Bromination–dehydrobromination route to some naturally occurring 1,6-dioxaspiro[4.4]-nonenes and -nonadienes

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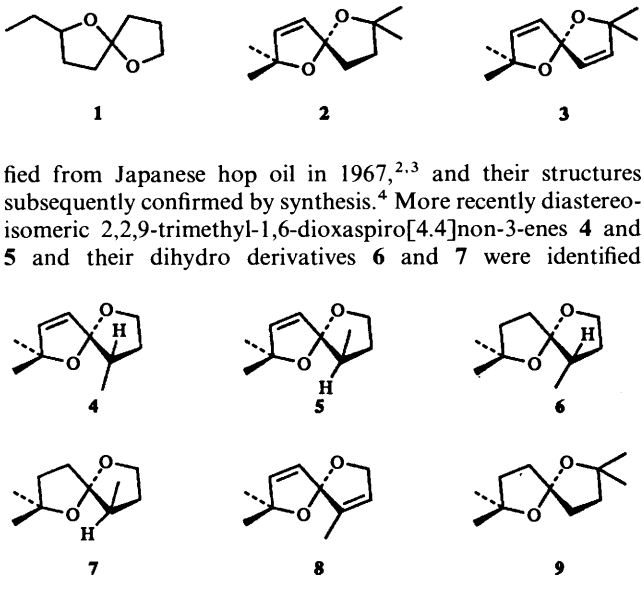
Bromination–dehydrobromination of saturated 1,6-dioxaspiro[4.4]nonanes afforded a variety of naturally occurring 1,6-dioxaspiro[4.4]-nonenes and -nonadienes, such as **2–5** and **8**, and can be applied to give unsaturated spirolactones, such as **27**.

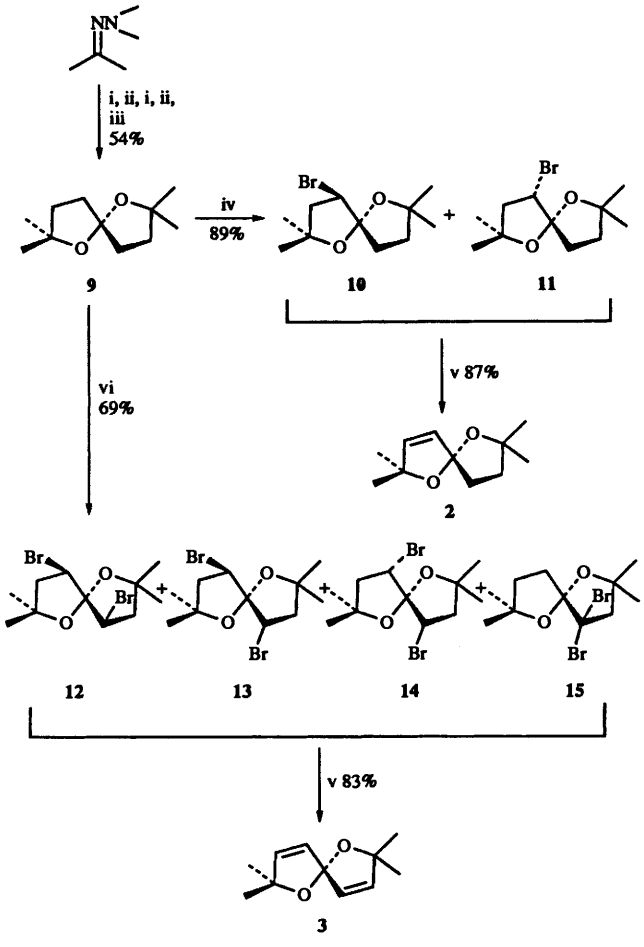
A number of natural compounds incorporating the 1,6-dioxaspiro[4.4]nonane unit have been identified, with the best known being chalcogran **1**, a beetle aggregation substance identified by Francke *et al.* in 1977.[1] The olefin 2,2,7,7-tetramethyl-1,6-dioxaspiro[4.4]non-3-ene **2**, and the related diene **3**, were identified from Japanese hop oil in 1967,[2,3] and their structures subsequently confirmed by synthesis.[4] More recently diastereoisomeric 2,2,9-trimethyl-1,6-dioxaspiro[4.4]non-3-enes **4** and **5** and their dihydro derivatives **6** and **7** were identified as new constituents of geranium oil, on the basis of spectral analysis and synthesis.[5] 2,2,9-Trimethyl-1,6-dioxaspiro[4.4]-nona-3,8-diene **8** was described as a low level component of the essential oil of *Artemisia salsoloides* by Weyerstahl *et al.*,[6] on the basis of spectral analysis of an impure sample (this is now confirmed by our synthesis). Compounds **4–8** are the only examples of 1,6-dioxaspiro[4.4]nonanes that follow the isoprene rule.



The reported syntheses[4,5,7] of several of these compounds involve mono- or di-alkylation of carbonyl substrates (ester or lactone) with an alkynyl derivative, followed by controlled hydrogenation of the triple bond and acid-catalysed spirocyclisation. Our recent studies[8] of direct bromination–dehydrobromination of saturated spiroketals appeared applicable to the synthesis of the unsaturated systems **2–5** and **8**, particularly when the necessary saturated precursors **6**, **7** and **9** appeared readily accessible by epoxide alkylation of suitable *N,N*-dimethylhydrazones.[9,10] These approaches are described in the present report.

Results and discussion

The synthesis of the spiroketal **9** had been reported by several workers,[3,4] but **9** is also readily acquired in satisfactory yield by repetitive alkylation (two-stage) of acetone *N,N*-dimethylhydrazone with 2,2-dimethyloxirane, followed by acidification of the dilithium diolate[9] (Scheme 1). The structure of **9** was confirmed by its NMR and mass spectra. The conversion of **9** into the olefinic spiroketal **2** commenced with monobromination, in the manner described previously,[8] which provided a mixture of *trans* and *cis* bromides **10** and **11** (55:45), in good yield (89%). This bromide mixture, on treatment with an excess of Bu^{t}OK in dry DMSO[8] at 20 °C, underwent smooth dehydrobromination to yield **2** in 87% yield (Scheme 1). The ^{1}H NMR data agreed with those reported previously,[3,4] and the new ^{13}C NMR data are concordant with **2**. The diene **3** was easily acquired in a similar way, except that the spiroketal **9** was first subjected to dibromination[8] in which four dibromides



Scheme 1 *Reagents:* i, BuLi; ii, 2,2-dimethyloxirane; iii, 10% HCl; iv, Br_2, $CaCO_3$, CCl_4; v, Bu^{t}OK, DMSO; vi, 2 Br_2, $CaCO_3$, CCl_4 (2 ×)

