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Structure Based Interference with Insect Behaviour - Cyclopropene Analogues of Pheromones Containing Z-Alkenes

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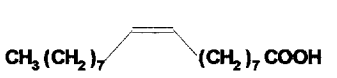
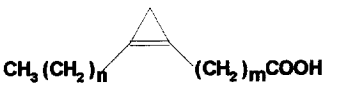
Abstract: Analogues of the pheromones of three insect species (*Musca domestica L., Plutella xylostella L. and Ephestia elutella Hbn.*) in which a Z-alkene has been replaced by a 1,2-disubstituted cyclopropene have been synthesised. The analogues interfere with normal mating behaviour for each species.,Copyright © 1996 Elsevier Science Ltd

It is well established that the cyclopropene fatty acid (CPFA) sterculic acid (2) is a potent inhibitor of the enzyme Δ^9-desaturase which desaturates stearic acid to oleic acid (1), introducing the Z-alkene in the latter;[1] although the mechanism of inhibition is not fully understood, the remarkable similarity in overall structure and stereochemistry of (1) and (2), coupled to the high strain and reactivity of the cyclopropene ring in the latter may be critical. Moreover, (3) is known to inhibit Δ^{12}-desaturase,[2] which generates the 12,13-double bond of linoleic acid from oleic acid, (4) to inhibit a Δ^5-desaturase in bacteria[3] and (5) to inhibit a Δ^{11}-desaturase in insects;[4] in each case, the inhibitor is closely related to the product of desaturation, except that a Z-alkene in the latter has been replaced by a cyclopropene.

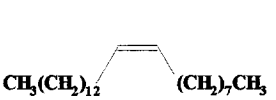


(1)

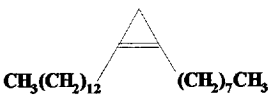


(2) n = 7, m = 7 (3) n = 4, m = 10
(4) n = 17, m = 3 (5) n = 2, m = 10

The cyclopropene ring is very close in shape to a Z-alkene, particularly in the direction of the orbitals of the π-bond; however, because of the high ring strain, it is much more reactive than the alkene. The pheromones of insects are often long-chain aldehydes, acetates and alcohols containing Z-alkenes. For example, two days after emergence from the pupal phase, female houseflies start producing a sex pheromone containing (Z)-9-tricosene (muscalure) (6) which acts as a short range attractant to male flies and increases the numbers of mating attempts made by males at females or inert targets. [5] We hypothesised that an analogue containing a 1,2-disubstituted cyclopropene at the same position as the alkene in a pheromone might reach its receptor site and cause the insect to respond, but that, once there, it might react so as to relieve its ring strain and block the receptor, thus disrupting insect behaviour.



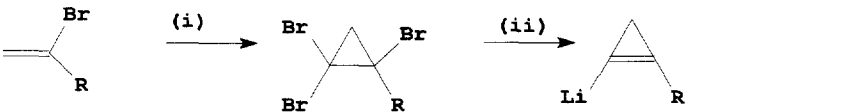
(6)



(7)

We now report the synthesis of such cyclopropene analogues, eg. (7) for Z-tricosene, for three species

of insect. In each case, the cyclopropene ring was obtained from a 2-bromoalk-1-ene by addition of dibromocarbene under phase transfer conditions to produce a 1,1,2-tribromocyclopropane, followed by reaction with 2.1 mol.equiv. of butyllithium to generate a 1-lithiocyclopropene (in the case of (**15**), 3.1 mol.equiv.):[6]



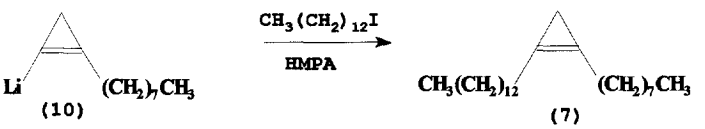
(8) R = $(CH_2)_7CH_3$ (9) R = $(CH_2)_7CH_3$ (10) R = $(CH_2)_7CH_3$

(11) R = $(CH_2)_3CH_3$ (12) R = $(CH_2)_3CH_3$ (13) R = $(CH_2)_3CH_3$

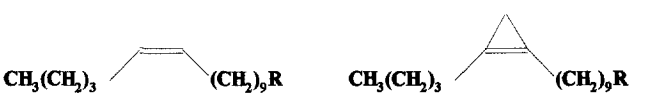
(14) R = $(CH_2)_8OCMe_2OMe$ (15) R = $(CH_2)_8OH$ (16) R = $(CH_2)_8OLi$

(i) $CHBr_3$, aq.NaOH, cetrimide (ii) 2.1 mol.equiv. BuLi (3.1 for (15))

This was then in each case coupled to an appropriate iodoalkane in the presence of HMPA to give the pheromone analogue. Thus the cyclopropene analogue (**7**) was prepared from the lithiocyclopropene (**10**) by alkylation with iodotridecane in the presence of HMPA:[7]

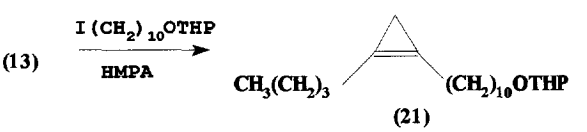


Female diamondback moths produce a pheromone blend which contains (**17**) and (**18**) which attracts males and elicits courtship behaviour.[8] Once again, the cyclopropene analogues (**19**) and (**20**) were synthesised as in Scheme 1.

