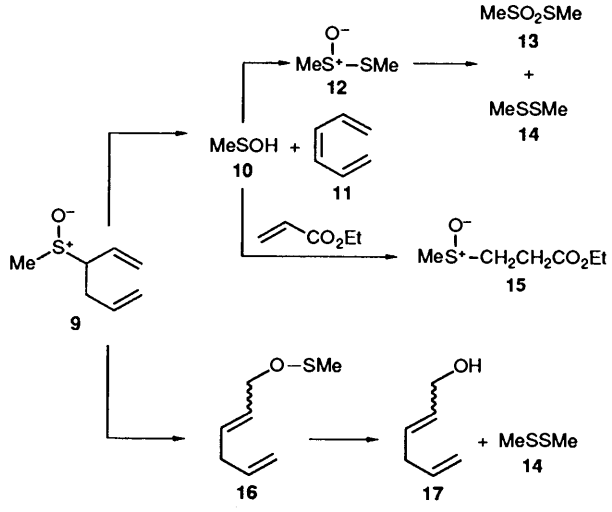
By oxidizing 2-methyl-1-prop-2-enylthioprop-1-ene[19] with 1.0 equiv. of *m*-CPBA in $CHCl_3$ at 23 °C, we obtained allyl vinyl sulphoxide **7** in 97% yield. This sulphoxide underwent [3,3]-sigmatropic rearrangement in $CHCl_3$ to give the sulphine **8**[20] in 90% yield after 30 h at room temperature (Scheme 3). We



Scheme 3

isolated **8** as a mixture of *E* and *Z* isomers (δ 8.92 for the *E* and δ 7.49 for the *Z* SCH=C protons), which were interconvertible.[21]

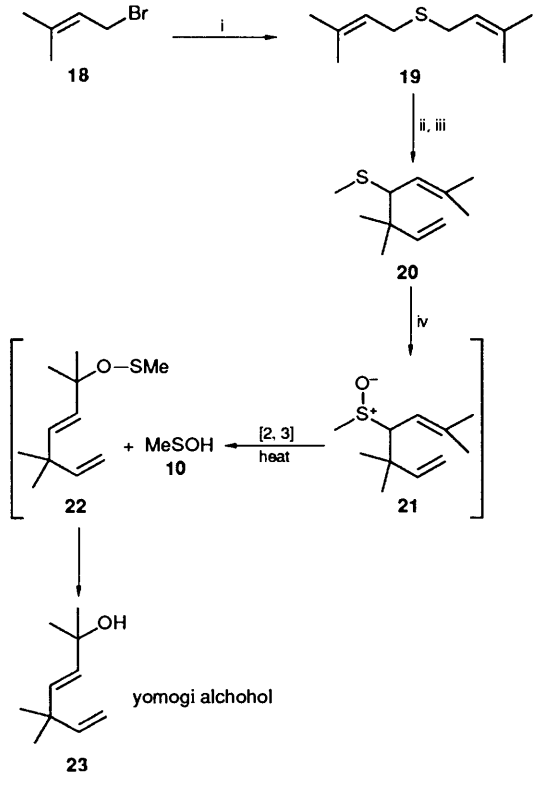
Thermolysis of the Sulphoxide **9**.—We oxidized 3-methylthiohexa-1,5-diene[22] with 1.0 equiv. of *m*-CPBA in CH_2Cl_2 at 0 °C to give the sulphoxide **9** in 89% yield. At 50 °C in $CDCl_3$ for 3 h, this sulphoxide remained unchanged. When **9** was heated at 77 °C in CCl_4 for 16 h, however, we isolated three products: *S*-methyl methanethiosulphinate[23] **12** (14%), *S*-methyl methanethiosulphonate[24] **13** (21%), and the allylic alcohol **17**[25] (21%) (Scheme 4). The alcohol **17** was



Scheme 4

obtained as a mixture of *E* and *Z* isomers with a ratio of 6.7:1 (= *E*/*Z*), as determined by ^1H NMR spectroscopy. The coupling constant for the CH_2O protons of the *Z* isomer was 5.6 Hz, which was consistent with that observed by Sota *et al.*[25] Also, a CCl_4 solution of the sulphoxide **9** in the presence of 5.0 equiv. of ethyl acrylate was heated at 77 °C for 16 h to give *S*-methyl methanethiosulphinate **12** (13%), the sulphoxide ester **15**[26] (39%), and allylic alcohol **17** (13%, Scheme 4).

Total Synthesis of Yomogi Alcohol **23**.[27]—We accomplished a total synthesis of yomogi alcohol in three steps from prenyl bromide **18**, a commercially available reagent (Scheme 5). We



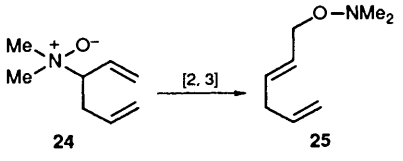
Scheme 5 *Reagents:* i, Na_2S; ii, BuLi; iii, MeI; iv, *m*-CPBA

converted the bromide **18** into the sulphide **19**[28] with Na_2S by following the procedure of Martinetz and Hiller.[29] The sulphide **19** was then treated with 1.4 equiv. of BuLi to effect the Stevens rearrangement.[30] *In situ*, 2 equiv. of MeI were added to give the sulphide **20**.[31] Oxidation of **20** with 1.0 equiv. of *m*-CPBA in 1,4-dioxane and water at room temperature produced the sulphoxide **21**. Although this sulphoxide was not isolated, it was detected by ^{1}H NMR spectroscopy. After 30 min, the reaction mixture was heated at 90 °C for 4.5 h to give yomogi alcohol **23** (53%).

We found that the yield of **23** was solvent-dependent in the one-flask reaction **20**→**21**→**22**→**23**. Use of an anhydrous solvent did not afford **23**; however, it was generated in organic solvents containing various amounts of water. A 1,4-dioxane solution containing 15% of water provided the best results. Ciuffarin *et al.*[31] observed the same solvent effect for the decomposition of MeOSAr to methanol (*cf.* **22**→**23**).

Similarly to the generation of the sulphoxide ester **15** from the sulphoxide **9** (see Scheme 4), we heated **21** in the presence of 5.0 equiv. of ethyl acrylate at 90 °C in 1,4-dioxane to give the sulphoxide ester **15** (11%).