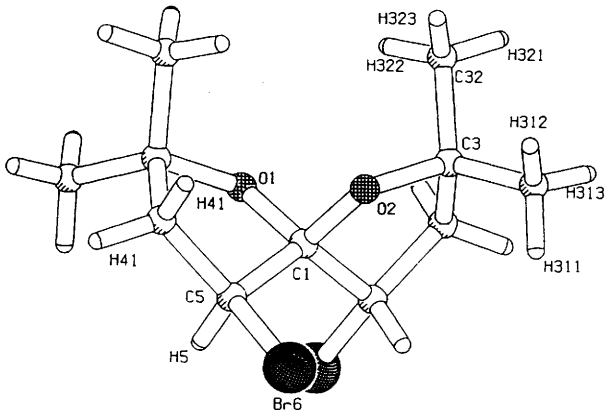
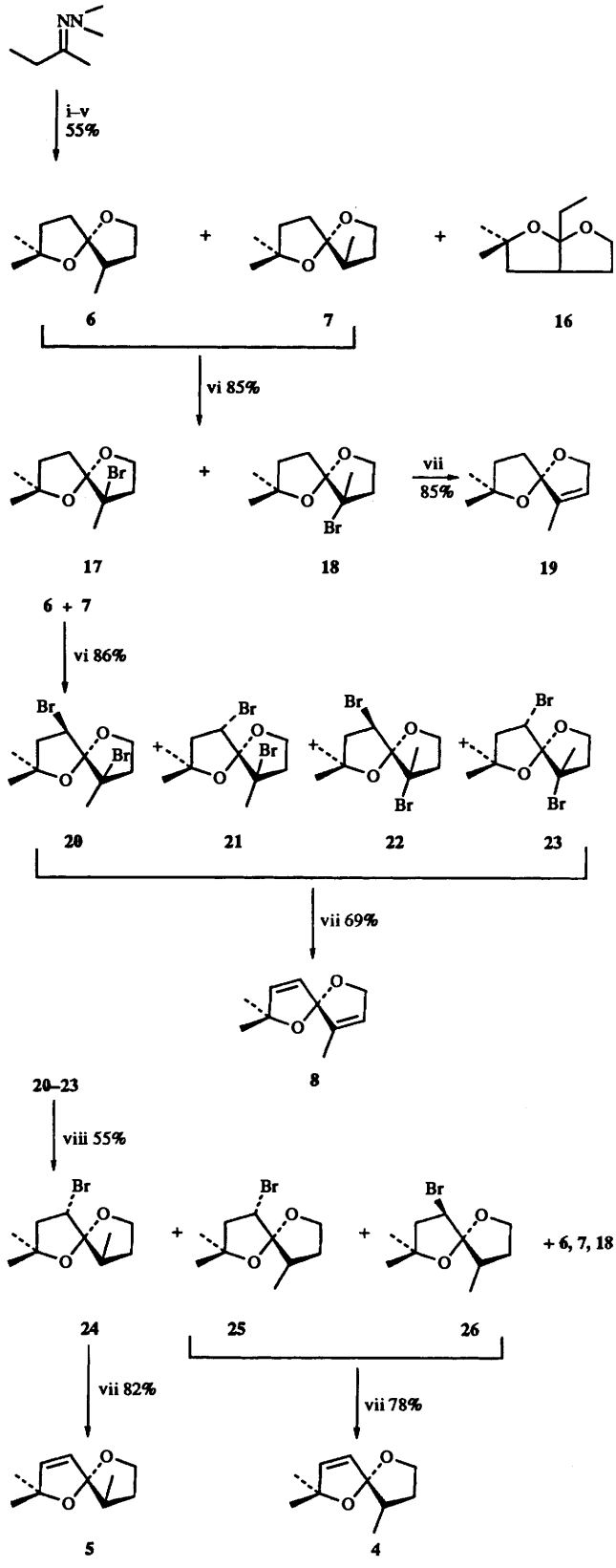


Fig. 1 PLUTON plot of one molecule of the dibromide **14**. Selected mean bond lengths (Å): Br(6)–C(5), 1.936; C(1)–O(2), 1.407; O(2)–C(3), 1.486; C(1)–C(5), 1.518; C(5)–C(4), 1.509; C(3)–C(31), 1.511. Selected mean bond angles (deg.): C(1)–O(2)–C(3), 109.6; O(2)–C(1)–O(1), 112.3; C(1)–C(5)–Br(6), 114.7; O(2)–C(1)–C(5), 101.9; O(1)–C(1)–C(5), 111.2.

were formed, three 4,9-dibromides (2:1:1; total 68%) **12**–**14** and one 4,4-dibromide **15** (9%) (Scheme 1). The isomers **12** and **14**, with two-fold symmetry axes, exhibit 6 ^{13}C NMR signals, whereas the isomers **13** and **15** each exhibit 11 signals. The isomers **13** and **15** were easily identified, as **15** lacks the CHBr signal in its ^{1}H NMR spectrum and shows a lowfield quaternary ^{13}C signal (66.2 ppm) for the *gem*-dibromomethylene carbon. Distinction between **12** and **14** was based initially on the multiplicity of the CHBr signals,[8] with that for the crystalline symmetrical dibromide (mp 72–73 °C) being a doublet of doublets at δ_H 4.21 (*J* 11 and 9 Hz) and that for the other symmetrical dibromide a doublet at δ_H 4.36 (*J* 5.6 Hz). This information, taken with the ^{13}C shifts of the spirocarbons (δ_C 110.5 and 118.0 ppm, respectively), and data on similar systems,[8] indicated that the crystalline isomer was **14**, and therefore the other was **12**. Our X-ray structure determination of the crystalline isomer confirmed these conclusions, and a PLUTON drawing is shown in Fig. 1. Treatment of a mixture of **12**–**14** with Bu^{t}OK in DMSO at room temperature led efficiently to the diene **3** (83%) whose ^{1}H NMR data matched those reported,[3,4] and whose ^{13}C NMR data are reported herein.

The spiroketals **4**–**7** were originally reported by Kaiser,[5] whose synthetic approach involved the addition of the lithium salt of 2-methylbut-3-yn-2-yl tetrahydropyran-2-yl ether to 3-methyltetrahydrofuran-2-one, hydrogenation under Lindlar conditions and acid-induced cyclisation. A more straightforward method utilises butanone *N*,*N*-dimethylhydrazone. Alkylation with 2,2-dimethyloxirane and then oxirane, followed by quenching and hydrazone hydrolysis, gave a mixture of **6** and **7** (72:28; 55%), together with the by-product **16**, resulting from α,α-dialkylation[11] (Scheme 2). The mixture of **6** and **7** (after removal of **16**) could be separated by preparative gas chromatography to provide **6** of 95% purity (5% of **7**) and **7** of 85% purity (15% of **6**). Distinction between **6** and **7** is based on the ^{13}C chemical shift of the 9-CH_3 group, with the signal at 13.3 ppm being assigned to **6**, and that at 17.1 ppm to **7**. This difference (3.8 ppm) reflects the γ-oxygen shielding effect, anticipated to be more pronounced for a γ-*syn* arrangement as present in **6**. However, samples of predominantly **6**, or predominantly **7**, when stored in $CDCl_3$, equilibrated to the same mixture of **6** and **7** (72:28) over a few days.