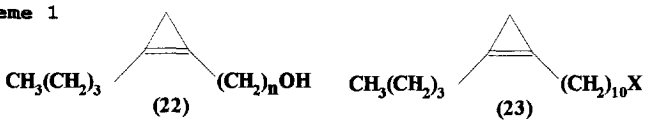


(**17**) R = CHO, (**18**) R = CH_2OAc (**19**) R = CHO, (**20**) R = CH_2OAc

The acetate (**20**) was prepared by coupling of 1-lithio-2-butylcyclopropene (**13**) to 10-iodo-1-tetrahydropyranyloxydecane to give (**21**), followed by deprotection with dilute acid to give the alcohol (**22**, n = 10) and acetylation of this using acetyl chloride and triethylamine.

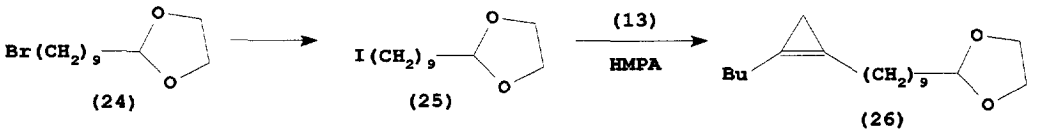


Scheme 1



The homologues (**22**, n = 4,6,8) were prepared in the same way. The aldehyde (**19**) could be prepared by coupling of the 1-lithio-2-butylcyclopropene (**13**) to 1,10-diiododecane to give (**23**, X = I). The product contained a small amount of the bromide (**23**, X = Br) presumably derived by halogen exchange in the coupling reaction. Reaction of the mixture with trimethylamine N-oxide led to (**19**), albeit only in low yield (25 %). In an alternative route, 10-bromodecan-1-ol was converted into the aldehyde by oxidation with PCC and then

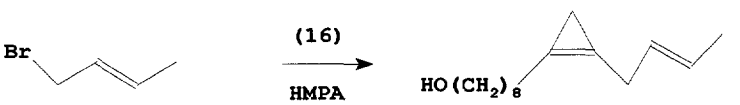
protected as the acetal (**24**) with ethan-1,2-diol and acid. The resulting bromide was converted into the corresponding iodide (**25**) using sodium iodide in acetone and this was coupled with 1-lithio-2-butyl-cyclopropene (**13**). The resulting acetal (**26**) was deprotected by reaction with dilute acid to give aldehyde (**19**).



Female warehouse moths *Ephestia elutella Hbn.* also produce a pheromone which, as in diamondback moths, attracts males and elicits courtship behaviour; in this case the main components are the alcohol (**27**) and acetate (**28**).[9] Once again, we have prepared the corresponding cylopropene analogues, (**29**) and (**30**). In this case, dec-9-yn-1-ol was first prepared by coupling of propargyl alcohol to 1-bromoheptane, using lithium amide, to produce dec-2-yn-1-ol, followed by a zipper reaction to move the alkyne to the alkyl terminus. Dec-9-yn-1-ol was treated with hydrogen bromide in the presence of tetraethylammonium bromide to give 9-bromo-dec-9-en-1-ol, which was protected with 2-methoxypropene to give (**14**) and then cyclopropanated by reaction with bromoform and base under phase transfer conditions to give (**15**) after deprotection.

(**27**) R = H, (**28**) R = Ac (**29**) R = H, (**30**) R = Ac

Reaction of this tribromide with 3.1 mol.equiv. of butyllithium in ether to give (**16**) followed by treatment with E-1-bromobut-2-ene in the presence of HMPA gave the desired analogue (**29**) which could be acetylated to give (**30**).



(**29**)

We have shown that each of the specific cyclopropene analogues above do indeed interfere with the mating behaviour of housefly (*Musca domestica L.*), the diamond-back moth (*Plutella xylostella L.*) or the warehouse moth (*Ephestia elutella Hbn.*) respectively and have obtained evidence that the inhibition is long-term. The effects occur with quantities of material which are similar to those at which the pheromones themselves elicit behaviour. In the case of the two moths, the cyclopropene analogue in each case also elicits a response in electroantennogram studies, albeit at a somewhat lower level than the pheromone. The full results of the biological assays will be presented elsewhere.

We thank Norsk-Hydro for supporting this work.

Experimental Section

Reagents were obtained from commercial suppliers and were used without further purification unless stated. Dichloromethane was distilled over calcium hydride. Diethyl ether and tetrahydrofuran were distilled over sodium wire. Petrol was either of boiling point 40 - 60 °C or 60 - 80 °C and was distilled. Reactions requiring anhydrous conditions were performed using oven dried glassware (250 °C) that was cooled under

