Isolation and Synthesis of 1,7-Dioxaspiro[5.5]undecane and 1,7-Dioxaspiro-[5.5]undecan-3-and -4-ols from the Olive Fly (*Dacus oleae*)

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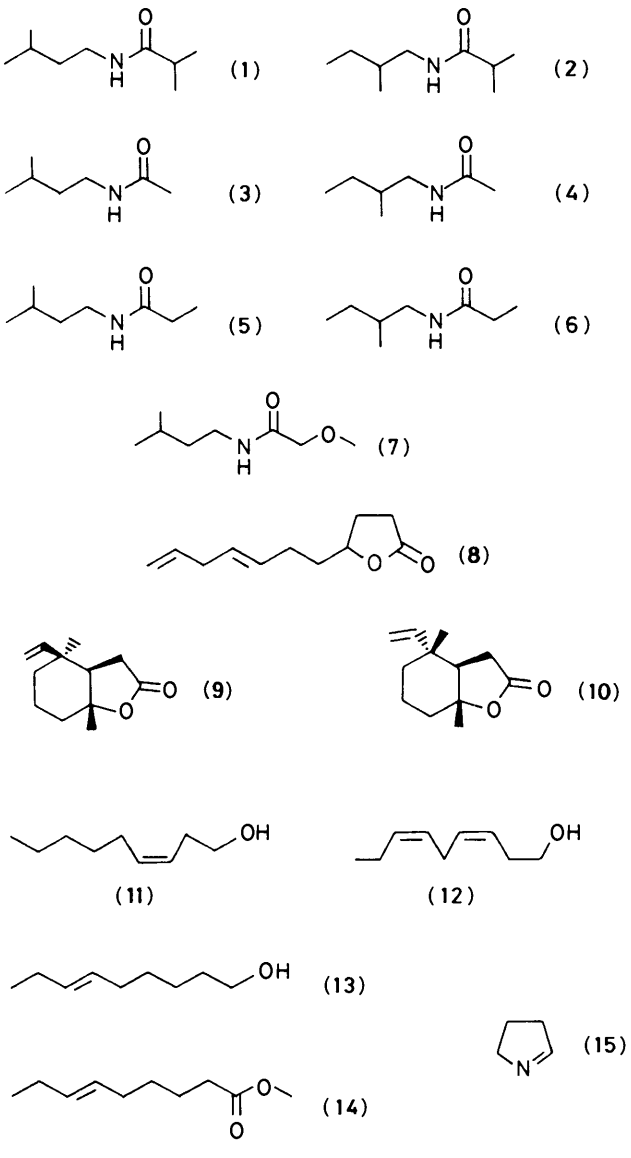
The major component of the sex pheromone of the olive fly has been shown to be 1,7-dioxaspiro[5.5]undecane (**16**). Two hydroxyspiroacetals, 1,7-dioxaspiro[5.5]undecan-3- and -4-ols (**17a**) and (**18a**), have also been isolated from the rectal glands of the female olive fly, and stereoselective syntheses of these developed.

Evidence for the importance of pheromones in controlling certain behavioural responses in fruit flies has been gathered over the past two decades. In general, most long-range sex pheromones are synthesized, stored in specialised glands, and released at a specific time of day, usually controlled by the light intensity. These long range attractants are normally emitted by the males (*e.g. Ceratitis capitata*,[1] *Dacus tryoni*[2] *and Anastrepha suspensa*[3]), but may be produced by the female (*e.g. Dacus oleae*[4]). The Queensland fruit fly (*Dacus tryoni*) is active at dusk, in common with most other species, and secretes a pheromone from glands associated with the posterior ventral regions of the rectum.[5] The Caribbean fruit fly (*Anastrepha suspensa*), olive fruit fly (*Dacus oleae*), Oriental fruit fly (*Dacus orientalis*), and melon fruit fly (*Dacus cucurbitae*) all have similar glands.[6,7]