Thermolysis of the Amine Oxide **24**.—By following the procedure of Craig and Purushothaman,[32] we obtained the amine oxide **24** (91%) from the corresponding amine[33] and 1.0 equiv. of *m*-CPBA. In $CDCl_3$ it underwent a [2,3]-sigmatropic rearrangement to the hydroxylamine **25** at 25 °C (k_1 = 3.8 ± 0.3 × 10^{-1} h^{-1} and a $t_{\frac{1}{2}}$ = 1.8 h; Scheme 6). Since a plot

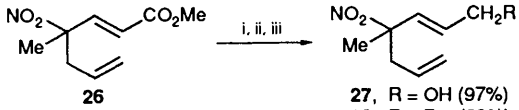


24 **25**

Scheme 6

of ln[**24**] *versus* reaction time gave a straight line, this rearrangement was first-order and irreversible.[18a]

Thermolysis of the Nitro Compound **29**.—Our synthesis of the tertiary allylic nitro compound **29** from the nitro ester **26**[34] involves three steps (Scheme 7). Ester **26** was reduced with 2.0



26

27, R = OH (97%)
28, R = Br (93%)
29, R = H (90%)

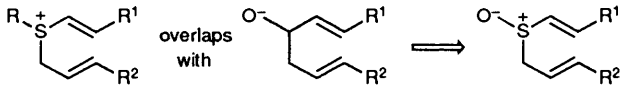
Scheme 7 *Reagents*: i, DIBAL-H, toluene; ii, LiBr, MsCl, collidine, DMF; iii, $LiEt_3BH$, THF

equiv. of diisobutylaluminium hydride (DIBAL-H)[35] in toluene to give the alcohol **27** (97%). Treatment of **27** with 2.0 equiv. of collidine, 1.0 equiv. of LiBr, and 2.0 equiv. of methanesulphonic acid gave the bromide **28** (93%).[36] Finally, reduction of **28** with 2.0 equiv. of $LiEt_3BH$[37] in THF at 0 °C afforded **29** (90%).

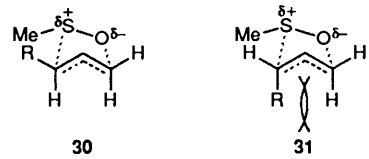
We found that most of **29** remained unchanged after 17 h at 110 °C in toluene although only 9% was recovered after it was heated in chlorobenzene at 132 °C for 17 h.

Discussion

Zwitterion-accelerated [3,3]-*Sigmatropic Rearrangements*.—Allyl vinyl sulphonium salts undergo [3,3]-sigmatropic rearrangement at much lower temperatures than that required by the corresponding sulphides.[38] In Evans' anionic oxy-Cope system, an oxide substituent attached to the C-3 position in hexa-1,5-dienes greatly accelerates the [3,3]-sigmatropic rearrangement.[9] Allyl vinyl sulphoxides **1**, possessing a semipolar S–O bond,[39] have both the three-coordinate sulphur (S^+) and the oxide (O^-) at the appropriate positions (Scheme 8). We



Scheme 8



30 **31**

R = $-CH_2CH{=}CH_2$

considered that these sulphoxides may inherit the charge accelerating effects from the sulphonium salt rearrangement[38] and the anionic oxy-Cope process.[9] Alternately, the effects of the charges might cancel to yield no rate acceleration.

The semipolar S–O bond of sulphoxides is zwitterionic in nature. Some evidence supports that a sulphoxide is favourably represented by a single bond (*i.e.*, S^+–O^-) rather than a double bond (*i.e.*, S=O).[39,40] For sulphoxides with aliphatic groups attached to S, the calculated bond orders are generally ≤1.5[41] (bond order = 1.4 for dimethyl sulphoxide)[42] and the S–O force constant is 6.95 × 10^{-5} dyne cm^{-1}.[43] This force constant is similar to those of the N–O linkage in pyridine *N*-oxides (6–7 × 10^{-5} dyne cm^{-1})[44] and those of single bonds in general (5–6 × 10^{-5} dyne cm^{-1}).[43,45] Double bond force constants, however, range from 10–12 × 10^{-5} dyne cm^{-1}.[43,45] Furthermore, experiments from the molecular refraction[40] and parachor[46] provide additional evidence to support that the sulphoxide S–O functionality possesses single bond character. On the other hand, the S–O bond length of dimethyl sulphoxide was determined to be 1.531 ± 0.0005 Å by Thomas *et al.*[47] and 1.47 ± 0.03 Å by Viswamitara and Kannan.[48] These values compare with the calculated bond length of 1.69 and 1.49 Å for the single and the double bonds, respectively.[49]

To determine whether an accelerating effect is present in rearrangement of a zwitterionic species, we measured the reaction rates of the sulphoxide **5** to the sulphine **6** and of the sulphide **3** to the thioketone **4**. At 23 °C under neutral conditions in $CDCl_3$, the reaction **5**→**6** (k_1 = 1.56 ± 0.04 × 10^{-1} h^{-1}) went 45 times faster than the reaction **3**→**4** (k_1 = 3.5 ± 0.1 × 10^{-3} h^{-1}). This acceleration factor was similar to that of an allyl aryl sulphoxide, which rearranges *ca.* 50 times faster than the corresponding sulphide at 100 °C, as observed by Makisumi *et al.*[16] These results indicate that the two opposite charges on S and O of sulphoxides did not cancel each other, but rather enhanced the reaction rate.

King and Harding[50] found that allyl vinyl sulphones undergo a [3,3]-rearrangement at 160–170 °C in the presence of a weak base.[51] We were able to convert the sulphoxide **5** into the sulphine **6** with completion over a wide range of temperatures (8–101 °C) under neutral conditions. The sulphoxide **7** also rearranged rapidly at room temperature to give the sulphine **8** in excellent yield (90%). Thus the zwitterion-accelerated [3,3]-sigmatropic rearrangements of sulphoxides should possess synthetic value.[20,52]

[2,3]-*Sigmatropic Rearrangement of Sulphoxides* **9** *and* **21**.—The allyl sulphoxide **9** might undergo [3,3]-sigmatropic rearrangement to give a vinyl sulphoxide, which is thermodynamically more stable.[53] In addition, the three-coordinate sulphur (S^+) in the sulphoxide **9** is in the same position as the

carbocation in Breslow's carbocationic Cope rearrangement, which has an enhanced reaction rate.[5] Kirmse *et al.*[33] reported a [3,3]-sigmatropic rearrangement on allyl vinyl sulphide CH_2=CHCH(SMe)CH_2CH=CH_2. This rearrangement takes place in the gas phase at 200 °C with $k = 6.0 \times 10^4$ s^{-1}.