Bromination of the mixture of **6** and **7** afforded in good yield two monobromides, the *trans* and *cis* isomers **17** and **18** (95:5), respectively, with no (secondary) 4-bromide being detectable. Distinction between **17** and **18** was made on the basis of the ^{13}C chemical shifts of the 9-CH_3 group,[8] as outlined above for compounds **6** and **7**. Dehydrobromination of the mixture of **17** and **18** cleanly provided the olefin **19** (Scheme 2), which was sensitive to even weakly acidic conditions. The use of $MgSO_4$ for drying, or re-dissolution in $CHCl_3$ *etc.*, led to rearranged



Scheme 2 *Reagents and conditions:* i, BuLi; ii, 2,2-dimethyloxirane; iii, LDA; iv, oxirane; v, 10% HCl; vi, Br_2, $CaCO_3$, CCl_4 (2×); vii, Bu^{t}OK, DMSO; viii, Bu_3SnH, AIBN, toluene, 90 °C

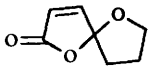
products (probably furan derivatives[8]), and consequently the NMR spectra of **19** were recorded immediately after isolation in [$^2H_6$]DMSO.[8]

Dibromination of the mixture of **6** and **7** (Scheme 2) led to three major 4,9-dibromides (*ca.* 56:23:21; 86%), with the major isomer being crystalline, mp 47–48 °C. These dibromides were separated and individually characterised, although the assignment of relative configurations between the possible structures **20–23** is uncertain. However, on the basis[8] that 4-H in the major isomer is a doublet (δ 4.47, J 6 Hz), we tentatively assign the major isomer as **20** or **22**, with the minor isomers being **21** and **23**, each of which showing 4-H as a doublet of doublets, at δ 4.31 (J 11 and 8.5 Hz) and δ 4.56 (J 9 and 9 Hz). Consideration of observed and calculated ^{13}C chemical shifts for **20–23**, indicated that the crystalline isomer is **20**, with the minor isomers, on this basis, being **21** and **23**. Natural compound **8** was readily acquired by double dehydrobromination of the mixture of **20–23** at 80 °C; its ^1H NMR spectrum matched that reported,[6] and the structure was fully concordant with the ^{13}C NMR and mass spectral data.

Controlled reduction of the mixture of the bromides **20**, **21** and **23** afforded three major 4-bromo derivatives (56:37:16; 55%) **24–26**, together with a minor 9-bromo derivative (8%) **18**, and a mixture of the fully reduced compounds **6** and **7** (72:28; 25%) (Scheme 2). The major monobromide could be separated from the mixture of minor monobromides and on dehydrobromination this major isomer provided only (9*R*)-2,2,9-trimethyl-1,6-dioxaspiro[4.4]non-3-ene **5** (82%). On this basis and spectroscopic grounds, the major monobromide has been tentatively assigned as **24**. Similarly, dehydrobromination of the mixture of minor isomers led only to (9*S*)-2,2,9-trimethyl-1,6-dioxaspiro[4.4]non-3-ene **4** (78%), and these minor isomers probably have structures **25** and **26** (Scheme 2).

The structures and relative configurations of **4** and **5** were confirmed by spectroscopic methods, and in particular the ^{13}C chemical shift of the 9-CH_3 group (13.1 ppm for **4**, but 15.4 ppm for **5**) for the reason outlined above. The olefinic spiroketals **4** and **5** readily equilibrated under mildly acidic conditions to a 70:30 mixture, as occurs naturally.[5]

Unsaturated spirolactones are also accessible by this procedure, and lactone **27** was synthesised because of its possible elaboration into the natural spiroketals **28** and **29**, bearing polyacetylene side chains.[12]



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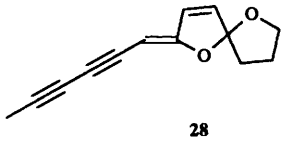

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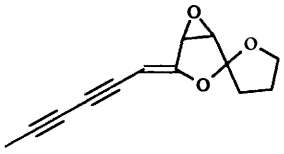

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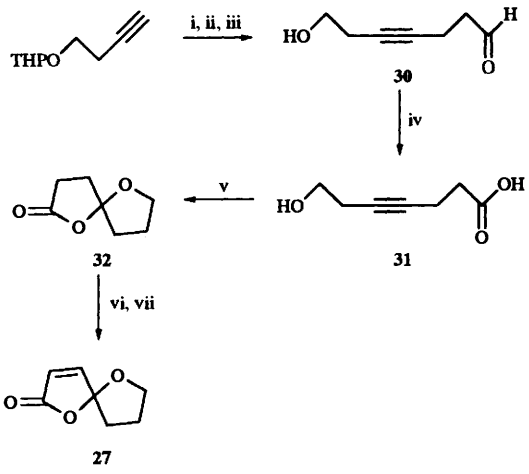
The route to **27** is summarised in Scheme 3, and the key step is a palladium(II)-induced cyclisation of the hydroxy alkynoic acid **31**. Cyclisation of this type has been achieved with Hg^{II},[13] but Pd^{II} appears to be cleaner and higher yielding. Bromination of the unstable saturated spiroketal **32**[14] provides a mixture of our monobromides, and dehydrobromination on silica, furnishes the unsaturated spirolactone **27**, although in low yield (15% from the hydroxy acid). Attempts are being made to improve the efficiency of this step. Simple adaptation would furnish other spirolactones of differing ring sizes.



Scheme 3 *Reagents and conditions:* i, BuLi, THF, −78 °C; ii, 2-(2-bromoethyl)-1,3-dioxolane; iii, AcOH, THF, H_2O (4:2:1), reflux; iv, Ag_2O, EtOH, H_2O; v, $Pd(PhCN)_2Cl_2$, THF, reflux; vi, Br_2, $CaCO_3$, $CHCl_3$; vii, SiO_2

This, and our previous report, demonstrate that bromination–dehydrobromination is a straightforward and useful approach for acquiring unsaturated spiroketals and spirolactones from their saturated precursors, and provides further opportunities for functionalisation based on the double bond. Some examples of this were recently described.[8]

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 MHz spectrometer using $CDCl_3$ and, in special cases, [$^2H_6$]-DMSO as solvents. Chemical shifts are relative to the signals of residual $CHCl_3$ at δ_H 7.24 ppm and δ_C 77.0 ppm, and DMSO at δ_H 2.49 ppm and δ_C 39.5 ppm. GC–MS data were acquired with a Hewlett-Packard MSD system combined with a 5890 GC system with a DB5 column. GC analyses were performed on a Shimadzu GC-14A instrument using a BP5 capillary column and temperature programming. High resolution mass spectra were obtained o. a Kratos MS-25RFA spectrometer.

Crystal structure analysis of the dibromide 14

Crystal data. $C_{11}H_{18}Br_2O_2$, M = 342.07, T = 298(2) K, λ = 0.710 73 Å, monoclinic, space group C_c, a = 11.320(6) Å, b = 11.499(2) Å, c = 10.332(4) Å, β = 91.84(2)°, V = 1344.2(9) Å^3, Z = 4, D_c = 1.690 mg cm^{-3}, μ(Mo-Kα) = 0.710 73 Å, absorption coefficient 6.012 mm^{-1}, F(000) = 680, 2.53 ≤ θ ≤ 24.96°.