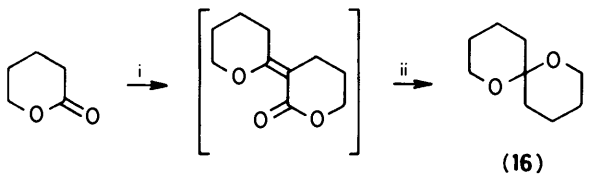
In recent years, several of these pheromone systems have been identified, and cover a diverse range of chemical types. The secretion from the rectal glands of male Queensland fruit flies (*Dacus tryoni*) and a related species (*Dacus neohumeralis*) was found to be largely a mixture of six aliphatic amides (**1**)—(**6**).[8] *N*-3-Methylbutylacetamide (**3**) was also identified from the melon fly (*Dacus cucurbitae*) together with the novel methoxyacetamide (**7**).[9] *N*-2-Methylbutylpropanamide (**6**) was found in the Oriental fruit fly (*Dacus orientalis*) in association with a lactone, (*E*)-5-hepta-3,6-dienyl-4,5-dihydrofuran-2(3*H*)-one (**8**).[10] Two isomeric γ-lactones, anastrephin (**9**) and *epi*-anastrephin (**10**), have been reported as major components of the sex and aggregation pheromones of the Mexican and Caribbean fruit flies, *Anastrepha ludens* and *Anastrepha suspensa*.[11,12] Nation *et al.* have reported anastrephin (**9**) and *epi*-anastrephin (**10**), together with (*Z*)-non-3-en-1-ol (**11**) and (*Z*,*Z*)-nona-3,6-dien-1-ol (**12**) as sex and aggregation pheromone components for *Anastrepha suspensa*.[13] Previously, (*E*)-non-6-en-1-ol (**13**) and methyl (*E*)-non-6-enoate (**14**) were identified from the volatiles produced by male Mediterranean fruit flies (*Ceratitis capitata*), and the latter was shown to be a male attractant in the field.[14] More recently, 3,4-dihydro-2*H*-pyrrole (Δ^1-pyrroline) (**15**) has been reported as the key component of the sex pheromone of the male Mediterranean fruit fly (*Ceratitis capitata*).[15]

This chemical diversity has been extended by our studies of the olive fruit fly (*Dacus oleae*). This species is a major pest of olives and is widely distributed throughout the Mediterranean basin and part of N. Africa. It is known that the female produces a volatile pheromone that attracts males,[4] and that the pheromone is stored in the rectal gland. We report that the major component of the sex pheromone of the olive fly is 1,7-dioxaspiro[5.5]undecane (**16**) together with two minor components 1,7-dioxaspiro[5.5]undecan-3-ol and -4-ol (**17a**), and (**18a**).

Results and Discussion

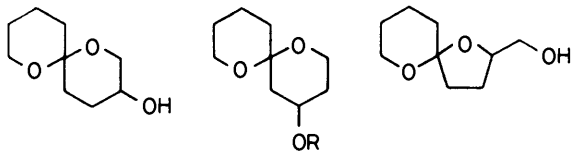
Analysis of the rectal glands, dissected from sexually mature adult flies (male or female), by means of solid-sample gas chromatography (s.s.g.c.)[16] indicated the presence of three female specific spiroacetals. The major component (*ca.* 300 ng per fly) was shown by high resolution mass spectrometry (h.r.m.s.) to have a molecular ion with an atomic composition of $C_9H_{16}O_2$, and two diagnostic ions at *m/z* 101 (100%, $C_5H_9O_2$) and *m/z* 98 (80, $C_6H_{10}O$). This enabled the compound to be

assigned as 1,7-dioxaspiro[5.5]undecane (**16**), from a consideration of the detailed fragmentation patterns of alkyl-1,6-dioxaspiro[4.4]nonanes[17] and alkyl-1,6-dioxaspiro[4.5]decanes.[18] The structure was confirmed by unambiguous synthesis of the spiroacetal (**16**) by the method of Erdmann[19] (Scheme 1) involving the dimerisation of δ-valerolactone. Comparison of its g.c. and m.s. properties with those of the natural product, showed them to be identical.



Scheme 1. *Reagents:* i, $Na^+ {}^-OEt$; ii, H_3^+O

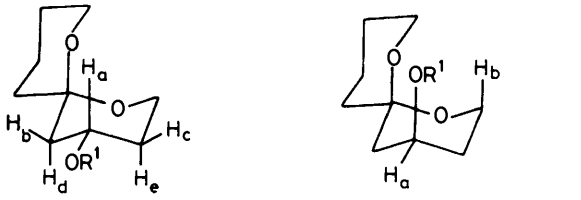
The two minor spiroacetals were each present at a level of *ca.* 10 ng per insect. Both components were shown to have a molecular ion *m/z* 172 ($C_9H_{16}O_3$), and diagnostic pairs of ions at *m/z* 98 ($C_6H_{10}O$), 101 ($C_5H_9O_2$) and *m/z* 114 ($C_6H_{10}O_2$), 117 ($C_5H_9O_3$). In particular, the ion pair at *m/z* 114, 117 indicated an additional hydroxy substituent on one ring. One component was assigned the structure 1,7-dioxaspiro[5.5]-undecan-3-ol (**17**) on the basis of the high relative intensity of ion *m/z* 98 (100%) compared to the ions *m/z* 101(29), 114(15), and 117(16), since elimination of water followed by a retro-Diels–Alder would give the ion *m/z* 98, in addition to the usual fragmentation pathway. This component readily isomerised to 1,6-dioxaspiro[4.5]decan-2-ylmethanol (**20**) when heated to 140 °C during s.s.g.c. Confirmation of the identity of the rearrangement product (**20**) was obtained by comparison with an authentic sample synthesized by the method of Ireland,[20] and this supported the assignment of the natural product as 1,7-dioxaspiro[5.5]undecan-3-ol (**17**). This thermal rearrangement could be minimised by using a solvent extract of the glands for analysis together with a lower injection temperature (≤100 °C). The other minor component had an ion at *m/z* 155 (*M* − 17), indicative of a hydroxy group, and an intense ion at *m/z* 127 strongly suggesting the structure to be 1,7-dioxaspiro[5.5]-undecan-4-ol (**18**). These structures have now been confirmed by unambiguous synthesis.