either dry nitrogen or argon and the experiments were conducted under a positive atmosphere of one of these gases. Organic solutions were dried over anhydrous magnesium sulphate, and, unless stated, were evaporated at 14 mmHg. Yields quoted are for the purified compounds unless stated. New compounds were homogeneous by tlc or by glc. Glc was conducted using a Perkin-Elmer Model F17 F.I.D. on a capillary column (30 m x 0.32 mm id Phase, DB5 split ratio of 50:1) using nitrogen as carrier gas. Tlc was performed using Aldrich silica gel 60 plates (F254). Compounds were visualised under an ultraviolet source or by exposure to iodine vapour. Column chromatography was conducted with Merck 7736 silica gel under medium pressure. Melting points are uncorrected. Infrared spectra were obtained as liquid films on a Perkin-Elmer 1600 FTIR spectrometer. Low resolution mass spectra were obtained on a Finnigan Mat 1020 spectrometer. Mass measurements refer to ^{79}Br isotope unless stated and were obtained from the Swansea Mass Spectrometry Service. Microanalyses were performed with a Carlo-Erba Model 1106 CHN analyser. Nmr spectra were recorded on a Bruker AC250 at 250 MHz for ^{1}H and 62.5 MHz for ^{13}C and in the latter case were either broad-band or gated decoupled.

2-Bromoalk-1-enes

(i) Dry hydrogen bromide was bubbled into an ice-cold stirred solution of tetraethylammonium bromide (30 g, 128 mmole) in dichloromethane (130 ml) until one equivalent had been absorbed by weight. The resulting yellow solution was warmed to room temperature and dec-1-yne (16 g, 115 mmole) was added. After 2 h at room temperature, the mixture was refluxed for a further 2 h. The cooled mixture was poured into ether (200 ml) and the precipitated salts filtered off on a sinter. The filter cake was washed with ether. After evaporating the combined ether fractions, the residual oil was distilled to give 2-bromodec-1-ene **(8)**[10] (23.4 g, 92 %) as a colourless oil (b.p. 57 - 59 °C at 0.5 - 0.6 mmHg) (Found M^+ 218.0625. $C_{10}H_{19}Br$ requires: 218.0670) which showed δ_H 5.55 (1 H, narrow q, J 1.2 Hz), 5.37 (1 H, narrow d , J 1.5 Hz), 2.4 (2 H, t, J 7 Hz), 1.5 - 1.7 (2 H, br, m), 1.2 - 1.4 (10 H, br, s), 0.9 (3 H, t, J 7 Hz); δ_c: 135, 116, 41.4, 31.9, 29.3, 29.22, 28.43, 27.9, 22.66, 14.06; ν_{max}: 1631, 883 cm^{-1}.

(ii) The above procedure was repeated using hex-1-yne and the solvent was removed carefully to give 2-bromo-hex-1-ene **(11)**[10] (85 %) (b.p. 25 °C at 18 mm Hg) which showed δ_H: 5.55 (1 H, br, s), 5.4 (1 H, br, s), 2.42 (2 H, br, t, J 7 Hz), 1.53 (2 H, pent, J 6.7 Hz), 1.33 (2 H, sext, J 6.89 Hz), 0.92 (3 H, t, J 7 Hz); δ_c: 134.8, 116.1, 41.1, 30.0, 21.5, 13.7; ν_{max} : 1630, 1465, 883 cm^{-1}.

(iii) The above procedure was repeated using pent-1-yne to give 2-bromopent-1-ene (78 %),[11] which showed δ_H: 5.5 (1 H, narrow doublet, J 1.2 Hz), 5.39 (1 H, narrow doublet, J 1.2 Hz), 2.4 (2 H, t, J 7.34 Hz), 1.6 (2 H, sext., J 7.37 Hz), 0.92 (3 H, t, J 7.3 Hz); δ_c : 134.6, 116.41, 43.4, 21.1, 12.86; ν_{max} : 1631, 1465 cm^{-1}.

(iv) The above procedure was repeated using but-1-yne and the solvent was removed by fractional distillation under atmospheric pressure to give 2-bromo-but-1-ene (62 %)[12,13] which showed δ_H: 5.6 (1 H, br.s), 5.35 (1 H, br.s), 2.4 (2 H, t, J 6.7 Hz), 1.1 (3 H, t, J 6.7 Hz); δ_C: 136.0, 114.9, 34.7, 12.9; ν_{max} : 1623, 1460 cm^{-1}.

10-Bromodec-9-en-1-ol

(a) Liquid ammonia (1 l) was decanted into a 2 litre 2-necked flask under a liquid nitrogen - methylated spirit

condenser protected by a soda guard tube. Lithium wire (0.2 g) was added to obtain a dark blue colour. Ferric nitrate (0.2 g) was added and the solution was stirred mechanically for 5 m. Lithium wire (6.26 g, 0.9 mole) was added over 40 m. Stirring was continued for a further 30 m, then propargyl alcohol (23 g, 0.41 mole) in ether (20 ml) was added dropwise with stirring over 20 m. After a further 30 m, 1-bromoheptane (66.1 g, 0.37 mole) in ether (20 ml) was added dropwise. Stirring was continued for 3 h and then the ammonia was allowed to evaporate overnight leaving a black gum. The product was carefully acidified to pH 1 with dil. sulphuric acid (10 %, 300 ml) yielding a pale yellow solution which was extracted with ether (3 x 300 ml). The ether extracts were washed with sat.aq. sodium bicarbonate (200 ml), dried, and evaporated to yield a yellow oil. Chromatography on silica eluting with 3:2 petrol and ether gave dec-2-yn-1-ol as a colourless liquid (48.1 g, 76 %)[14] which showed δ_H: 4.25 (2 H, t, J 2.18 Hz), 2.2 (2 H, tt, J 2.14, 6.9 Hz), 1.7 (1 H, br, s), 1.6 - 1.25 (10 H, m), 0.85 (3 H, t, J 7.0 Hz); δ_c: 86.6, 78.2, 51.3, 31.65, 28.8, 28.7, 28.5, 22.5, 18.7, 14.0; ν_{max} 3330, 2225, 1460, 1015 cm^{-1}.