Structure determination. The unit-cell parameters were obtained by least squares on the setting angles for 25 reflections with 2θ = 20–25° using an Enraf-Nonius CAD-4 four-circle diffractometer[15] (monochromatic Mo-Kα radiation, λ 0.710 73 Å. A unique data set was measured at 295 K within $2\theta_{max}$ = 50° limit conventional $2\theta/\omega$ scan mode). Of the 2625 independent reflections obtained, 1009 with $I > 2\sigma(I)$ were considered 'observed' and were used in the full matrix least squares refinement after being corrected for absorption using the Ψ scan method. The intensities of 3 standard reflections, measured every 250 reflections through the data collection, showed only small random variations. The structure was solved by the Patterson heavy-atom method in SHELXS 86.[16] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen parameters were located and refined, and secondary extinction corrections were not applied. Neutral scattering factors for non-hydrogen atoms were taken from Ibers and Hamilton.[17] Final atomic coordinates, and

equivalent isotropic thermal parameters, bond lengths and bond angles, anisotropic thermal parameters, hydrogen coordinates, and structure amplitudes have been deposited at the Cambridge Crystallographic Data Centre.†

2,2,7,7-Tetramethyl-1,6-dioxaspiro[4.4]nonane 9

To a stirred and cooled (−78 °C) solution of acetone *N*,*N*-dimethylhydrazone (2.22 g, 22 mmol) in dry THF (30 cm^3) under a nitrogen atmosphere was added dropwise butyllithium (13.8 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 22 mmol) over a period of 5 min. The reaction mixture was stirred at −78 °C for 2 h, during which a white solid formed. 2,2-Dimethyloxirane (1.6 g, 22 mmol) in dry THF (2 cm^3) was then added dropwise to it at this temperature and the reaction mixture was allowed to warm to room temperature and stirred for 2 h, after which butyllithium (13.8 cm^3, 22 mmol) was added dropwise to the re-cooled (−78°) mixture. On completion of the addition, the reaction mixture was allowed to warm to 20 °C and stirred for 4 h. Again, 2,2-dimethyloxirane (1.6 g, 22 mmol) in dry THF (2 cm^3) was added dropwise to it at −78 °C and the reaction mixture was finally allowed to warm to room temperature and stirred overnight. Diethyl ether (ether) (30 cm^3) and then 10% hydrochloric acid were added to it until the system was acidic, and after stirring for 1 h, the organic layer was separated and the aqueous layer further extracted with ether (4 × 30 cm^3). The combined ether layers were washed with aqueous saturated $NaHCO_3$ (2 × 30 cm^3), brine (2 × 40 cm^3), dried ($MgSO_4$), and then concentrated under reduced pressure to give a residue (4 g), consisting of one major volatile product. Purification of the crude product by flash chromatography on silica (ether–hexane, 0:10→1:10) yielded the spiroketal **9** as an oil (2.2 g, 54%) [Found: $(M - CH_3)^+$ 169.1227. $C_{10}H_{17}O_2$ $(M - CH_3)$ requires $M - CH_3$, 169.1224]; δ_H 1.13 and 1.30 (each 6 H, s, 2 × 2- and 7-CH_3) and 1.64–2.03 (8 H, m, 3-, 4-, 8- and 9-H_2); δ_C 29.0 and 30.2 (2 × 2- and 7-CH_3), 36.5 (C-3 and -8), 37.6 (C-4 and -9), 81.1 (C-2 and -7) and 115.2 (C-5); *m*/*z* (GC–MS) 169 ($M - CH_3$, 64%), 126 (41), 115 (100), 111 (16), 99 (72), 97 (60), 93 (24), 77 (14), 71 (18) and 70 (27).

4-Bromo-2,2,7,7-tetramethyl-1,6-dioxaspiro[4.4]nonanes 10 and 11

The spiroketal **9** (0.7 g, 3.8 mmol) was added to a suspension of $CaCO_3$ (0.57, 5.7 mmol) in CCl_4 (5 cm^3), followed by bromine (0.61 g, 3.8 mmol) in CCl_4 (5 cm^3) over 5 min, after which the solution was filtered and dried ($MgSO_4$), concentrated under reduced pressure and then chromatographed on silica (ether–hexane, 0:10→1:10) to give an oil (0.89 g, 89%), consisting of the isomers **10** and **11**. A portion of this mixture was separated by HPLC (2.5% EtOAc in hexane) to afford **10** and **11** (*ca.* 54:46).

Isomer **10** [Found: $(M - CH_3)^+$, 247.0333. $C_{10}H_{16}{}^{79}BrO_2$ $(M - CH_3)$ requires $(M - CH_3)$, 247.0329]; δ_H 1.14, 1.30, 1.33 and 1.42 (each 3 H, s, 2 × 2- and 7-CH_3), 1.65–2.32 (5 H, m, 3- and 8-H_2 and 9-H), 2.62 (1 H, dd, *J* 14.5 and 6, 9-H) and 4.26 (1 H, dd, *J* 6 and 1.5, 4-H); δ_C 28.7, 30.0, 30.1 and 31.7 (2 × 2- and 7-CH_3), 35.8 (C-8), 37.5 (C-9), 47.1 (C-3), 55.3 (C-4), 81.3 (C-7), 83.8 (C-2) and 116.7 (C-5); *m*/*z* (GC–MS) 249 ($M - CH_3$, 16%), 247 ($M - CH_3$, 16), 125 (41), 115 (100), 113 (12), 109 (68), 97 (38) and 70 (18).

Isomer **11** [Found: $(M - CH_3)^+$, 247.0336. $C_{10}H_{16}{}^{79}BrO_2$ $(M - CH_3)$ requires $(M - CH_3)$, 247.0329]; δ_H 1.17, 1.23, 1.34 and 1.36 (each 3 H, s, 2 × 2- and 7-CH_3), 1.68–2.29 (6 H, m, 3-, 8- and 9-H_2) and 4.05 (1 H, dd, *J* 10.6 and 9.4, 4-H); δ_C 28.0, 29.5, 29.8 and 30.6 (2 × 2- and 7-CH_3), 31.3 (C-8), 37.3 (C-9), 46.3 (C-3), 48.8 (C-4), 79.5 (C-7), 82.9 (C-2) and 113.1 (C-5); *m*/*z* (GC–MS) 249 ($M - CH_3$, 17%), 247 ($M - CH_3$, 22), 167 (11), 125 (44), 115 (100), 113 (10), 109 (76), 107 (12), 97 (46) and 70 (18).

2,2,7,7-Tetramethyl-1,6-dioxaspiro[4.4]non-3-ene 2

To a stirred solution of a mixture of the bromides **10** and **11** (0.2 g, 0.76 mmol) in dry DMSO (5 cm^3) was added portionwise Bu^{t}OK (0.17 g, 1.5 mmol) under a nitrogen atmosphere. A brown colour appeared immediately, and the reaction mixture was stirred overnight. GC examination indicated that the bromides had reacted completely and water was added and the system was extracted with pentane (4 × 20 cm^3). The combined organic phases were washed with water, separated, dried ($MgSO_4$), concentrated and chromatographed on silica (ether–hexane, 0:10→1:10) to give an oil (0.12 g, 87%) (Found: M^+, 182.1301. $C_{11}H_{18}O_2$ requires *M*, 182.1302); δ_H 1.16, 1.24, 1.32 and 1.34 (each 3 H, s, 2 × 2- and 7-CH_3), 1.73–2.27 (4 H, m, 8- and 9-H_2), 5.52 (1 H, d, *J* 5.5, 3-H) and 5.95 (1 H, d, *J* 5.5, 4-H); δ_C 28.2, 28.5, 28.6 and 29.8 (2 × 2- and 7-CH_3), 37.6 and 37.7 (C-8 and -9), 81.5 (C-7), 86.3 (C-2), 118.2 (C-5), 127.5 (C-3) and 139.8 (C-4); *m*/*z* (GC–MS) 182 (M^+, 0.4%), 167 (23), 113 (42), 109 (100), 95 (14), 69 (16), 67 (10), 55 (13), 43 (48) and 41 (20).