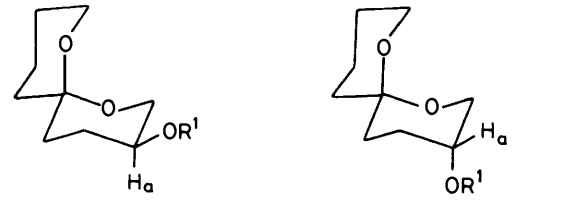
(**17**) (**18**) R = H (**20**)
(**19**) R = Me

1,7-Dioxaspiro[5.5]undecan-4-ol (**18**) was prepared from the alkyne (**23**), obtained by the method of Deslongchamps[21] (Scheme 2). The methoxyacetal (**26**) was the preferred substrate for reduction of the alkyne to the alkene as the hydroxyacetal (**23**) (as the -ynone) was prone to over-reduction. The diastereoisomers (**18a**) and (**18b**) (ratio *ca.* 17:1) were separated and the corresponding dinitrobenzoate esters (**21a**) and (**21b**) prepared.

From the ^1H n.m.r. data of (**18a**) it was observed that the signal for H_a (δ4.04) was significantly deshielded by a 1,3-diaxial interaction with a ring oxygen, and appeared as seven evenly spaced lines, intensity ratio 1:2:3:4:3:2:1, due to two coupling constants of 11 Hz (axial-axial) and two coupling constants of 5.5 Hz (axial-equatorial); thus, H_a was axial and the hydroxy was equatorial. The remaining four protons on carbons adjacent to oxygen had similar chemical shifts to each other, as two were equatorial (deshielded by hyperconjugation) and two were axial and had a 1,3-diaxial interaction with an oxygen. Thus, the ^1H n.m.r. data indicated that (**18a**) was exclusively in the anomerically stabilised conformation, as shown. The ^1H n.m.r. of the dinitrobenzoate ester (**21a**) also showed a septuplet for H_a (δ5.53, 1 H, dddd, *J* 5.5, *J'* 11.5 Hz). From the ^1H n.m.r. spectrum of (**18b**) it was apparent that H_a and H_b had similar chemical shifts (δ3.96—4.1) as H_b had two 1,3-diaxial interactions with oxygens. The ^1H n.m.r. of the corresponding



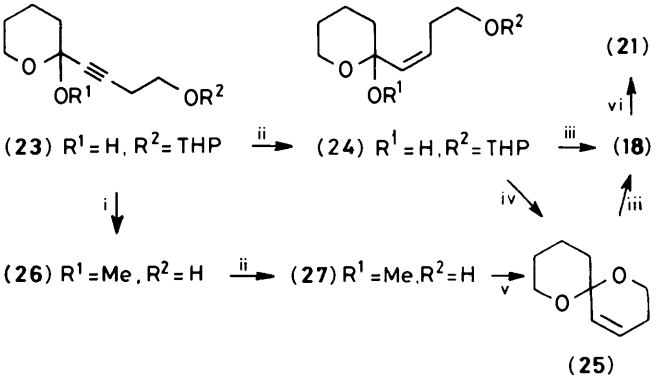
(4*S*, 6*S* – (**18a**)[a] R¹ = H (4*R*, 6*S* – (**18b**)[a] R¹ = H
(4*S*, 6*S* – (**21a**)[a] R¹ = DNB (4*R*, 6*S* – (**21b**)[a] R¹ = DNB



(3*S*, 6*S* – (**17a**)[a] R¹ = H (3*R*, 6*S* – (**17b**)[a] R¹ = H
(3*S*, 6*S* – (**22a**)[a] R¹ = DNB (3*R*, 6*S* – (**22b**)[a] R¹ = DNB