On the other hand, the allyl sulphoxide **9** may undergo [2,3]-sigmatropic rearrangement to give a sulphenate ester. This type of rearrangement, in general, is reversible and greatly favours allyl sulphoxides.[54] We intended to determine what effect the zwitterion would have on the rearrangement of the sulphoxide **9**.

After pyrolysing the sulphoxide **9** in CCl_4 at 77 °C for 16 h, we obtained *O*-methyl methanethiosulphinate **12** (14%), *S*-methyl methanethiosulphonate **13** (21%), and the allylic alcohol **17** (21%; Scheme 4). According to the following two reports, we believe that **12** and **13** came from methylsulphenic acid **10**. Shelton and Davis[55] showed that alkylsulphenic acids (RSOH) can self-condense quickly in acidic media to give *S*-alkyl alkylthiosulphinates [RS(O)SR]. Backer and Kloosterziel[56] found that *S*-methyl methanethiosulphinate **12** is unstable and rapidly decomposes to *S*-methyl methanethiosulphonate **13** and methyl disulphide **14** (b.p. 109 °C).

We believe that the unstable methylsulphenic acid **10** was generated from the sulphoxide **9** during pyrolysis by a *syn* elimination. The by-product, hexa-1,3,5-triene **11** (b.p. 76–79 °C),[57] was not isolated because of its volatility. In a control experiment, however, we were able to trap MeSOH with ethyl acrylate to give the adduct **15** in 39% yield (Scheme 4).[26]

The presence of acid **10** in the reaction mixture could also account for the formation of allylic alcohol **17**. This alcohol could be derived from the [2,3]-rearrangement of the sulphoxide **9** to sulphenate ester **16**, followed by an S–O bond cleavage. Ciuffarin *et al.*[31] found that sulphenate esters are unstable in acidic media with trace amounts of water present. In addition, sulphenic acids (*e.g.*, MeSOH) are extremely powerful nucleophiles towards compounds containing two-coordinate sulphur that is directly attached to a leaving group.[58] Similarly to **9**, the sulphoxide **21** underwent a [2,3]-sigmatropic rearrangement to give the sulphenate ester **22** (Scheme 5) at 90 °C; this sulphenate ester then reacted with MeSOH **10**, generated *in situ*, to give yomogi alcohol **23**.

We obtained **17** as a mixture of regioisomers (E/Z = 6.7:1). The stereoselectivity[59,60] most likely comes from the energy difference between the two five-membered cyclic transition states **30** and **31** in the conversion of the sulphoxide **9** into the sulphenate ester **16**. The transition state **30**, leading to *E*-**17**, should be thermodynamically more stable than the transition state **31**.[61] Substituent R (=CH_2CH=CH_2) in **31** holds an axial position and thus has more steric congestion than the equatorial R in **30**.

Total Synthesis of Yomogi Alcohol **23**.—Yomogi alcohol possesses antibacterial and antifungal activities.[62] It was first isolated from the essential oil of *Artemisia feddei, Lev et Van*,[27] and was identified as a constituent in a variety of *Artemesia* plants. The isolated yield, however, is always low and varied according to the geographical area where the plant is grown.[63]

We thought that yomogi alcohol **23** could be synthesized from the sulphide **20** by a one-flask process (Scheme 5)—isolation of the sulphoxide **21** would not be necessary. Okazaki *et al.*[64] found that sterically crowded sulphoxides decompose readily at the S–C bond to form carbenium ions and sulphenate anions. The sulphoxide moiety of **21** resides in a sterically congested area. We therefore believe that the sulphoxide **21** would decompose to give MeSOH. Meanwhile, the sulphoxide **21** would also be in equilibrium with the sulphenate ester **22**. Methylsulphenic acid (MeSOH), which is generated *in situ*, could then cleave the S–O bond in the sulphenate ester **22** to yield **23**.

We obtained yomogi alcohol **23** from the commercially available prenyl bromide **18** in three steps. Based on the results of the reaction **9**→**17**, we expected that the dienol **23** would be generated preferentially in the *E* form. Indeed, our spectroscopic data for the product from the reaction of **20** with *m*-CBPA were consistent with those reported for yomogi alcohol **23**[28] and, in addition, we detected only one isomer by GC.

Yomogi alcohol **23**, a tertiary allylic alcohol, was previously synthesized by Evans and Andrews from **20** through a two-step process.[65] Although the use of thiophiles in the preparation of allylic alcohols are well documented,[65] no external thiophile is required in our synthesis of yomogi alcohol.

In order to prove that MeSOH was generated, we heated the sulphoxide **21** in the presence of 5.0 equiv. of ethyl acrylate. The sulphoxide ester **15** was isolated in 11% yield. The decomposition of the sulphoxide **21** to MeSOH was, therefore, a minor pathway and did not reduce the yield of yomogi alcohol significantly.

Sigmatropic Rearrangement of the Amine Oxide **24**.—The N–O bond in amine oxides is more polar in nature than the S–O bond in sulphoxides.[66] The *d*-orbital of the S atom can be used to form a π-bond in sulphoxides; however, the N atom does not have the corresponding, low energy *d*-orbital.[66] The N–O bond in amine oxides therefore possesses more zwitterionic character than the S–O bond in sulphoxides. This zwitterionic character may promote a [3,3]-sigmatropic rearrangement of amine oxide **24**. In addition, the positive charge in amine oxide **24** resides in the same position as that in the substrate of Breslow's carbocationic Cope rearrangement.[5]

Alternatively, the amine oxide **24** may undergo a [2,3]-sigmatropic rearrangement. In the allylic amine oxide–hydroxylamine rearrangement, equilibrium usually favours the hydroxylamine.[67]

Kirmse *et al.*[33] showed that the amine CH_2=CHCH(NMe_2)-CH_2CH=CH_2 undergoes a [3,3]-sigmatropic rearrangement in the gas phase at 200 °C with $k = 1.12 \times 10^6$ s^{-1}. Our experimental results indicate that the corresponding amine oxide **24** preferred a [2,3]- instead of a [3,3]-sigmatropic rearrangement (Scheme 6). At 25 °C, the rearrangement rate (k_1) for **24**→**25** was $3.8 \pm 0.3 \times 10^{-1}$ h^{-1}. This value was consistent with that ($k_1 = 4.3 \times 10^{-1}$ h^{-1} at 30 °C) for a closely related rearrangement reported by Wragg *et al.*,[68] which involves the conversion of *N*-methyl-*N*-prop-2-enylaniline oxide into *N*-methyl-*O*-allyl-*N*-phenylhydroxylamine.