(b) Lithium wire (5.4 g, 0.779 mole) was added in portions to dry 1,3-diaminopropane (460 ml) under an argon atmosphere. Stirring was continued for 30 m followed by heating at 70 °C until the blue colour was discharged (about 90 m). The resulting suspension was cooled to 25 °C and potassium t-butoxide (58.3 g, 0.52 mol) was added, followed by stirring at room temperature for a further 20 m. Dec-2-yn-1-ol (20 g, 0.13 mol) was added dropwise over 10 min. After stirring for 45 m the mixture was poured into ice (1 kg), extracted with CH_2Cl_2 (4 x 200 ml) and the combined organic extracts were washed with water (2 x 200 ml), dried and the solvent was evaporated to give dec-9-yn-1-ol (17.5 g, 83.5%)[15] which showed δ_H: 3.58 (2 H, t, J 6.5 Hz), 2.13 (2 H, dt, J 2.6, 6.9 Hz), 1.9 (1 H, t, J 2.6 Hz), 1.6 - 1.2 (12 H, m); δ_c: 84.5, 70.6, 62.6, 32.5, 29.0, 28.8, 28.4, 28.2, 25.45, 18.1; ν_{max}: 3331 cm^{-1}.

(c) Dry hydrogen bromide was bubbled into an ice-cold stirred solution of tetraethylammonium bromide (28.52 g, 0.135 mole) in dichloromethane (100 ml) until one equivalent of the gas had been absorbed by weight. The resulting solution was warmed to room temperature and dec-9-yn-1-ol (19 g, 0.1233 mole) was added. The mixture was stirred for 2 h, refluxed for a further 2 h, cooled, and then poured into ether (200 ml). The precipitated salts were filtered off through a short silica pad, washed with ether (100 ml) and the combined ether layers washed with sat.aq. sodium bicarbonate, dried, and evaporated. The residue was chromatographed on silica eluting with 5:2 petrol and ether to give a first fraction, 2,10-dibromodec-1-ene (4.0 g, 11 %) which showed δ_H: 5.5 (1 H, q, J 1.26 Hz), 5.38 (1 H, d, J 1.5 Hz), 3.4 (2 H, t, J 6.8 Hz), 2.41 (2 H, dt, J 0.93, 7.5 Hz), 1.75 (2 H, pent, J 6.7 Hz), 1.55 (2 H, br, m), 1.40 (2 H, br, m), 1.3 (8 H, br, s); δ_c: 134.7, 116.16, 41.27, 33.78, 32.7, 28.32, 28.16, 28.02, 27.8, 27.7. The second fraction was 10-bromodec-9-en-1-ol (22 g, 76 %) which showed δ_H 5.54 (1 H, q, J 1.3 Hz), 5.37 (1 H, d, J 1.6 Hz), 3.63 (2 H, t, J 6.5 Hz), 2.4 (2 H, dt, J 0.9, 7.8 Hz), 1.6 - 1.5 (4 H, br, m), 1.4 (1 H, br, s), 1.35 - 1.25 (6 H, m); δ_c: 134.7, 116, 62.8, 41.2, 32.5, 29.1, 28.1, 27.6, 25.5, 20.1; ν_{max}: 3345, 1630, 1461, 883 cm^{-1}.

1,1,2-Tribromo-2-octylcyclopropane (9)

Freshly prepared aq. sodium hydroxide (50 %, 36 g in 36 ml of water) was added to a rapidly stirred solution of

2-bromodec-1-ene (19.65 g, 0.09 mole), bromoform (46.1 g, 0.18 mole) and cetrimide (3.0 g) at such a rate that the internal reaction temperature remained below 70 °C, cooling in an ice bath when necessary. The mixture was stirred rapidly for 14 h at ambient temperature. When g.l.c. showed no starting material was left, the product was diluted with dichloromethane (500 ml) and brine (200 ml). The aqueous phase was extracted with dichloromethane (3 x 300 ml). The combined organic layers were dried and evaporated to yield a viscous black oil. The excess of bromoform was distilled off at 0.2 mm Hg and the residue was diluted with ether (200 ml). Filtration and evaporation of the ether gave a brown oil which was distilled to give *1,1,2-tribromo-2-octylcyclopropane* (**9**) (27.6 g, 78 %) (b.p. 110 °C and 0.05 mm Hg) (Found: C, 34.19; H, 4.88. $C_{11}H_{19}Br_3$ requires C: 34.03; H, 4.94 %) which showed δ_H 1.96 - 2.08 (2 H, m), 1.94 (1 H, d J 9.2 Hz), 1.82 (1 H, d, J 9.2 Hz), 1.7 (2 H, m), 1.2 - 1.4 (10 H, m), 0.89 (3 H, t, J 6.7 Hz); δ_c : 45.7, 41.6, 37.9, 33.0, 31.7, 29.5, 29.1, 28.8, 27.5, 22.5, 14.0; ν_{max} : 2929, 2858, 1464, 691 cm^{-1}.