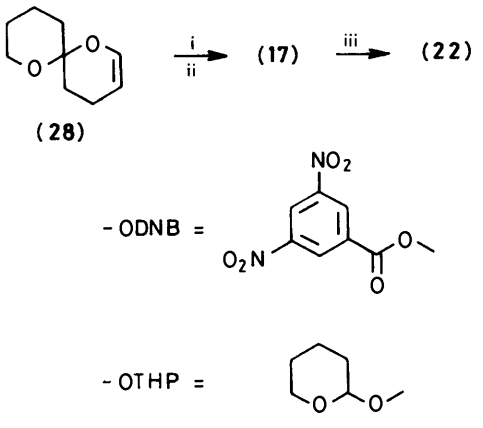
[a] Only one enantiomer shown

dinitrobenzoate (**21b**) showed a narrow, complex multiplet for H_a (δ5.46), and a multiplet for H_b (δ4.15) with coupling constants (1 H, m, $J = J'$ 12, J'' 3 Hz) consistent with the structure shown. The stereoselectivity of the reaction could be accounted for by epimerisation at the spiro-carbon atom C-6 favouring the sterically less hindered diasteroisomer (**18a**). The substituent in (**18b**) is axial and whilst a change to equatorial would lead to release of steric strain this would seem to be unfavourable (as observed by ^1H n.m.r.) due to the concomitant loss of anomeric stabilisation.



Scheme 2. *Reagents:* i, MeOH, H^+; ii. H_2, Pd (5% on $BaSO_4$), quinoline; iii, THF, H_2O, conc. HCl; iv, THF, conc. HCl; v, CSA, CH_2Cl_2; vi, 3,5-DNBCl, pyridine

1,7-Dioxaspiro[5.5]undecan-3-ol (**17**) was prepared by hydroboration of 1,7-dioxaspiro[5.5]undec-2-ene (**28**) (Scheme 3) obtained by the method of Ireland.[20] The diastereoisomers (**17a**) and (**17b**) (ratio *ca.* 1:3) were separated and their corresponding dinitrobenzoate esters (**22a**) and (**22b**) formed. It was observed that the signal for H_a in the ^1H n.m.r. of ester (**22a**) (δ 5.15) appeared as seven equally spaced lines, intensity ratio 1:2:3:4:3:2:1 [cf. (**21a**)] with coupling constants (1 H, dddd, *J* 11.8, *J'* 5.4 Hz) consistent with H_a axial as shown. Similarly the signal for H_a in the ^1H n.m.r. of ester (**22b**) was a narrow complex multiplet (δ 5.18) corresponding to H_a being equatorial. Again, the anomerically stabilised conformations were observed. Co-elution studies showed that the natural hydroxyspiroacetals were identical with the (**17a**) and (**18a**) diastereoisomers. The regioselectivity of the hydroboration reaction is similar to that observed for dihydropyrans,[22] whilst the stereoselectivity may in part be due to steric effects (attack from less hindered face).



Scheme 3. *Reagents:* i, BH_3.THF; ii, NaOH, H_2O_2; iii, DNBCl, py

Field trials with the racemic mixture of the spiroacetal (**16**) have been carried out in Southern Spain (Granada). Triangular, sticky 'delta' traps baited with rubber septa impregnated with 1—50 mg of the spiroacetal (**16**) caught large numbers of olive flies, of which more than 99% were males and less than 1% were females. Similar unbaited traps caught no flies. These results indicate that the synthetic compound is acting in a similar way to the pheromone produced by the female fly in having specific attraction for male flies.

Spiroacetals have been found as pheromones for a wide range of insect species, but this is the first report of spiroacetals in Diptera. All the previously known spiroacetal pheromones contained unbranched carbon skeletons and, with one exception, contained 9, 11 or 13 carbon atoms,[23] with no further oxygen substituents. Since our initial communications[24,25] two other novel hydroxyspiroacetals (**29**) and (**30**) have been isolated from the mandibular gland secretion of a bee of the genus Andrena.[26] Stereospecific syntheses of 1,7-dioxaspiro[5.5]undecane (**16**),[27,28] 1,7-dioxaspiro[5.5]undecane-3-ol (**17**)[29] and 1,7-dioxaspiro[5.5]undecan-4-ol (**18**)[27] have been reported, as well as two syntheses of racemic-(**18**)[30,31] and racemic (**16**).[32]

Experimental

N.m.r. spectra were recorded on Perkin-Elmer Hitachi R24 (^1H; 60 MHz) and Bruker AM360 (^1H; 360 MHz, ^{13}C; 90 MHz) spectrometers. The samples were dissolved in deuteriochloroform unless otherwise stated and chemical shifts are reported as δ values (relative to an internal $SiMe_4$ standard). I.r. spectra were recorded on a Perkin-Elmer 298 spectrometer, and mass spectra obtained using a Kratos MS30 spectrometer. All m.p.s are uncorrected.