Decomposition of the Nitro Compound **29**.—The nitro group also possesses zwitterionic character. Unlike amine oxides, the O^- in allylic nitro compounds does not participate in [2,3]-sigmatropic rearrangements. On the other hand, the nitroalkene **29** could undergo a [3,3]-sigmatropic rearrangement to give the thermodynamically more stable product, in which a C–C double bond is in conjugation with the nitro group.[69] Nevertheless, we found that **29** did not give the [3,3]-sigmatropic rearrangement product at 132 °C for 17 h. Instead, a large mass was lost under the pyrolytic conditions. We believe that **29** may have decomposed by *cis* elimination to give nitrous acid and volatile 4-methylhepta-2,4,6-triene.[70]

Conclusions

[3,3]-Sigmatropic rearrangement of the allyl vinyl sulphoxide **5** to γ,δ-unsaturated sulphine **6** under neutral conditions was 45 times faster than that of the sulphide **3** to the thioketone **4**. Similarly, the allyl vinyl sulphoxide **7** rearranged to the sulphine **8** under neutral conditions. These results indicate the existence of the zwitterion-accelerated rearrangement. The acceleration effect resulting from the charges in a dipolar, ionic

moiety did not cancel out. Instead, the sulphoxide functionality significantly facilitated the rearrangement.

On the other hand, zwitterionic moieties, such as sulphoxide and amine oxide, attached to the C-3 position of hexa-1,5-dienes did not accelerate the [3,3]-sigmatropic rearrangement. Instead, the [2,3]-sigmatropic rearrangement prevailed. By use of the [2,3] process as the key step, an efficient total synthesis of yomogi alcohol was accomplished in three steps from prenyl bromide **18**.

Experimental

All reactions were carried out in oven-dried glassware (120 °C) under an atmosphere of dry nitrogen. Ethyl acetate and hexanes from Tilley Chemical Co. were dried and distilled over CaH_2. Benzene, tetrahydrofuran (THF), 1,4-dioxane, and toluene from J. T. Baker Chemical Co. were freshly distilled from Na–benzophenone. Chloroform, dichloromethane, *N*,*N*-dimethylformamide (DMF) and carbon tetrachloride from J. T. Baker Chemical Co. were freshly distilled over CaH_2. *m*-Chloroperoxybenzoic acid (*m*-CPBA), ethyl acrylate, diisobutylaluminium hydride (DIBAL-H), lithium triethylborohydride ($LiEt_3BH$), lithium bromide, collidine, and methanesulphonyl chloride were purchased from Aldrich Chemical Co. and were used directly without purification. M.p.s were obtained by a Büchi 510 melting point apparatus and are uncorrected. Analytical thin layer chromatography (TLC) was performed on precoated plates (silica gel GHLF), purchased from Analtech Inc. Visualization of spots on TLC was done by use of UV light and/or 2.5% phosphomolybdic acid in ethanol with heating. Mixtures of ethyl acetate and hexanes were used as eluents. Gas chromatography analyses were performed on a Hewlett-Packard 5794 instrument equipped with a 12.5-m cross-linked methyl silicone gum capillary column (0.2-mm i.d.). Purification by gravity column chromatography was carried out by use of EM Reagents Silica Gel 60 (particle size 0.063–0.200 mm, 70–230 mesh ASTM) or Woelm aluminium oxide (Woelm basic, activity grade 1). Separations by radial thin-layer chromatography were performed on a model 7924T Chromatotron from Harrison Research. The plates (1, 2 or 4 mm thickness) were coated with EM Reagents Silica Gel 60 PF_{254} containing gypsum. Constant reaction temperature was maintained by a model 2800 bath and circulator from Forma Scientific. IR spectra were measured on a Perkin-Elmer 599B, 710B, or Fourier-Transform 1600 spectrophotometer. The wavenumbers reported are referenced to the polystyrene 1601 cm^{-1} absorption. ^1H NMR spectra were obtained on either a Varian CFT-20 (80 MHz) or a Varian XL-400 (400 MHz) spectrometer. [^2H]-$CHCl_3$ was used as solvent and Me_4Si was used as internal standard. ^{13}C NMR spectra were recorded on a Varian XL-400 spectrometer at 101 MHz and $CDCl_3$ was used as solvent. Carbon-13 chemical shifts were referenced to the centre of the $CDCl_3$ triplet (δ 77.0); *J* coupling constants are in Hz. High-resolution mass spectra were obtained by means of a VG Analytical 70-S mass spectrometer.

Kinetics.—The kinetics of the rearrangement reactions were determined by monitoring the concentration of starting material as a function of reaction time by ^1H NMR spectroscopy (80 MHz). The reaction temperatures were controlled by a thermostatted circulator bath. The rate constants for the irreversible first-order reactions were calculated from the best straight line of the linear least squares plot of ln(concentration of starting material) *versus* reaction time. The slope of the plot of ln(concentration of starting material) *versus* reaction time was equal to $-k$. The rate constants for the reversible first-order reactions were calculated from the best straight line of ln[(concentration of starting material) − (concentration of starting material at equilibrium)] *versus* reaction time. The slope of this plot gave k_{obsd}, where $k_{obsd} = k_1 + k_{-1}$. The forward rate constant (k_1) was calculated by combination of $k_{obsd} = k_1 + k_{-1}$ and $K_{eq} = k_1/k_{-1}$. Correlation coefficients were greater than 0.99 in all cases. The indicated errors of the calculated parameters were obtained from the standard deviations of the line fit.

2,4-*Dimethyl*-3-(*prop*-2-*enylsulphinyl*)*pent*-2-*ene* **5**.—*m*-CPBA (80%, 84.5 mg, 0.392 mmol, 1.0 equiv.) was added to a stirred solution of compound **3**[18] (66.7 mg, 0.392 mmol, 1.0 equiv.) in $CHCl_3$ (2.0 cm^3) at 23 °C. Stirring was continued at 23 °C for 30 min after which the reaction mixture was diluted with diethyl ether (15 cm^3), washed with 10% aqueous KOH (5 cm^3), dried ($MgSO_4$), filtered, and concentrated to give **5** as a colourless oil (95%, 69.4 mg, 0.372 mmol). Compound **5** rearranged at room temperature to give **6**.