4,9-Dibromo-2,2,7,7-tetramethyl-1,6-dioxaspiro[4.4]nonanes 12–14

The title compounds were prepared using the bromination procedure described for the preparation of compounds **10** and **11**.

Isomer **14**, mp 72–73°C [Found: M^+, 326.9420. $C_{10}H_{15}{}^{79}Br{}^{81}BrO_2$ $(M - CH_3)$ requires *M*, 326.9414]; δ_H 1.23 and 1.38 (each 6 H, s, 2 × 2- and 7-CH_3), 2.30 (2 H, d, *J* 11, 3- and 8-H), 2.31 (2 H, d, *J* 9, 3- and 8-H) and 4.21 (2 H, dd, *J* 11 and 9, 4- and 9-H); δ_C 28.5 and 30.4 (2 × 2- and 7-CH_3), 44.5 (C-4 and -9), 45.8 (C-3 and -8), 81.0 (C-2 and -7) and 110.5 (C-5); *m*/*z* (GC–MS) 329 ($M - CH_3$, 4%), 327 ($M - CH_3$, 8), 325 ($M - CH_3$, 5), 195 (26), 193 (26), 165 (17), 123 (32), 113 (48), 95 (13), 69 (33) and 43 (100).

Isomer **12** [Found: $(M - CH_3)^+$, 326.9420. $C_{10}H_{15}{}^{79}Br{}^{81}BrO_2$ $(M - CH_3)$ requires $(M - CH_3)$, 326.9414] (Found: C, 39.0; H, 5.5%. $C_{11}H_{18}Br_2O_2$ requires C, 38.60; H, 5.26%); δ_H 1.36 and 1.48 (each 6 H, s, 2 × 2- and 7-CH_3), 2.30 (2 H, d, *J* 14.5, 3- and 8-H), 2.69 (2 H, dd, *J* 14.5 and 5.6, 3- and 8-H) and 4.36 (2 H, d, *J* 5.6, 4- and 9-H); δ_C 29.8 and 32.5 (2 × 2- and 7-CH_3), 46.7 (C-3 and -8), 53.7 (C-4 and -9), 84.4 (C-2 and -7) and 118.0 (C-5); *m*/*z* (GC–MS) 329 ($M - CH_3$, 5%), 327 ($M - CH_3$, 10), 325 ($M - CH_3$, 6), 195 (32), 193 (32), 165 (26), 123 (35), 113 (36), 95 (10), 69 (28) and 43 (100).

Isomer **13** [Found: $(M - CH_3)^+$, 326.9417. $C_{10}H_{15}{}^{79}Br{}^{81}BrO_2$ $(M - CH_3)$ requires $(M - CH_3)$, 326.9414]; δ_H 1.18, 1.29, 1.34, 1.40 (each 3 H, s, 2 × 2- and 7-CH_3), 2.18–2.46 (4 H, m, 3- and 8-H_2), 4.47 (1 H, dd, *J* 10.5 and 9.4, 4-H or 9-H) and 4.52 (1 H, dd, *J* 10 and 7.4, 9-H or 4-H); δ_C 28.4, 28.5, 28.9 and 30.2 (2 × 2- and 7-CH_3), 46.9 and 48.1 (C-3 and -8), 49.5 and 50.9 (C-4 and -9), 80.6 and 81.3 (C-2 and -7) and 112.4 (C-5); *m*/*z* (GC–MS) 329 ($M - CH_3$, 3%), 327 ($M - CH_3$, 6), 325 ($M - CH_3$, 4), 195 (54), 193 (54), 165 (18), 123 (36), 113 (78), 95 (17), 69 (47) and 43 (100).

2,2,7,7-Tetramethyl-1,6-dioxaspiro[4.4]nona-3,8-diene 3

The diene **3** was obtained as an oil, utilising the procedure for dehydrobromination described for the preparation of compound **2** (Found: M^+, 180.1150. $C_{11}H_{16}O_2$ requires *M*, 180.1146); δ_H 1.28 and 1.36 (each 6 H, s, 2 × 2- and 7-CH_3), 5.51 (2 H, d, *J* 5.6, 3- and 8-H) and 6.01 (2 H, d, *J* 5.6, 4- and 9-H); δ_C 28.1 and 28.7 (2 × 2- and 7-CH_3), 86.5 (C-2 and -7), 121.4 (C-5), 126.9 (C-3 and -8) and 139.9 (C-4 and -9); *m*/*z* (GC–MS) 180 (M, 6%), 165 (83), 123 (18), 122 (16), 96 (14), 95 (10), 79 (14) and 67 (16).

† For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1995, Issue 1.

2,2,9-Trimethyl-1,6-dioxaspiro[4.4]nonane 6 and 7

To a stirred and cooled (−78 °C) solution of butanone *N,N*-dimethylhydrazone (4.0 g, 35 mmol) in dry THF (50 cm^3) was added dropwise under a nitrogen atmosphere butyllithium (22 cm^3 of 1.6 mol dm^{-3} solution in hexane, 35 mmol). The reaction mixture was stirred at −78 °C for 1.5 h, during which time a white solid formed. 2,2-Dimethyloxirane (2.5 g, 35 mmol) in dry THF (5 cm^3) was added dropwise to the reaction mixture and it was allowed to warm to room temp. and stirred for 2.5 h. Lithium diisopropylamide (70 mmol; prepared by reaction of butyllithium and diisopropylamine at −30 °C for 3.5 h in dry THF) in THF (50 cm^3) was added at −78 °C and the reaction mixture was allowed to warm to 0 °C and stirred for 4 h. Then, ethylene oxide (*ca.* 3 g, 70 mmol) was added to it at −78 °C and the reaction mixture was finally allowed to warm to 20 °C, and stirred overnight. Hydrochloric acid (10%) was added until the mixture was acidic, and after stirring for 1 h the mixture was extracted with ether. The combined ether extracts were washed with saturated aqueous $NaHCO_3$, brine, dried ($MgSO_4$), concentrated and chromatographed on silica (ether–hexane, 0:10→2:10) to give a mixture of the title compounds **6** and **7** in the ratio 72:28 (Found: M^+, 170.1301. $C_{11}H_{18}O_2$ requires *M*, 170.1302).