Isolation, S.s.g.c. and G.c.m.s. of the Natural Products.—Sexually mature adult flies (7 days old, either male or female) were frozen on solid carbon dioxide and the rectal glands extirpated, placed in a glass capillary (5 glands per tube), and sealed with a flame. Gas chromatographic analysis was performed with a solid sample injector/heater[16] at 140 °C for 5 min, then injected onto a 3 m × 3 mm analytical column containing FFAP (5% on Diatomite C AAW, and temperature programmed from 100—245 °C at 6 °C min^{-1}. Co-elution studies were conducted with synthetic samples of (**17**) and (**18**) and an extract of the natural products. Direct injection gave the following retention times; (**17a**) and natural product, 21.4; (**17b**), 19.2; (**18a**) and natural product, 21.0; (**18b**) 16.0 min. Mass spectra of the natural products were as follows; (**16**), *m/z* 156 (M^+, 18%), 111(15), 101(100), 100(50), 98(80), 83(26), 56(23), 55(48), 43(31), and 41(28); (**17a**), *m/z* 172 (M^+, 5%), 142 (18), 127(3), 117(16), 114(15), 101(29), 98(100), 83(12), and 55(14); (**18a**), *m/z* 172 (M^+, 4%), 155(15), 127(35), 117(100), 114(57), 101(69), 98(77), 83(14), and 55(42).

Synthesis of 1,7-*Dioxaspiro*[5.5]*undecane* (**16**).—δ-Valerolactone (20 g) in absolute ethanol (50 ml) was added dropwise to a stirred solution of sodium (2.3 g) in absolute ethanol (50 ml) at 5—10 °C. After addition, the mixture was refluxed for 3 h and the alcohol was distilled to leave a residue which was dissolved in hot water and acidified with dilute hydrochloric acid. The product was then co-distilled with water. Work-up and distillation afforded (**16**) (10.2 g, 65%), b.p. 77—78 °C at 13 mmHg; δ_H (360 MHz) 1.20—1.45 (8 H), 1.63 (2 H), 1.95 (2 H), 3.52 (2 H), and 3.65 (2 H); δ_C (90 MHz) 19.01 (t), 25.89 (t), 36.24 (t), 60.24 (t), and 94.91 (s); *m/z* 156 (M^+, 18%), 111(14), 101(100), 100(51), 98(84), 83(26), 56(21), 55(40), 43(31), and 41(28).

Hydrogenation of 1-(2-*Hydroxytetrahydropyran*-2-*yl*)-4-*tetrahydropyran*-2-*yloxybut*-1-*yne* (**23**).—The alkyne (**23**)[21] (16 g, 62.5 mmol) was dissolved in dry methanol (150 ml), 5% palladium on barium sulphate (250 mg) and quinoline (0.7 ml) were added, and the solution was placed under an atmosphere of hydrogen. After the rapid initial uptake of hydrogen the reaction was stopped, filtered, and the methanol removed completely to afford crude (*Z*)-1-(2-hydroxytetrahydropyran-2-yl)-4-tetrahydropyran-2-yloxybut-1-ene (**24**) as an oil (15.8 g, 98%), $\nu_{max.}$ 3 500 br cm^{-1} (OH); δ_H (60 MHz) 1.4—2.0 (12 H, m), 2.2—2.8 (3 H, m), 3.3—4.2 (6 H, m), 4.6 (1 H, br s), 5.25 (1 H, d, *J* 12 Hz), and 5.5 (1 H, m).

Protection–Deprotection of 1-(2-*Hydroxytetrahydropyran*-2-*yl*)-4-*tetrahydropyran*-2-*yloxybut*-1-*yne* (**23**).—The alkyne (**23**)[21] (12.7 g, 50 mmol), dissolved in dry methanol (200 ml), was treated with Amberlite resin (IR-118) (2 g) and stirred for 24 h. Filtration and removal of solvent, followed by chromatography (Florosil: diethyl ether) afforded 4-(2-methoxytetrahydropyran-2-yl)but-3-yn-1-ol (**26**) as a pale yellow oil (7.9 g, 86%), $\nu_{max.}$ 3 400br cm^{-1} (OH); δ_H (60 MHz) 1.3—2.2 (6 H, m), 2.4—2.9 (3 H, m), 3.4 (3 H, s), and 3.6—4.2 (4 H, m).