1,1,2-Tribromo-2-butylcyclopropane (12)

The above procedure was repeated using 2-bromohex-1-ene to give *1,1,2-tribromo-2-butylcyclopropane* (**12**) (82 %) (bp 53 - 55 °C at 0.2 mmHg) (Found: C, 25.15; H, 3.2. $C_7H_{11}Br_3$ requires C, 25.11; H, 3.31) which showed δ_H: 1.5 - 2.1 (6 H, m, including two doublets at δ 1.94 and 1.9 with J 9.2 Hz), 1.35 (2 H, sext., J 7.2 Hz), 0.9 (3 H, t, J 7.2 Hz); δ_c : 45.7, 41.3, 37.9, 33.0, 29.7, 22.0, 13.93; ν_{max} : 2954, 2859, 1465, 691 cm^{-1}.

1,1,2-Tribromo-2-(10-hydroxyoctyl)cyclopropane (15)

(a) 2-Methoxypropene (11.35 g, 15.1 ml, 0.157 mole) and pyridinium toluene-4-sulphonate (0.02 mole eq., 0.4 g) were added to a stirred solution of 10-bromodec-9-en-1-ol (18.5 g, 0.078 mole) in dry ether (80 ml) at 0 °C. An exothermic reaction was observed. After stirring at room temperature for 15 m, t.l.c. showed no starting material was left, and the mixture was quenched with sat.aq. sodium bicarbonate (20 ml); the aqueous layer was extracted with ether (2 x 50 ml), the combined organic layers were dried and evaporated to give 2-bromo-10-((1-methoxy-1-methyl)ethoxy)dec-1-ene (23.6 g, 97 %) which showed δ_H: 5.6 (1 H, br.s), 5.4 (1 H, br.s), 3.42 (2 H, t, J 6.3 Hz), 3.2 (3 H, s), 2.5 (2 H, t, J 7.0 Hz), 1.6 (4 H, m), 1.45 (8 H, br.s), 1.38 (6 H, s).

(b) Bromoform (39 g, 0.154 mole) was stirred with triethylamine (4 drops), in dichloromethane (50 ml) for 10 m when cetrimide (2.5 g) was added followed by 2-bromo-10((1-methoxy-1-methyl)ethoxy)dec-1-ene (23.6 g, 0.077 mole). Aq. sodium hydroxide (50 %, 30.9 g, in water 31 ml) was cooled to ~30 °C and added slowly to the rapidly stirred mixture at 5 °C. After 48 h at room temperature the ^1H n.m.r. spectrum showed no starting material. The mixture was diluted with dichloromethane (500 ml) and brine (200 ml). The aqueous layer was washed with dichloromethane (3 x 300 ml) and the combined organic layers were dried, and evaporated to give thick brown oil. The excess of bromoform was distilled off at 0.2 mm Hg and 30 °C and the residue was diluted with ether (200 ml). The precipitate was filtered off and the solvent evaporated to give yellow oil, which was stirred with methanol (50 ml), water (15 ml) and p-toluene sulphonic acid (1 g) for 1 h. The product was extracted with dichloromethane (3 x 150 ml). The combined organic layers were washed with water (150 ml), dried and evaporated; chromatography on

silica eluting with 1:1 petrol and ether gave *1,1,2-tribromo-2-(10-hydroxyoctyl)cyclopropane* (**15**) (17.3 g, 55 %) (Found: C, 32.65, H: 5.06. $C_{11}H_{19}OBr_3$ requires: C, 32.46; H, 4.7) which showed δ_H: 3.64 (2 H, t, J 6.45 Hz), 1.9 - 2.15 (3 H, m, including a doublet at δ 1.95 with J 9.2 Hz), 1.82 (1 H, d, J 9.2 Hz), 1.7 (2 H, m), 1.55 (2 H, m), 1.45 (1 H, s), 1.35 (8 H, br, m); δ_c: 63.16, 46, 42, 38.25, 33.3, 32.9, 29.5, 29.4, 29.00, 27.00, 25.8; δ_{max} : 3340 cm^{-1}.

1-Iodotridecane

Iodine (12.66 g, 50 mmole) in dry dichloromethane (200 ml) was added dropwise with stirring to 1,2-bis(diphenylphosphino)ethane (10 g, 25 mmole) in dry dichloromethane (100 ml) at 0 °C under nitrogen. Tridecan-1-ol (8 g, 40 mmole) in dry dichloromethane (20 ml) was then added. The ice bath was removed and the mixture was stirred for 2 h at 25 °C. When t.l.c. showed no starting material, ether (250 ml) and then petrol (200 ml) were added; the precipitated salts were removed by filtration through a pad of silica and washed with 2:1 petrol and ether. The solvent was evaporated and the residue was purified by flash chromatography eluting with petrol to give 1-iodotridecane (10.78 g, 87 %)[16] as a colourless oil, which showed δ_H: 3.2 (2 H, t, J 7 Hz), 1.8 (2 H, pent., J 6.5 Hz), 1.25 (20 H, br, s), 0.9 (3 H, t, J 7 Hz); δ_C: 33.57, 31.9, 30.5, 29.6, 29.5, 29.4, 29.3, 28.5, 22.67, 14.1, 7.2.