Isomer **6**, δ_H 0.97 (3 H, d, *J* 6.2, 9-CH_3), 1.12 and 1.31 (each 3 H, s, 2 × 2-CH_3), 1.66–1.99 (7 H, m, 3-, 4- and 8-H_2, 9-H), 3.69 (1 H, ddd, *J* 8.5, 8 and 7, 7-H) and 3.89 (1 H, ddd, *J* 8.5, 8 and 2.5, 7-H); δ_C 13.3 (9-CH_3), 28.3 and 29.9 (2 × 2-CH_3), 32.2 (C-8), 33.7 (C-3), 37.4 (C-4), 39.7 (C-9), 65.0 (C-7), 81.7 (C-2) and 115.3 (C-5); *m/z* (GC–MS) 170 (M, 3%), 155 (50), 125 (30), 115 (100), 114 (19), 112 (30), 101 (44), 97 (76), 83 (16), 73 (18), 71 (22) and 70 (50).

Isomer **7**, δ_H 0.93 (3 H, d, *J* 7, 9-CH_3), 1.14 and 1.30 (each 3 H, s, 2 × 2-CH_3), 1.66–1.99 (7 H, m, 3-, 4- and 8-H_2 and 9-H) and 3.81 (2 H, m, 7-H_2); δ_C 17.0 (9-CH_3), 28.8 and 30.1 (2 × 2-CH_3), 32.1 (C-8), 32.6 (C-3), 37.3 (C-4), 40.1 (C-9), 64.6 (C-7), 81.1 (C-2) and 117.3 (C-5); *m/z* (GC–MS) 155 (M − CH_3, 62%), 125 (27), 115 (100), 112 (34), 101 (34), 99 (20), 97 (70), 83 (20), 71 (25) and 70 (38).

9-Bromo-2,2,9-trimethyl-1,6-dioxaspiro[4.4]nonanes 17 and 18

The title compounds were obtained as oils, by using the standard conditions outlined above for the preparation of **10** and **11**.

Isomer **17** (Found: M^+, 248.0403. $C_{10}H_{17}{}^{79}BrO_2$ requires *M*, 248.0407); δ_H 1.14 and 1.30 (each 3 H, s, 2 × 2-CH_3), 1.81 (3 H, s, 9-CH_3), 1.68–2.40 (6 H, m, 3-, 4- and 8-H_2) and 3.92 (2 H, m, 7-H_2); δ_C 26.2 (9-CH_3), 28.2 and 30.0 (2 × 2-CH_3), 34.1 (C-8), 37.6 (C-3), 42.2 (C-4), 64.4 (C-7), 71.3 (C-9), 84.1 (C-2) and 117.2 (C-5); *m/z* (GC–MS) 250 (M, 1%), 248 (M, 1), 235 (13), 153 (23), 133 (13), 115 (80), 111 (38), 97 (38), 95 (26), 81 (13), 70 (18), 69 (54) and 43 (100).

Isomer **18** [Found: M^+, 233.0178. $C_9H_{14}{}^{79}BrO_2$ (M − CH_3) requires *M*, 233.0173]; δ_H 1.26 and 1.35 (each 3 H, s, 2 × 2-CH_3), 1.70 (3 H, s, 9-CH_3), 1.80–2.26 (5 H, m, 3- and 8-H_2 and 4-H), 2.69 (1 H, ddd, *J* 12, 10 and 8, 4-H), 3.77 (1 H, ddd, *J* 16, 8 and 0.5, 7-H) and 3.92 (1 H, ddd, *J* 16, 8 and 3.4, 7-H); δ_C 27.4 (9-CH_3), 30.1 (2 × 2-CH_3), 30.1 (C-8), 37.2 (C-3), 40.7 (C-4), 63.0 (C-7), 63.5 (C-9), 83.2 (C-2) and 115.3 (C-5); *m/z* (GC–MS) 250 (M, 1%), 248 (M, 1), 235 (18), 233 (18), 153 (25), 139 (10), 115 (100), 111 (38), 97 (42), 95 (22), 70 (16) and 69 (52).

2,2,9-Trimethyl-1,6-dioxaspiro[4.4]non-8-ene 19

Using the standard conditions outlined above for the preparation of **10** and **11** the title compound was obtained as an oil (Found: M^+, 168.1151. $C_{10}H_{16}O_2$ requires *M*, 168.1146); δ_H 1.09 and 1.22 (each 3 H, s, 2 × 2-CH_3), 1.62 (3 H, ddd, *J* 2, 2 and 2, 9-CH_3), 1.65–2.10 (4 H, m, 3- and 4-H_2), 4.20 (1 H, ddq, *J* 13, 2 and 2, 7-H), 4.34 (1 H, ddq, *J* 13, 2 and 2, 7-H) and 5.70 (1 H, ddq, *J* 2, 2 and 2, 8-H); δ_C 10.8 (9-CH_3), 28.0 and 29.2 (2 × 2-CH_3), 34.1 (C-3), 37.4 (C-4), 71.0 (C-7), 80.7 (C-2), 119.3 (C-5), 123.8 (C-8) and 135.5 (C-9); *m/z* (GC–MS) 168 (M, 6%), 153 (5), 150 (33), 136 (9), 135 (76), 107 (11), 96 (9), 95 (100) and 79 (14).

4,9-Dibromo-2,2,9-trimethyl-1,6-dioxaspiro[4.4]nonanes 20, 21 and 23

Total yield 56%. Isomer **20** was crystalline, mp 47–48 °C [Found: (M − CH_3)$^+$, 312.9262. $C_9H_{13}{}^{79}Br^{81}BrO_2$ (M − CH_3) requires (*M* − CH_3), 312.9258]; δ_H 1.30 and 1.46 (each 3 H, s, 2 × 2-CH_3), 2.05 (3 H, s, 9-CH_3), 2.27 (1 H, d, *J* 14, 3-H), 2.35–2.60 (2 H, m, 8-H_2), 2.73 (1 H, dd, *J* 14 and 6, 3-H), 3.85–4.06 (1 H, m, 7-H_2) and 4.47 (1 H, d, *J* 6, 4-H); δ_C 26.9 and 29.5 (2 × 2-CH_3), 31.9 (9-CH_3), 44.8 (C-8), 47.4 (C-3), 53.8 (C-4), 64.0 (C-7), 69.1 (C-9), 83.8 (C-2) and 115.4 (C-5); *m/z* (GC–MS) 330 (M, 1%), 328 (M, 3), 326 (M, 1), 315 (10), 313 (20), 195 (86), 193 (84), 191 (24), 189 (24), 181 (43), 179 (47), 113 (74), 110 (36), 109 (38), 69 (75) and 43 (100).

Isomer **21** was obtained as an oil (Found: M^+, 327.9500. $C_{10}H_{16}{}^{79}Br^{81}BrO_2$ requires: *M*, 327.9294); δ_H 1.25 and 1.36 (each 3 H, s, 2 × 2-CH_3), 1.89 (3 H, s, 9-CH_3), 2.27 (1 H, d, *J* 14, 3-H), 2.21–2.73 (4 H, m, 3- and 8-H_2), 3.95 (1 H, ddd, *J* 8, 8 and 6.51, 7-H), 4.09 (1 H, ddd, *J* 8, 8 and 5, 7-H) and 4.31 (1 H, dd, *J* 11 and 8.5, 4-H); δ_C 28.4, 29.7 and 30.3 (2 × 2-CH_3 and 9-CH_3), 41.7 (C-8), 43.6 (C-4), 48.3 (C-3), 64.7 (C-7), 65.0 (C-9), 80.6 (C-2) and 111.8 (C-5); *m/z* (GC–MS) 315 (M − CH_3, 13%), 313 (M − CH_3, 13), 311 (M − CH_3, 13), 195 (62), 193 (58), 191 (58), 189 (19), 179 (36), 113 (82), 110 (33), 109 (36), 69 (70) and 55 (100).