Compound **5**: δ_H(80 MHz; $CDCl_3$) 1.23 (d, *J* 3.4, 3 H, CH_3), 1.33 (d, *J* 3.6, 3 H, CH_3), 1.89 (s, 3 H, CH_3C=C), 1.94 (s, 3 H, CH_3C=C), 3.15–3.75 (m, 3 H, SCH_2 + $CHMe_2$) and 5.10–5.95 (m, 3 H, CH_2=CH); ν_{max}(neat)/cm^{-1} 3070w, 2980s, 2920m, 2860m, 1630m (C=C) and 1050s (S–O).

2,4,4-*Trimethylhept*-6-*ene*-3-*thione* S-*Oxide* **6**.—The sulphoxide **5** (69.4 mg, 0.372 mmol) was dissolved in $CHCl_3$ (3.7 cm^3) and the solution was kept at room temperature for 30 h. The reaction mixture was then concentrated and the crude product was purified by Chromatotron (1 mm plate; 20% EtOAc in hexanes as eluent) to give the sulphine **6** as a colourless oil (96%, 66.6 mg, 0.357 mmol): TLC R_f 0.56 (20% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 110 °C) t_R 5.41 min; δ_H(80 MHz; $CDCl_3$) 1.18 [s, 6 H, $C(CH_3)_2$], 1.50 [d, *J* 6.9, 6 H, $CH(CH_3)_2$], 2.25 (d, *J* 6.9, 2 H, CH_2), 2.65–2.96 (m, 1 H, $CHMe_2$), 4.94–5.19 (m, 2 H, CH_2=C) and 5.47–6.00 (m, 1 H, CH=C); δ_C(101 MHz; $CDCl_3$) 19.66 (q, CH_3), 26.33 (q, CH_3), 35.43 (d, $CHMe_2$), 42.79 (s, CMe_2), 44.89 (t, CH_2), 119.34 (t, CH_2=), 133.73 (d, CH=) and 213.92 (s, S=C); ν_{max}(neat)/cm^{-1} 2960s, 1720w, 1460w, 1370w, 1270w, 1090s, 1000m and 920w (Found: M^+, 186.1079. Calc. for $C_{10}H_{18}OS$: *M*, 186.1079).

2-*Methyl*-1-*prop*-2-*enylsulphinylprop*-1-*ene* **7**.[21]—*m*-CPBA (80%, 421 mg, 1.95 mmol, 1.0 equiv.) was added to a stirred solution of 2-methyl-1-(prop-2-enylthio)prop-1-ene[20] (250 mg, 1.95 mmol, 1.0 equiv.) in $CHCl_3$ (13.0 cm^3) at 23 °C. Stirring was continued at the same temperature for 30 min after which the reaction mixture was diluted with diethyl ether (30 cm^3), washed with 10% aqueous KOH (10 cm^3), dried ($MgSO_4$), filtered, and concentrated to give **7** as a colourless oil (97%, 272 mg, 1.88 mmol). Compound **7** rearranged at room temperature to give **8**.

Compound **7**: δ_H(80 MHz; $CDCl_3$) 1.92 (s, 3 H, CH_3), 1.97 (s, 3 H, CH_3), 3.47 (d, *J* 4.8, 2 H, CH_2), 5.15–6.10 (m, 4 H, CH_2=CH + CH=C); ν_{max}(neat)/cm^{-1} 2970s, 2920m, 2860m and 1050s (S–O).

(E)- *and* (Z)-2,2-*Dimethylpent*-4-*ene*-1-*thial* S-*Oxide* **8**.[21]—A solution of the sulphoxide **7** (81.7 mg, 0.566 mmol) dissolved in $CHCl_3$ (4.0 cm^3) was kept at room temperature for 30 h after which it was concentrated and the crude product was purified by Chromatotron (1-mm plate; 20% EtOAc in hexanes as eluent) to give sulphine **8** as a colourless oil (90%, 73.5 mg, 0.510 mmol): TLC R_f 0.56 (20% EtOAc in hexanes); δ_H(80 MHz; $CDCl_3$) 1.20 (s, 6 H, 2 × CH_3, *E* isomer), 1.37 (s, 6 H, 2 × CH_3, *Z* isomer), 2.22 (d, *J* 7.2, 2 H, CH_2, *E* isomer), 2.38 (d, *J* 7.2, 2 H, CH_2, *Z* isomer), 4.90–5.20 (m, 2 H, CH_2=C), 5.50–6.05 (m, 1 H, CH=C), 7.49 (s, 1 H, SCH=C, *Z* isomer) and 8.92 (s, 1 H, SCH=C, *E* isomer); ν_{max}(neat)/cm^{-1} 3060w, 2950s, 2920s, 2880m, 1640w, 1465m, 1385w, 1365w, 1315w, 1280w, 1250m, 1130m,

1070m, 1030m, 1000m, 920m, 810w and 750w (Found: M^+, 144.0610. Calc. for $C_7H_{12}OS$: 144.0609).

3-*Methylsulphinylhexa*-1,5-*diene* **9**.—*m*-CPBA (80%, 57.4 mg, 0.266 mmol, 1.0 equiv.) was added to a stirred solution of 3-methylthiohexa-1,5-diene[23] (34.1 mg, 0.266 mmol, 1.0 equiv.) in CH_2Cl_2 (2.6 cm^3) at 0 °C and stirring was continued for 30 min. The mixture was then diluted with dichloromethane (10 cm^3), washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), filtered, and concentrated to give a colourless oil. Purification of the crude product by gravity column chromatography (100% EtOAc) gave the sulphoxide **9** as a colourless oil (89%, 34.1 mg, 0.236 mmol): TLC R_f 0.27 (100% EtOAc); δ_H($CDCl_3$; 80 MHz) 2.43, 2.52 (2 × s, 3 H, CH_3), 2.55–3.40 (m, 3 H, $SCHCH_2$) and 4.90–5.95 (m, 6 H, 2 × $CH{=}CH_2$); ν_{max}(neat)/cm^{-1} 3060w, 2990w, 2960w, 2900w, 1630m, 1430w, 1410m, 1290w, 1030s (S–O), 990s, 920s and 680w; *m*/*z* (rel. int.) 81 ($M^{\bullet+}$ − ·MeSO, 100), 80 (37), 79 (57), 77 (14), 55 (15), 53 (63), 41 (71) and 39 (33).