Hydrogenation of 4-(2-*Methoxytetrahydropyran*-2-*yl*)*but*-3-*yn*-1-*ol* (**26**).—The alkyne (**26**) (7.6 g, 41 mmol) was hydrogenated in methanol, over 5% palladium on barium sulphate poisoned with quinoline, in the presence of sodium hydrogen carbonate. After the initial rapid uptake of hydrogen, the reaction was stopped, the solution filtered, and the solvent removed. The product was dissolved in dichloromethane, filtered, and the solvent removed to give (*Z*)-4-(2-methoxy-

tetrahydropyran-2-yl)but-3-en-1-ol (**27**) as a pale yellow oil (7.54 g, 98%) $\nu_{max.}$ 3 400br cm^{-1} (OH); δ_H (60 MHz) 1.3—2.2 (6 H, m), 2.3—3.0 (3 H, m), 3.5 (3 H, s), 3.6—4.2 (4 H, m), and 5.4 6.0 (2 H, m).

Cyclisation of (Z)-4-(2-*Methoxytetrahydropyran*-2-*yl*)*but*-3-*en*-1-*ol* (**27**).—The monoene (**27**) (7.2 g, 38.7 mmol) was dissolved in dichloromethane (200 ml) and camphorsulphonic acid (0.2 g) added. The reaction was stirred for 10 min and then washed with saturated aqueous sodium hydrogen carbonate. The organic layer was dried ($NaHCO_3/Na_2SO_4$), filtered, and evaporated. Fractional distillation of the crude product afforded two compounds as clear colourless liquids. 1,7-Dioxaspiro[5.5]undec-4-ene (**25**) (4.06 g, 68%), b.p. 85—88 °C at 16 mmHg; δ_H (60 MHz) 1.3—1.8 (6 H, m), 1.8—2.3 (2 H, m), 3.5—4.0 (4 H, m), 5.6 (1 H, dm, *J* 11 Hz), and 5.9 (1 H, dm); *m/z* 154 (M^+, 3%), 126(21), 124(21), 109(34), 99(92), and 96(100) and 4-methoxy-1,7-dioxaspiro[5.5]undecane (**19**) (1.8 g, 25%), b.p. 110—115 °C at 16 mmHg; δ_H (60 MHz) 1.4—2.0 (10 H, m), 3.1 (3 H, s), and 3.4—4.0 (5 H, m); *m/z* 155 (78%, *M* − MeO), 141(21), 131(38), 128(22), 113(38), 101(53), 99(41), 98(100), 86(37), 71(97), 58(60), 55(79), 43(72), and 41(79).

Cyclisation of (Z)-1-(2-*Hydroxytetrahydropyran*-2-*yl*)-4-*tetrahydropyran*-2-*yloxybut*-1-*ene*—(**24**) The monoene (**24**) (1 g, 3.9 mmol) was dissolved in tetrahydrofuran (25 ml) and concentrated hydrochloric acid was added dropwise to the solution which was then stirred for 18 h. Work-up and distillation afforded 1,7-dioxaspiro[5.5]undec-4-ene (**25**) as a clear colourless liquid (0.47 g 78%), b.p. 80—110 °C at 16 mmHg (Kugelrohr). Spectral details of the major component (**25**) were as before, but g.c.m.s. indicated the presence of *ca.* 10% 1,7-dioxaspiro[5.5]undecane, due to over-reduction of the alkyne.