Isomer **23** was obtained as an oil (Found: M^+, 327.9500, $C_{10}H_{16}{}^{79}Br^{81}BrO_2$ requires: *M*, 327.9492); δ_H 1.17 and 1.36 (each 3 H, s, 2 × 2-CH_3), 1.82 (3 H, s, 9-CH_3), 2.31–2.58 (4 H, m, 3- and 8-H_2), 4.00–4.19 (2 H, m, 7-H_2), 4.56 (1 H, dd, *J* 9 and 9, 4-H); δ_C 27.4, 28.7 and 29.8 (2 × 2-CH_3 and 9-CH_3), 42.6 (C-8), 47.9 (C-4), 49.0 (C-3), 65.8 (C-7), 67.9 (C-9), 81.1 (C-2) and 113.2 (C-5); *m/z* (GC–MS) 330 (M, 1%), 328 (M, 2), 326 (M, 1), 195 (75), 193 (72), 191 (13), 189 (16), 181 (46), 179 (46), 113 (84), 110 (32), 109 (31), 99 (14), 95 (15), 81 (22), 69 (88) and 55 (100).

4-Bromo-2,2,9-trimethyl-1,6-dioxaspiro[4.4]nonane 24–26

To a stirred solution of the mixture of 4,9-dibromo-2,2,9-trimethyl-1,6-dioxaspiro[4.4]nonanes **20**, **21** and **23** (0.78 g, 2.4 mmol) in dry THF (5 cm^3) under a nitrogen atmosphere was added tributyltin hydride (0.69 g, 2.4 mmol), followed by AIBN (*ca.* 50 mg). The reaction mixture was heated to 90 °C and stirred for 50 min, after which combined GC–MS analysis indicated that the monobromides had been produced but that the dibromides had not reacted completely. Additional tributyltin hydride (1.8 mmol) was added in several portions until the dibromides had been consumed. Water (10 cm^3) was then added and the mixture extracted with ether (3 × 20 cm^3). The combined ether extracts were dried ($MgSO_4$), concentrated and separated by flash chromatography on silica (ether–hexane, 0:5→1:5) followed by HPLC (2.5% EtOAc in hexane) to give the products as an oil consisting of **25** and **26** (32:68; 0.18 g, 30%), **24** (0.15 g, 25%), **18** (0.048 g, 8%), and the mixture of **6** and **7** (72:28; 0.1 g, 25%).

Isomers **25** and **26** (Found: M^+, 248.0400. $C_{10}H_{17}{}^{79}BrO_2$ requires *M*, 248.0407); δ_H 0.97 and 1.13 (each 3 H, d, *J* 6.5, 2 × 9-CH_3), 1.15, 1.32, 1.36 and 1.38 (each 3 H, s, 4 × 2-CH_3), 1.70–2.61 (10 H, m, 2 × 3- and 8-H_2 and 2 × 9-H), 3.69 (1 H, ddd, *J* 19, 9 and 7, 7-H), 3.73 (1 H, ddd, *J* 19, 9 and 7, 7-H), 3.91 (1 H, ddd, *J* 8, 8 and 3.6, 7-H), 4.01 (1 H, ddd, *J* 8, 8 and 2.4, 7-H), 4.08 (1 H, dd, *J* 10.4 and 9.5, 4-H) and 4.42 (1 H, dd, *J* 6.7 and 4.5, 4-H); δ_C 13.0 and 14.8 (2 × 9-CH_3), 28.9, 29.3, 30.4 and 30.6 (4 × 2-CH_3), 32.3 and 33.8 (2 × C-8), 36.5 and 40.0

(2 × C-9), 46.2 and 47.8 (2 × C-3), 47.3 and 54.3 (2 × C-4), 65.8 and 66.7 (2 × C-7), 79.9 and 81.3 (2 × C-2) and 112.9 and 115.3 (2 × C-5); *m/z* (GC–MS for the shorter-retention-time isomer) 235 (M − CH_3, 4%), 233 (M − CH_3, 4), 195 (11), 193 (11), 153 (18), 113 (32), 111 (32), 101 (100) and 69 (28); *m/z* (GC–MS for the longer-retention-time isomer) 235 (M − CH_3, 4%), 233 (M − CH_3, 4), 195 (16), 193 (16), 153 (18), 113 (46), 111 (38), 101 (100), 69 (33).

Isomer **24** (Found: M^+, 248.0410. $C_{10}H_{17}{}^{79}BrO_2$ requires *M*, 248.0407); δ_H 1.12 (3 H, d, *J* 7, 9-CH_3), 1.17 and 1.34 (each 3 H, s, 2 × 2-CH_3), 1.56–2.36 (5 H, m, 3- and 8-H_2 and H-9), 3.93 (1 H, dd, *J* 8 and 8, 7-H), 3.96 (1 H, dd, *J* 8 and 1.6, 7-H) and 4.08 (1 H, dd, *J* 9.8 and 9.8, 4-H); δ_C 14.4 (9-CH_3), 29.0 and 30.3 (2 × 2-CH_3), 33.8 (C-8), 40.0 (C-9), 46.4 (C-4), 46.8 (C-3), 66.7 (C-7), 79.7 (C-2) and 114.1 (C-5); *m/z* (GC–MS) 235 (M − CH_3, 2%), 233 (M − CH_3, 2), 195 (9), 193 (9), 153 (14), 113 (28), 111 (33), 101 (100) and 69 (28).

2,2,9-Trimethyl-1,6-dioxaspiro[4.4]non-3-ene Diastereoisomer 4

Dehydrobromination of a mixture of **25** and **26** gave the title compound as an oil (Found: M^+, 168.1151. $C_{10}H_{16}O_2$ requires *M*, 168.1146); δ_H 0.84 (3 H, d, *J* 7, 9-CH_3), 1.17 and 1.23 (each 3 H, s, 2 × 2-CH_3), 1.58 (1 H, m, 8-H), 1.92–2.01 (2 H, m, 8- and 9-H), 3.60 (1 H, ddd, *J* 10, 7.8 and 6.5, 7-H), 3.70 (1 H, ddd, *J* 10, 8 and 2, 7-H), 5.47 (1 H, d, *J* 5.6, 4-H) and 6.12 (1 H, d, *J* 5.6, 3-H); δ_C 13.1 (9-CH_3), 27.0 and 28.5 (2 × 2-CH_3), 31.6 (C-8), 39.3 (C-9), 64.9 (C-7), 85.9 (C(2), 118.4 (C-5), 125.6 (C-3) and 140.5 (C-4); *m/z* (GC–MS) 168 (M, 3%), 153 (28), 125 (18), 123 (100), 113 (93), 109 (18), 97 (21), 96 (14), 95 (59) and 82 (32).