Thermolysis of 3-*Methylsulphinylhexa*-1,5-*diene* **9**.—A solution of the sulphoxide **9** (296 mg, 2.05 mmol) dissolved in carbon tetrachloride (20.5 cm^3) was heated under reflux for 16 h. The mixture was then concentrated and the residue was purified by gravity column chromatography. The initial eluent contained 20% EtOAc in hexanes; finally, the polarity was increased to 100% EtOAc. A mixture of (2*E*)- and (2*Z*)-hexa-2,5-dien-1-ols **17** was obtained as a colourless oil (21%, 42.4 mg, 0.432 mmol, *E*:*Z* 6.7:1, as determined by ^1H NMR spectroscopy). *S*-Methyl methanethiosulphonate **13** (21%, 27.7 mg, 0.219 mmol) and *S*-methyl methanethiosulphinate **12** were isolated (14%, 16.2 mg, 0.143 mmol).

Compound **17**: TLC R_f 0.53 (40% EtOAc in hexanes); δ_H($CDCl_3$; 400 MHz) 2.81 (dd, *J* 5.2 and 6.4, 2 H, $CH_2C{=}C$, *E* isomer), 2.85 (dd, *J* 6.4 and 6.4, 2 H, $CH_2C{=}C$, *Z* isomer), 4.11 (d, *J* 4.4, 2 H, CH_2O, *E* isomer), 4.21 (d, *J* 5.6, CH_2O, *Z* isomer), 5.00–5.08 (m, 2 H, $C{=}CH_2$) and 5.69–5.84 (m, 3 H, CH=CH and CH=C); ν_{max}(neat)/cm^{-1} 3300br (OH), 3060m, 2990m, 2970m, 2860s, 1620m, 1410m, 1370m, 1070m, 960s, 990s and 905s; *m*/*z* (rel. int.) 98 (M^+, 2), 80 ($M^{\bullet+}$ − H_2O, 25), 79 (19), 68 (17), 67 (31), 57 (100), 55 (17), 54 (31), 53 (19), 43 (19), 41 (59), 39 (54), 32 (10) and 31 (23). The spectroscopic data for this compound were consistent with those reported in the literature.[25]

Compound **13**: TLC R_f 0.37 (40% EtOAc in hexanes); δ_H($CDCl_3$; 80 MHz) 2.69 (s, 3 H, SCH_3) and 3.30 (s, 3 H, CH_3SO_2); ν_{max}(neat)/cm^{-1} 3010w, 2990w, 2920m, 1410m (S–CH_3), 1300s (SO_2), 1120s (SO_2), 950s, 740s and 700w; *m*/*z* (rel. int.) 126 ($M^{\bullet+}$, 58), 81 (72), 79 (53), 64 (30), 63 (66), 47 (100), 46 (36) and 45 (69). The spectroscopic data of this compound were consistent with those reported in the literature.[30]

Compound **12**: TLC R_f 0.20 (40% EtOAc in hexanes); δ_H($CDCl_3$; 80 MHz) 2.66 (s, 3 H, SCH_3), 2.97 (s, 3 H, CH_3SO); ν_{max}(neat)/cm^{-1} 2980w, 2910m, 1420m (S–CH_3), 1270m (S–CH_3), 1060s (S–O), 930m, 745w and 670m; the spectroscopic data of this compound were consistent with those reported in the literature.[23]

Thermolysis of 3-*Methylsulphinylhexa*-1,5-*diene* **9** *in the Presence of Ethyl Acrylate*.—Ethyl acrylate (750 mg, 7.50 mmol, 5.0 equiv.) was added to a solution of **9** (216 mg, 1.50 mmol, 1.0 equiv.) in carbon tetrachloride (15.0 cm^3) and the mixture was heated at reflux for 16 h. After this it was concentrated under reduced pressure and purified by gravity column chromatography. The initial eluent contained 40% EtOAc in hexanes; finally, the polarity was increased to 100% EtOAc. A mixture of (2*E*)- and (2*Z*)-hexa-2,5-dien-1-ols **17** was obtained as a colourless oil (13%, 19.1 mg, 0.195 mmol) followed by *S*-methyl methanethiosulphinate **12** (13%, 10.6 mg, 0.096 mmol) and ethyl 3-methylsulphinylpropionate **15** (39%, 96.1 mg, 0.585 mmol). The spectroscopic data of **12** and **17** were identical with those listed above.

Compound **15**: TLC R_f 0.09 (100% EtOAc); δ_H($CDCl_3$; 80 MHz) 1.27 (t, *J* 7.1, 3 H, CCH_3), 2.59 (s, 3 H, SCH_3), 2.60–3.00 [m, 4 H, $(CH_2)_2$] and 4.28 (q, *J* 7.1, 2 H, OCH_2); ν_{max}(neat)/cm^{-1} 2970m, 2910m, 1715s (C=O), 1420m, 1370m, 1340m, 1290m, 1240m, 1170m, 1030s (S–O), 985w, 940w, 850w and 780w; *m*/*z* (rel. int.) 164.05 ($M^{\bullet+}$, 14), 149 ($M^{\bullet+}$ − ·CH_3, 21), 119 ($M^{\bullet+}$ − ·OEt, 23), 101 ($M^{\bullet+}$ − ·MeSO, 14), 84 (16), 73 (29), 64 (32), 63 (15), 55 (100) and 41 (21). The spectroscopic data for this compound were consistent with those reported in the literature.[26]