Hydration of 1,7-*Dioxaspiro*[5.5]*undec*-4-*ene* (**25**).—The spiroacetal (**25**) (4 g, 26 mmol) was dissolved in tetrahydrofuran (80 ml) and water (20 ml) and concentrated hydrochloric acid (4 ml) were added with stirring to the solution. After 18 h, neutralisation and extraction with ether afforded the crude 4-hydroxyspiroacetal (**18**). The diastereoisomers (**18a**) and (**18b**) were separated by flash chromatography (silica/diethyl ether). (4*S*,6*S*)- and (4*R*,6*R*)-1,7-dioxaspiro[5.5]undecan-4-ol (**18a**) (2.6 g, 60%), white crystals, m.p. 50 °C (from 40—60 °C light petroleum) (lit.,[30] 48—49 °C) (Found: C, 62.65; H, 9.35. $C_9H_{16}O_3$ requires C, 62.77, H, 9.36%); $\nu_{max.}$ 3 400br cm^{-1} (OH); δ_H (360 MHz) 1.29 (1 H, dd, J_{bd} 12, J_{ad} 11 Hz, H_d), 1.43—1.60 (5 H, m), 1.65 (1 H, dm, *J* 12 Hz), 1.75—1.91 (2 H, m), 1.99 (1 H, ddd, J_{ab} 5.5, J_{bc} 2, J_{bd} 12 Hz, H_b), 2.9 (1 H, br s), 3.51—3.74 (4 H, m), and 4.04 (1 H, dddd, $J_{ae} = J_{ad}$ 11, $J_{ab} = J_{ac}$ 5.5 Hz, H_a); δ_C (90 MHz) 18.53(t), 25.13(t), 35.07(t), 35.54(t), 45.26(t), 58.85(t), 60.39(t), 64.16(d), and 97.36(s); *m/z* 172 (M^+, 4%), 155(12), 127(33), 117(100), 114(54), 101(86), 98(77), 83(17), 71(32), and 55(52); (4*S*,6*R*)- and (4*R*,6*S*)-1,7-dioxaspiro[5.5]undecan-4-ol (**18b**) (0.21 g, 5%), b.p. 60—70 °C at 0.08 mmHg (Kugelrohr) had $\nu_{max.}$ 3 520br cm^{-1} (OH); δ_H (360 MHz) 1.45—1.75 (7 H, m), 1.8—1.94 (3 H, m), 3.61—3.77 (3 H, m), and 3.96—4.1 (3 H, m); δ_C (90 MHz) 18.22(t), 25.09(t), 32.35(t), 35.55(t), 40.90(t), 55.35(t), 61.0(t), 64.95(d), and 97.44(s); *m/z* 172 (M^+, 6%), 155(11), 127(24), 117(100), 114(37), 101(78), 98(38), 83(10), 71(15) and 55(15).

Cyclisation and Hydration of (Z)-1-(2-*Hydroxytetrahydropyran*-2-*yl*)-4-*tetrahydropyran*-2-*yloxybut*-1-*ene* (**24**).—The monoene (**24**) (10.2 g, 40 mmol) was dissolved in tetrahydrofuran (100 ml) and water (20 ml) was added to it; concentrated hydrochloric acid (4 ml) was then added dropwise to the stirred solution. After 4 h, work-up and purification as described previously gave (4*S*,6*S*)- and (4*R*,6*R*)-1,7-dioxaspiro[5.5]undecan-4-ol (**18a**) (3.63 g. 53%) and (4*R*, 6*S*)- and (4*S*, 6*R*)-1,7-dioxaspiro[5.5]undecan-4-ol (**18b**) (0.22 g, 3%); spectral details as before.

Esterification of 1,7-*Dioxaspiro*[5.5]*undecan*-4-*ols* (**18a**) *and* (**18b**).—The hydroxyspiroacetals (**18a**) and (**18b**) were treated with 3,5-dinitrobenzoyl chloride in pyridine to afford the corresponding 3,5-dinitrobenzoate esters (**21a**) and (**21b**) in good yield. (4*S*,6*S*)- and (4*R*,6*R*)-4-(3,5 Dinitrobenzoyloxy)-1,7-dioxaspiro[5.5]undecane, (**21a**), m.p. 152—153 °C (from diethyl ether–pentane) (Found: C, 52.3; H, 4.95; N, 7.55. Calc. for $C_{16}H_{18}N_2O_8$: C, 52.46; H, 4.95; N, 7.65); δ_H (360 MHz) 1.50—1.92 (8 H, m), 2.10—2.24 (2 H, m), 3.69 (2 H, m), 3.88 (2 H, m) 5.53 (1 H, dddd, *J* 5.5, *J'* 11.5 Hz, H_a), 9.11 (2 H, s), 9.20 (1 H, s); *m/z* 366 (M^+, 14%), 336(7), 267(9), 266(10), 195(20), 155(97), 109(17), 101(37), 99(100), 98(72), 96(59), 75(29), and 41(70). (4*R*,6*S*)- and 4*S*,6*R*)-4-(3,5-Dinitrobenzoyloxy)-1,7-dioxaspiro-[5.5]undecane, (**21b**), m.p. 127—128 °C (from diethyl ether–pentane) (Found: C, 52.5; H, 4.95; N, 7.5. Calc. for $C_{16}H_{18}N_2O_8$: C, 52.46; H, 4.95; N, 7.65); δ_H 1.45—1.70 (5 H, m), 1.77 (1 H, m), 1.83—1.92 (2 H, m), 1.97—2.09 (2 H, m), 3.70 (1 H, m), 3.76—3.9 (2 H, m), 4.15 (1 H, m, $J = J' = 12$, $J'' = 3$ Hz, H_b), 5.46 (1 H, m, H_a), and 9.20 (3 H, s); *m/z* 366 (M^+, 4%), 336(2), 267(6), 266(6), 195(22), 155(76), 109(13), 101(39), 99(100), 98(36), 96(51), 75(35), 55(80), and 41(55).