13-(2-Octylcycloprop-1-enyl)tridecane (7)

Butyllithium (16 ml, 1.6 M) was added dropwise to a stirred solution of 1,1,2-tribromo-2-octylcyclopropane (3.91 g, 10 mmole) in dry diethyl ether (40 ml) at -78 °C, under nitrogen. The mixture was allowed to warm to 25 °C, stirred for 30 m and cooled to 0 °C when HMPA (3.8 ml, 3.2 g, 11 mmole) and then 1-iodotridecane (3.41 g, 11 mmole) were added dropwise. After stirring for 18 h at room temperature, water (70 ml) and ether (70 ml) were added. The aqueous layer was extracted with ether (2 x 70 ml). The combined ether layers were washed with water (3 x 70 ml), dried and evaporated. Chromatography eluting with petrol gave *13-(2-octylcycloprop-1-enyl)tridecane* (**7**) (2.0 g, 60 %) as a colourless oil (Found: M + H^+ 334.3596. $C_{24}H_{46}$ requires 334.3599), which showed δ_H: 2.38 (4 H, t, J 7.1 Hz), 1.54 (4 H, br, t, J 6.9 Hz), 1.27 (30 H, br.s), 0.89 (6 H, t, J 6.89 Hz), 0.78 (2 H, s); δ_c: 109.5, 32.1, 29.9, 29.6, 29.5, 27.6, 2.62., 25.9, 25.1, 22.9, 22.6, 14.2, 13.9, 7.5; ν_{max}: 2855, 1466, 1377, 1009, 721 cm^{-1}.

10-(2-Butylcycloprop-1-enyl)decan-1-yl acetate (20)

(i) Butyllithium (2.2 mole eq., 22 ml) was added dropwise with stirring to 1,1,2-tribromo-2-butylcyclopropane (**12**) (5 g, 0.015 mole) in ether (50 ml) at -78 °C, under nitrogen. The reaction was allowed to reach room temperature and stirred for 30 m and then cooled in an ice bath and HMPA (2.2 mole eq. 5.87 g) added dropwise followed by 1-iodo-10-tetrahydropyranyloxydecane[17] (0.95 mole eq., 5.2 g). After 14 h. at room temprature, the mixture was quenched by the dropwise addition of water (50 ml) followed by ether (100 ml). The aqueous layer was washed with ether (2 x 50 ml). The combined extracts were washed with water (2 x 75 ml), dried, and evaporated to give a yellow oil. Chromatography on silica eluting with petrol and ether (5:1) gave 10-(2-butylcycloprop-1-enyl)-1-

tetrahydropyranyloxydecane (**21**) (2.9 g, 58 %) as a colourless oil, which showed δ_H: 4.58 (1 H, br, s), 3.89 (1 H, m), 3.70 (1 H, m), 3.55 (1 H, m), 3.35 (1 H, m), 2.35 (4 H, m), 1.8 - 1.2 (26 H, m), 0.93 (3 H, t, J 7.3 Hz), 0.77 (2 H, s).

(ii) Pyridinium toluene-4-sulphonate (0.2 g, 0.8 mmole) was added to 10-(2-butylcycloprop-1-enyl)-1-tetrahydropyranyloxydecane (1.8 g, 5.35 mmole) in ethanol (20 ml), stirred at 55 °C (oil bath temperature) for 3 h when t.l.c. showed no starting material, and then diluted with ether (15 ml) and water (10 ml). The aqueous layer was washed with ether (2 x 15 ml). The combined ether layers were washed with sat.aq. sodium bicarbonate (10 ml) and water (5 ml), dried and evaporated to give a pale yellow oil; short column chromatography eluting with 2:1 petrol and ether afforded *10-(2-butylcycloprop-1-enyl)decan-1-ol* (**22**, n = 10) (0.99 g, 74 %) (Found: M + H^+ 253.2531. $C_{17}H_{32}O$ + H requires: 253.2531), which showed δ_H: 3.58 (2 H, t, J 6.5 Hz), 2.32 (4 H, br, t, J 6.9 Hz), 1.4 - 1.6 (6 H, m), 1.2 - 1.38 (14 H, br, s), 0.86 (3 H, t, J 7.3 Hz), 0.71 (2 H, s); δ_c: 109.3, 63.0, 32.8, 29.5, 29.4, 29.4, 29.4, 27.4, 26.0, 25.7, 22.45, 13.9, 7.35 (the remaining signals were obscured by the others); ν_{max} : 3450 cm^{-1}.