3,3,6-*Trimethyl*-4-*methylsulphinylhepta*-1,5-*diene* **21**.[66]—*m*-CPBA (80%, 437 mg, 2.02 mmol, 1.0 equiv.) was added to a stirred solution of 3,3,6-trimethyl-4-methylthiohepta-1,5-diene[31] (**20**, 373 mg, 2.02 mmol, 1.0 equiv.) in CH_2Cl_2 (20 cm^3) at 0 °C. Stirring was continued for 30 min after which the mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (3 × 15 cm^3). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated to give a colourless liquid. Purification of the liquid by gravity column chromatography (100% EtOAc as eluent) gave the sulphoxide **18** as a colourless oil (83%, 338 mg, 1.69 mmol) which solidified on cooling: m.p. 39.0–40.0 °C; TLC R_f 0.27 (100% EtOAc); δ_H($CDCl_3$; 80 MHz) 1.14, 1.16, 1.21, 1.28 (4 × s, 3 H, CH_3), 1.67, 1.76, 1.82, 1.92 (4 × d, *J* 1.3, 3 H, $CH_3C{=}C$), 2.32, 2.41 (2 × s, 3 H, CH_3SO), 2.74 (d, *J* 11.2, 1 H, CH), 3.45 (d, *J* 11.2, 1 H, CH), 4.80–6.20 (m, 4 H, CH=C + $CH{=}CH_2$); ν_{max}(neat)/cm^{-1} 3083w, 2967s, 2914s, 2871m, 1972w, 1738w, 1710w, 1665w, 1639w, 1447m, 1414m, 1379m, 1363m, 1292w, 1241m, 1189m, 1039s (S–O), 912s, 851m and 685w; *m*/*z* (rel. int.) 137 ($M^{\bullet+}$ − ·MeSO, 73), 107 (17), 95 (100), 93 (15), 81 (31), 69 (25), 67 (32), 57 (35), 55 (37), 53(16), 43 (48), 41 (62) and 39 (20).

Thermolysis of 3,3,6-*Trimethyl*-4-*methylsulphinylhepta*-1,5-*diene* **21** *in the Presence of Ethyl Acrylate*.—Ethyl acrylate (338 mg, 3.38 mmol, 5.0 equiv.) was added to a solution of **21** (135 mg, 0.676 mmol, 1.0 equiv.) in 1,4-dioxane (7.0 cm^3) and the solution was heated at 90 °C for 16 h. It was then concentrated under reduced pressure and purified by gravity column chromatography. The initial eluent contained 20% EtOAc in hexanes; finally, the polarity was increased to 100% EtOAc. Ethyl 3-methylsulphinylpropionate **15** was obtained as a colourless oil (11%, 12.4 mg, 0.0755 mmol), the spectroscopic data for which were identical with those listed above.

Yomogi Alcohol **23**, [(3E)-2,5,5-*Trimethylhepta*-3,6-*dien*-2-*ol*].—*m*-CPBA (80%, 42.9 mg, 0.199 mmol, 1.0 equiv.) was added to a stirred solution of the sulphide **20**[31] (36.6 mg, 0.199 mmol, 1.0 equiv.) in 1,4-dioxane (0.83 cm^3) and water (0.17 cm^3) at room temperature and the reaction mixture was stirred for 30 min and then heated at 90 °C for 4.5 h. It was then cooled and diluted with diethyl ether (10 cm^3). The aqueous layer was separated and washed with saturated aqueous $NaHCO_3$ (2.5 cm^3) and brine (2.5 cm^3), dried ($MgSO_4$), filtered, and concentrated to give a yellow liquid. Purification of this by gravity column chromatography (10% EtOAc in hexanes as eluent) gave yomogi alcohol **23** as a colourless liquid (53%, 16.3 mg, 0.106 mmol): TLC R_f 0.39 (20% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 70 °C; duration 2.00 min; increment rate 10 °C min^{-1}; final temperature 250 °C); t_R 2.77 min; δ_H($CDCl_3$; 80 MHz) 1.10 [s, 6 H, $(CH_3)_2CCH{=}C$], 1.31 [s, 6 H, $(CH_3)_2COH$], 4.70–4.95 (m, 2 H, $CH_2{=}C$) and 5.45–5.95 (m, 3 H, CH=CH + CH=C); ν(neat)/cm^{-1} 3371br (OH), 3083w, 2967s, 2929m, 2870w, 2360w, 1726w, 1639w (C=C), 1461w, 1412w, 1376m, 1360m, 1288w, 1233w, 1133m, 1043w, 977m, 911s, 805w and 740w; *m*/*z* (rel. int.) 139 ($M^{\bullet+}$ − H_2O, 25), 121 (26), 96 (18), 93 (27), 85 (35),

81 (22), 79 (18), 67 (16), 59 (48), 55 (19), 43 (100), 41 (36), 40 (17) and 39 (17). The spectroscopic data for this compound were consistent with those reported in the literature.[27]

N,N-*Dimethylhexa*-1,5-*dien*-3-*amine* N-*Oxide* **24**.—The method of Craig and Purushothaman was followed.[32] *m*-CPBA (80%, 147 mg, 0.683 mmol, 1.0 equiv.) was added to a stirred solution of *N*,*N*-dimethylhexa-1,5-dien-3-amine[34] (75.3 mg, 0.601 mmol, 1.0 equiv.) in $CHCl_3$ (3.0 cm^3) at 0 °C. Stirring was continued for 30 min after which the solution was chromatographed through a column packed with alkaline alumina (25% methanol in $CHCl_3$ as eluent). After concentration at 0 °C, *N*-oxide **24** was obtained (91%, 77.5 mg, 0.549 mmol). Compound **24** rearranged at room temperature to give **25**.

Compound **24**: δ_H($CDCl_3$; 80 MHz) 3.01 (s, 3 H, CH_3), 3.17 (s, 3 H, CH_3), 3.20–3.60 (m, 3 H, $CHCH_2$) and 4.80–5.60 (m, 6 H, 2 × $CH{=}CH_2$); ν_{max}(neat)/cm^{-1} 957 (m, N–O).

O-*Hexa*-2.5-*dienyl*-N,N-*dimethylhydroxylamine* **25**.—A solution of the *N*-oxide **24** (244 mg, 1.95 mmol, 1.0 equiv.) in $CHCl_3$ (9.0 cm^3) was kept at room temperature for 7 h and then concentrated under reduced pressure at 0 °C to give the pure hydroxylamine **25** (100%, 244 mg, 1.95 mmol); δ_H($CDCl_3$; 80 MHz) 2.58, 2.62 (2 × s, 3 H, CH_3, *E* and *Z* isomers), 2.65–2.85 (m, 2 H, $C{=}CCH_2C{=}C$), 4.14 (d, *J* 4.5, 2 H, CH_2O), 4.80–5.15 (m, 3 H, $CH{=}CH_2$ + CH=C) and 6.05–6.25 (m, 1 H, CH=C); δ_C($CDCl_3$; 100 MHz) 36.40 (t, CH_2), 47.81, 49.88 (2 × q, CH_3, *E* and *Z* isomers), 72.34 (t, CH_2O), 117.68 (t, CH_2=), 127.07 (d), 133.58 (d) and 136.68 (d); ν_{max}(neat)/cm^{-1} 3030w, 2930s, 2880s, 2840s, 2750s, 1710w, 1660w, 1630m, 1460m, 1420m, 1350w, 1200w, 990s, 965s, 910s, 800w and 750w; *m*/*z* (rel. int.) 93 (21), 81 ($M^{\bullet+}$ − ·$ON(CH_3)_2$, 51), 80 (29), 79 (57), 77 (25), 61 (100), 60 (64), 53 (29), 43 (21), 42 (32) and 41 (61).