Hydroboration of 1,7-*Dioxaspiro*[5.5]*undec*-2-*ene* (**28**).—The spiroacetal (**28**)[20] (1.0 g, 6.49 mmol) was dissolved in dry tetrahydrofuran (60 ml) at 0 °C, under dry nitrogen. Borane–tetrahydrofuran complex (BH_3.THF, 1 M solution in THF; 10 ml, 10 mmol) was added dropwise to the reaction mixture which was then stirred at 0 °C for 1 h, and at room temperature for 96 h. The reaction was worked up at 0 °C by the addition of sodium hydroxide (3 M; 20 ml, 60 mmol) followed by hydrogen peroxide (30% w/v; 3.4 ml, 30 mmol), and stirred at room temperature for 4 h. Extraction and repeated flash column chromatography (silica-diethyl ether) afforded the 3-hydroxyspiroacetals (**17a**) and (**17b**) as colourless viscous oils in a ratio of *ca.* 1:3. (3*S*,6*S*)- and (3*R*,6*R*)-1,7-Dioxaspiro[5.5]undecan-3-ol (**17a**) (0.22 g, 20%) and $\nu_{max.}$ 3 420br cm^{-1} (OH); δ_H (360 MHz) 1.44—1.65 (6 H, m), 1.70—1.86 (4 H, m), 3.25—3.39 (2 H, m), and 3.56—3.70 (4 H, m); δ_C (90 MHz) 18.77(t), 25.21(t), 28.12(t), 34.69(t), 34.89(t), 60.54(t), 64.68(t), 66.03(d), and 94.48(s); *m/z* 172 (M^+, 3%), 142(9), 117(11), 114(10), 101(28), 99(16), 98(100), 83 (19), 55(57), and 43(74). (3*S*,6*R*)-and (3*R*,6*S*)-1,7-Dioxaspiro[5.5]-undecan-3-ol (**17b**) (0.63 g, 56%) had $\nu_{max.}$ 3 430br cm^{-1} (OH); δ_H (360 MHz) 1.35—1.72 (7 H, m), 1.76—1.91 (2 H, m), 2.0 (1 H, m), and 3.55—3.80 (6 H, m); δ_C (90 MHz) 18.55(t), 25.33(t), 25.38(t), 29.92(t), 35.29(t), 60.82(t), 64.25(d), 64.72(t), and 95.25(s); *m/z* 172 (M^+, 4%), 142(10), 117(16), 114(13), 101(34), 99(16), 98(100), 83(23), 55(66), and 43(96).

Esterification of 1,7-*Dioxaspiro*[5.5]*undecan*-3-*ols* (**17a**) *and* (**17b**).—The hydroxyspiroacetals (**17a**) and (**17b**) were treated with 3,5-dinitrobenzoyl chloride in pyridine to afford the corresponding 3,5-dinitrobenzoate esters (**22a**) and (**22b**) in good yield. (3*S*,6*S*)- and (3*R*,6*R*)-3-(3,5-Dinitrobenzoyloxy)-1,7-dioxaspiro[5.5]undecane, (**22a**) m.p. 154—155 °C (from pentane–toluene) (lit.,[29] 155 °C) (Found: C, 52.7; H, 5.1; N, 7.9. Calc. for $C_{16}H_{18}N_2O_8$: C, 52.5; H, 5.0; N, 7.7%); δ_H (360 MHz) 1.50—1.92 (8 H, m), 2.0—2.19 (2 H, m), 3.65—3.9 (4 H, m), 5.15 (1 H, dddd, *J* 11.8, *J'* 5.4 Hz), 9.15 (2 H, s), and 9.23 (1 H, s); *m/z* 336 (0.4%, *M* − NO), 311(1), 266(7), 195(30), 98(100), 75(35), 55(60), and 43(63). (3*S*,6*R*)- and (3*R*,6*S*)-3-(3,5-Dinitrobenzoyloxy)-1,7-dioxaspiro[5.5]undecane, (**22b**), m.p. 171—172 °C (from pentane–toluene) (lit.,[29] 173 °C) (Found: C, 52.4; H, 5.0; N, 7.7. Calc. for $C_{16}H_{18}N_2O_8$: C, 52.5; H, 5.0; N, 7.7%); δ_H (360 MHz) 1.49—1.99 (9 H, m), 2.31 (1 H, m), 3.69 (2 H, m), 3.94 (2 H,

m), 5.18 (1 H, m), 9.20 (2 H, s), and 9.26 (1 H, s); *m/z* 336 (0.1%, *M* − NO), 311(1), 266(3), 195(12), 98(68), 75(39), 55(82), and 41(100).

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