(iii) 10-(2-Butylcycloprop-1-enyl)-decan-1-ol (**22**, n = 10) (0.45 g, 1.78 mmole) in ether (10 ml) was treated with triethylamine (1.2 mol.equiv., 0.3 ml) followed by acetyl chloride (1.15 mol.equiv., 0.146 ml) at 0 °C. A dense white precipitate immediately formed. The reaction was allowed to reach room temperature and stirred for 15 m when t.l.c. showed no starting material; water (5 ml) was added followed by ether (20 ml). The aqueous layer was extracted with ether (2 x 10 ml). The combined organic layers were washed with water (10 ml), dried and evaporated to give *10-(2-butyl-1-cycloprop-1-enyl)decan-1-yl acetate* (**20**) (0.43 g, 82 %) (Found: C, 77.88; H, 11.41. $C_{19}H_{34}O_2$ requires: C, 77.49; H, 11.64) which showed δ_H: 4.05 (2 H, t, J 6.7 Hz), 2.4 (4 H, br, t, J 6.9 Hz), 2.05 (3 H, s), 1.4 - 16 (6 H, m), 1.25 - 1.4 (14 H, br, s), 0.92 (3 H, t, J 7.2 Hz), 0.77 (2 H, s); δ_c: 171.3, 109.3, 64.6, 29.6, 29.5, 29.4, 29.2, 28.6, 27.4, 26, 25.9, 25.7, 22.45, 21.0, 13.9, 7.4; ν_{max} : 1872, 1743, 1237, 1038 cm^{-1}.

8-(2-Butylcycloprop-1-enyl)octan-1-yl acetate

(i) The above experiment was repeated using 1-iodo-8-tetrahydropyranyloxyoctane[18] to give 8-(2-butylcycloprop-1-enyl)-1-tetrahydropyranyloxyoctane (48 %) which showed δ_H: 4.58 (1 H, br, s), 3.85 (1 H, m), 3.72 (1 H, m), 3.57 (1 H, m), 3.35 (1 H, m), 2.35 (4 H, m), 1.8 - 1.2 (22 H, m), 0.98 (3 H, t, J 7.2 Hz), 0.75 (2 H, s).

(ii) Deprotection of the alcohol as above gave 8-(2-butylcycloprop-1-enyl)octan-1-ol (**22**, n = 8) (0.82 g, 78%) which showed δ_H: 3.6 (2 H, t, J 6.6 Hz), 2.37 (4 H, br.t, J 6.8 Hz), 1.2 - 1.6 (13 H, m, including the hydroxyl group), 0.92 (3 H, t, J 7.3 Hz), 0.76 (2 H, s); δ_c: 109.2, 109.1, 62.9, 32.6, 29.4, 29.2, 29.2, 27.2, 25.85, 25.6, 22.3, 13.7, 7.2; ν_{max} : 3356, 1008 cm^{-1}.

(iii) Acetylation as above gave 8-(2-butylcycloprop-1-enyl)octan-1-yl acetate (92%) (Found: M + H^+ 267.2324. $C_{17}H_{30}O_2$ + H requires: 267.2324) which showed δ_H: 4.08 (2 H, t, J 6.7 Hz), 2.36 (4 H, br, t, J 6.6 Hz), 2.02 (3 H, s), 1.45 - 1.6 (6 H, m), 1.25 - 1.4 (10 H, m), 0.89 (3 H, t, J 7.3 Hz), 0.75 (2 H, s); δ_c: 171.2, 109.4, 109.3, 64.6, 29.6, 29.3, 29.2, 28.6, 27.4, 26.0, 25.9, 25.7, 22.5, 21.0, 13.9, 7.4; ν_{max}: 1740 cm^{-1}.

6-(2-Butylcycloprop-1-enyl)hexan-1-yl acetate

(i) The above experiment was repeated using 1-iodo-6-tetrahydropyranyloxyhexane[19] to give 6-(2-butylcyclo-prop-1-enyl)-1-tetrahydropyranyloxyhexane (50 %) (δ_H: 4.57 (1 H, t, J 2.8 Hz), 3.85 (1 H, m), 3.70 (1 H, dt, J 6.7, 9.5 Hz), 3.55 (1 H, m), 3.4 (1 H, dt, J 6.53, 9.5 Hz), 2.37 (4 H, t, J 7.06 Hz), 1.7 - 1.3 (18 H, m), 0.91 (3 H, t, J 7.26 Hz), 0.76 (2 H, s); δ_c: 109.4, 109.3, 67.65, 62.35, 30.8, 29.7, 29.55, 29.2, 27.3, 26.1, 26.0, 25.7, 25.5, 22.5, 19.7, 13.9, 7.4).

(ii) Deprotection of the alcohol as above gave *6-(2-butylcycloprop-1-enyl)hexan-1-ol* (**22**, n = 6) (82 %) (Found: C, 79.4; H, 12.3. $C_{13}H_{24}O$ requires: C, 79.53, H, 11.95) which showed δ_H: 3.6 (2 H, t, J 6.5 Hz), 2.34 (4 H, br, t, J 7 Hz), 1.3 - 1.6 (13 H, m, including the hydroxyl group), 0.87 (3 H, t, J 7.3 Hz), 0.73 (2 H, s); δ_c: 109.5, 109.2, 63.9, 32.76, 29.5, 29.2, 27.35, 25.95, 25.74, 25.56, 22.5, 13.9, 7.4; ν_{max}: 3363, 1850 cm^{-1}.

(iii) Acetylation as above gave *6-(2-butylcyclprop-1-enyl)hexan-1-yl acetate* (77 %) (Found: C, 75.87; H, 10.62. $C_{15}H_{26}O_2$ requires: C, 75.58; H, 11.00) which showed δ_H: 4.01 (2 H, t, J 6.7 Hz), 2.34 (4 H, t, J 7 Hz), 2.00 (3 H, s), 1.3 - 1.6 (12 H, m), 0.87 (3 H, t, J 7.4 Hz), 0.73 (2 H, s); δ_c: 171.2, 109.6, 109.2, 64.6, 29.55, 29.0, 28.6, 27.3, 25.9, 25.7, 22.5, 21, 13.9, 7.4; ν_{max} : 1743, 1238 cm^{-1}.