(2E)-4-*Methyl*-4-*nitrohepta*-2,6-*dien*-1-*ol* **27**.—The procedure of Battersby *et al.* was followed.[36] Diisobutylaluminium hydride (DIBAL-H; 1.5 mol dm^{-3} in toluene; 840 mm^3, 1.24 mmol, 2.0 equiv.) was added to a stirred solution of (2*E*)-methyl 4-methyl-4-nitrohepta-2,6-dien-1-oate[35] **26** (123 mg, 0.619 mmol, 1.0 equiv) in toluene (0.62 cm^3) at 0 °C. The reaction was stirred at 0 °C for 2 h. The mixture was then quenched with 10% aqueous HCl (5 cm^3) at 0 °C and warmed to room temperature. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 × 10 cm^3). The combined organic layers were washed with brine (10 cm^3), dried ($MgSO_4$), filtered, and concentrated to give a colourless oil. Purification of the oil by Chromatotron (2 mm plate; 40% EtOAc in hexanes as eluent) gave the nitro alcohol **27** as a colourless oil (97%, 103 mg, 0.602 mmol): TLC R_f 0.44 (40% EtOAc in hexanes); δ_H($CDCl_3$; 80 MHz) 1.67 (s, 3 H, CH_3), 2.69–2.83 (m, 2 H, CH_2CNO_2), 4.22 (d, *J* 3.4, 2 H, CH_2O) and 4.90–6.20 (m, 5 H, CH_2=CH + CH=CH); ν_{max}(neat)/cm^{-1} 3350br (OH), 2995w, 2910w, 2880w, 1730w, 1645w, 1540s (NO_2), 1450w, 1440w, 1420w, 1390m, 1350m (NO_2), 1090w, 1020w, 1000m, 980m, 930m, 810w and 800w [Found: M^+, 125.0968. Calc. for $C_8H_{13}O$: ($M^{\bullet+}$ − ·NO_2) 125.0966].

(2E)-1-*Bromo*-4-*methyl*-4-*nitrohepta*-2,6-*diene* **28**.—The conditions used were a modification of Collington and Meyers' procedure.[37] Lithium bromide (87.7 mg, 1.01 mmol, 1.0 equiv.), dissolved in dimethylformamide (1.6 cm^3), was added to a stirred solution of the nitro alcohol **27** (174 mg, 1.01 mmol, 1.0 equiv.) and 2,4,6-collidine (246 mg, 2.03 mmol, 2.0 equiv.) at room temperature. The solution was cooled to 0 °C and methanesulphonyl chloride (232 mg, 2.03 mmol, 2.0 equiv.) was added dropwise. The mixture was stirred at room temperature for 16 h and then quenched with water and extracted with diethyl ether (2 × 15 cm^3). The combined organic layers were washed with saturated aqueous $CuSO_4$ (2 × 10 cm^3), water (10 cm^3) and brine (10 cm^3), dried ($MgSO_4$), filtered, and concentrated to give the allylic bromide **28** (93%, 219 mg, 0.935 mmol); δ_H($CDCl_3$; 80 MHz) 1.68 (s, 3 H, CH_3), 2.70–2.81 (m, 2 H, CH_2CNO_2), 4.09 (d, *J* 5.4, 2 H, CH_2Br) and 4.95–6.25 (m, 5 H, CH_2=CH + CH=CH); ν_{max}(neat)/cm^{-1} 3083w, 2986w, 2932w, 2878w, 1676w, 1642w, 1542s (NO_2), 1438w, 1386m, 1372m, 1349m (NO_2), 1321w, 1253w, 1175m, 1044w, 996w, 969m, 930m, 845w and 750w [Found: M^+, 187.0123. Calc. for $C_8H_{12}Br$: ($M^{\bullet+}$ − ·NO_2) 187.0122].

(6E)-4-*Methyl*-4-*nitrohepta*-1,6-*diene* **29**.—Super-Hydride ($LiEt_3BH$; 1.0 mol dm^{-3} in THF; 1.77 cm^3, 1.77 mmol, 2.0 equiv.) was added to a stirred solution of (2*E*)-1-bromo-4-methyl-4-nitrohepta-2,6-diene (**28**, 207 mg, 0.885 mmol, 1.0 equiv.) in THF (1.0 cm^3) at 0 °C. The mixture was stirred at 0 °C for 1 h and then at room temperature for an additional hour after which the reaction was quenched with water (5 cm^3) at 0 °C. The mixture was then warmed to room temperature when the aqueous layer was separated and extracted with diethyl ether (2 × 15 cm^3). The combined organic layers were washed with brine (10 cm^3), dried ($MgSO_4$), filtered, and concentrated to give an oil. Purification of this by gravity column chromatography (10% EtOAc in hexanes as eluent) gave the nitro compound **29** as a colourless oil (90%, 123 mg, 0.793 mmol); TLC R_f 0.58 (10% EtOAc in hexanes); δ_H($CDCl_3$; 80 MHz) 1.64 (s, 3 H, CH_3CNO_2), 1.76 (dd, *J* 2.3 and 4.7, 3 H, CH_3), 2.65–2.80 (m, 2 H, CH_2CNO_2), 4.90–6.05 (m, 5 H, CH_2=CH and CH=CH); ν_{max}(neat)/cm^{-1} 3080w, 2920s, 2860s, 1640m (C=C), 1540s (NO_2), 1450s, 1385s, 1345s (NO_2), 1170w, 1000m, 970m, 930m, 860w, 840w and 725m [Found: M^+, 109.1018. Calc. for C_8H_{13}: ($M^{\bullet+}$ − ·NO_2) 109.1017].

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