2,2,9-Trimethyl-1,6-dioxaspiro[4.4]non-3-ene Diastereoisomer 5

Dehydrobromination of **24** gave the title compound as an oil (Found: M^+, 168.1150. $C_{10}H_{16}O_2$ requires *M*, 168.1146); δ_H 0.86 (3 H, d, *J* 6, 9-CH_3), 1.20 and 1.71 (each 3 H, s, 2 × 2-CH_3), 1.52 (1 H, m, 8-H), 2.05–2.10 (2 H, m, 8- and 9-H), 3.72 (2 H, dd, *J* 7.2 and 5.8, 7-H_2), 5.60 (1 H, d, *J* 5.7, 3-H) and 6.06 (1 H, d, *J* 5.7, 4-H); δ_C 15.4 (9-CH_3), 27.8 and 28.3 (2 × 2-CH_3), 32.6 (C-8), 41.8 (C-9), 65.0 (C-7), 85.6 (C-2), 120.7 (C-5), 124.9 (C-3) and 139.8 (C-4); *m/z* (GC–MS) 168 (M, 3%), 153 (28), 125 (18), 123 (90), 113 (100), 109 (16), 97 (16), 95 (61), 82 (32) and 67 (44).

2,2,9-Trimethyl-1,6-dioxaspiro[4.4]nona-3,8-diene 8

Dehydrobromination of a mixture of **20**, **21** and **23** gave the title compound as an oil (Found: M^+, 166.0989. $C_{10}H_{14}O_2$ requires *M*, 166.0990); δ_H 1.30 and 1.37 (each 3 H, s, 2 × 2-CH_3), 1.63 (3 H, ddd, *J* 2, 2 and 2, 9-CH_3), 4.37 (1 H, ddq, *J* 13, 2 and 2, 7-H), 4.59 (1 H, ddq, *J* 13, 2 and 2, 7-H), 5.50 (1 H, d, *J* 5.6, 3-H), 5.73 (1 H, ddq, *J* 2, 2 and 2, 8-H) and 6.06 (1 H, d, *J* 5.6, 4-H); δ_C 11.5 (9-CH_3), 27.7 and 28.8 (2 × 2-CH_3), 72.5 (C-7), 86.6 (C-2), 123.6 (C-5), 124.2 (C-8), 125.5 (C-3), 135.5 (C-9) and 140.9 (C-4); *m/z* (GC–MS) 166 (M, 20%), 151 (42), 109 (8), 107 (8), 95 (12), 82 (14), 81 (9), 79 (13), 67 (18) and 43 (100).

7-Hydroxyhept-4-ynoic acid 31

To a stirred and cooled (−78 °C) solution of 4-(tetrahydropyran-2-yloxy)but-1-yne (4.0 g, 26 mmol) in dry THF (150 cm^3) under a nitrogen atmosphere butyllithium (9.4 cm^3 of 2.5 mol dm^{-3} solution in hexane, 23.5 mmol) was added dropwise, and the reaction mixture was stirred at −78 °C for 3 h. A solution of 2-(2-bromoethyl)-1,3-dioxolane (5 g, 27.6 mmol) in HMPA (*ca.* 6 cm^3) and dry THF (20 cm^3) was added dropwise. The reaction was allowed to warm to room temperature and stirred overnight. Water was added, and the aqueous system was extracted with ether (3×), and the combined ether extracts were washed with brine, dried ($MgSO_4$), chromatographed on silica (EtOAc–hexane, 0:10→3:10) to give an oil (5.4 g, 82%). Combined samples of this oil (8 g) were deprotected with AcOH–THF–H_2O (4:2:1) (200 cm^3) under refluxing, to give 7-hydroxyhept-4-ynal **30** (3.1 g, 78%); δ_H 2.13–2.50 (4 H, m, 3- and 6-H_2), 2.58–2.66 (2 H, m, 2-H_2), 3.64 (2 H, t, *J* 6, 7-H_2) and 9.23 (1 H, s, CHO); δ_C 12.0 (C-3), 23.0 (C-6), 42.8 (C-2), 61.2 (C-7), 77.9 (C-4), 80.2 (C-5) and 200.9 (C-1). The aldehyde **30** was oxidised with Ag_2O to give 7-hydroxyhept-4-ynoic acid **31** in 80% yield, δ_H 2.34–2.65 (6 H, m, 2-, 3- and 6-H_2), 3.66 (2 H, t, *J* 6, 7-H_2) and 6.58 (br s, OH); δ_C 14.6 (C-3), 22.9 (C-6), 33.6 (C-2), 61.2 (C-7), 77.8 (C-4), 80.4 (C-5) and 177.4 (C-1).

1,6-Dioxaspiro[4.4]non-3-en-2-one 27

The acid **31** (0.5 g, 3.5 mmol), without further purification, was refluxed in dry THF (50 cm^3) in the presence of a catalytic amount of $Pd(PhCN)_2Cl_2$ (*ca.* 10 mg) for 2 h. After filtration and concentration, the residue was examined by GC–MS, which showed one major, volatile product **32**, δ_H 1.95–2.71 (8 H, m, 3-, 4-, 8- and 9-H_2) and 3.98–4.09 (2 H, m, 7-H_2); δ_C 23.5 (C-8), 29.2 (C-3), 31.2 (C-9), 36.1 (C-4), 69.1 (C-7), 116.3 (C-5) and 176.7 (C-2); *m/z* (GC–MS) 140 (M − 2 H, 0.6%), 112 (8), 97 (18), 84 (21), 83 (35), 82 (18), 70 (52), 69 (50), 68 (22), 57 (33), 56 (67), 55 (81) and 41 (100).

The crude spirolactone **32** was dissolved in dry $CHCl_3$ (20 cm^3), in which $CaCO_3$ powder (1.4 g, 14 mmol) was suspended, and bromine in dry $CHCl_3$ (1:1 v/v) was added dropwise to it to effect monobromination of the spirolactone. GC–MS examination indicated that the product consisted of four major monobromides in the ratio 16:35:38:11. This monobromide mixture was filtered, concentrated and then dehydrobrominated by column chromatography on silica [ether–light petroleum (bp 40–60 °C), 0:10→5:10] to give the unsaturated spirolactone **27** (74 mg, 15% calculated from the acid **31**) [Found: (M − CO)$^+$, 112.0525. $C_6H_8O_2$ (M − CO) requires (*M* − CO), 112.0522]; δ_H 2.15 (4 H, m, 8- and 9-H_2), 4.05 and 4.22 (each 1 H, m, 7-H_2) and 6.12 and 7.09 (each 1 H, ABq, *J* 5.6, 3- and 4-H); δ_C 24.3 (C-8), 35.4 (C-9), 70.7 (C-7), 114.5 (C-5), 124.3 (C-4), 151.9 (C-3) and 170.0 (C-2); *m/z* (GC–MS) 112 (M − CO, 6%), 99 (13), 96 (41), 95 (12), 82 (23), 68 (12), 55 (100), 54 (58) and 53 (18).

Acknowledgements

We are indebted to the University of Queensland for the award of a postdoctoral research fellowship (to Y. Q. T.) and support for this work.

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Paper 4/06491G
Received 24*th October* 1994
Accepted 30*th January* 1995