4-(2-Butylcycloprop-1-enyl)butan-1-yl acetate (22, n = 4)

(i) The above experiment was repeated using 1-iodo-4-tetrahydropyranyloxybutane[20] to give 4-(2-butylcyclo-prop-1-enyl)-1-tetrahydropyranyloxybutane (53 %) (δ_H: 4.5 (1 H, t, J 2.9 Hz), 3.87 (1 H, m), 3.74 (1 H, m), 3.52 (1 H, m), 3.42 (1 H, m), 2.4 (4 H, m), 1.45 - 1.9 (12 H, m), 1.3 (2 H, sext., J 6.9 Hz), 0.9 (3 H, t, J 7.2 Hz), 0.7 (2 H, s); δ_c : 109.7, 109.05, 98.8, 67.3, 62.5, 30.75, 29.5, 29.45, 25.8, 25.7, 25.5, 24.15, 22.45, 17.6, 13.8, 7.4).

(ii) Deprotection of the alcohol as above affored *4-(2-butylcycloprop-1-enyl)butan-1-ol* (**22**, n = 4) (88%) (Found, M^+ + H: 169.1592. $C_{11}H_{20}O$ + H requires: 169.1592) which showed δ_H: 3.6 (2 H, t, J 6.3 Hz), 2.34 (4 H, m), 1.7 (1 H, br, s), 1.4 - 1.6 (6 H, m), 1.3 (2 H, m), 0.86 (3 H, t, J 7.2 Hz), 0.73 (2 H, s); δ_c: 109.9, 108.96, 62.7, 32.5, 29.57, 25.8, 25.7, 24.0, 22.86, 13.9, 7.4; ν_{max} : 3331, 1070 cm^{-1}.

(iii) Acetylation as above gave *4-(2-butylcyclprop-1-enyl)butan-1-yl acetate* (84%) (Found: M^+ + NH_4: 228.1964. $C_{13}H_{22}O_2$ + NH_4 requires: 228.1964) which showed δ_H: 4.04 (2 H, t, J 6.3 Hz), 2.4 (4 H, m), 2.0 (3 H, s), 1.45 - 1.65 (6 H, m), 1.32 (2 H, sext., J 6.9 Hz), 0.87 (3 H, t, J 7.3 Hz), 0.74 (2 H, s); δ_c: 171.2, 110.1, 108.7, 64.3, 29.5, 28.3, 25.68, 25.6, 23.8, 22.45, 20.9, 13.8, 7.37; ν_{max} : 1743, 1239 cm^{-1}.

2-(9-Bromononyl-1,3-dioxacyclopentane (24)

(i) 10-Bromodecanol[21](0.084 mole, 20 g) in dichloromethane (20 ml) was added to a stirred suspension of PCC (0.168 mole, 36.38 g) in dichloromethane (200 ml). The mixture was stirred at room temperature for one hour then refluxed for two hours, when t.l.c. showed no starting material, and then cooled, diluted with ether (300 ml), filtered

through a silica pad and the solvent evaporated to give 10-bromodecanal (16.8 g, 85 %) which was used without purification, and showed υ_{max}: 1725, 1459, 1265, 1116 cm^{-1}.

(ii) 1,2-Ethanediol (5 mol. eq., 19.78 g) was added to 10-bromodecanal (15 g, 0.663 mole) and pTSA (1.2 g, 0.0063 mole) in benzene (100 ml) and stirred at reflux for 3 h to separate the water by Dean Stark apparatus, then cooled and quenched with sat.aq. sodium bicarbonate (10 ml) and water (10 ml). The product was extracted with ether (2 x 100 ml), the combined ether layers were washed with water (2 x 50 ml), dried and evaporated to give 2-(9-bromononyl)-1,3-dioxacyclopentane (**24**)[22] (16.3 g, 91.5 %) (δ_H: 4.84 (1 H, t, J 4.7 Hz), 4.05-3.8 (4 H, m), 3.4 (2 H, t, J 6.8 Hz), 1.85 (2 H, pent, J 6.7 Hz), 1.63 (2 H, m), 1.5-1.3 (12 H, m); υ_{max}: 2927, 2856, 1132, 1036 cm^{-1}).

2-(9-Iodononyl)-1,3-dioxacyclopentane (25)

2-(9-Bromononyl)-1,3-dioxacyclopentane (14.5 g, 0.05 mole) was added to a stirred solution of sodium iodide (38.9 g, 0.25 mole) in dry acetone (150 ml). Sodium bicarbonate (4.36 g, 0.05 mole) was added and the mixture was refluxed for 5 h, when ^1H n.m.r. showed no starting material. The reaction was cooled and the solvent evaporated. Water (30 ml) was added and the mixture was extracted with ether (3 x 50 ml). The ether layers were washed with water (30 ml) and brine (30 ml), dried and evaporated to give a pale yellow oil. Chromatography on silica eluting with 5:1 petrol and ether gave 2-(9-iodononyl)-1,3-dioxacyclopentane (**25**) (15.2 g, 90 %) (Found: M^+ + H: 327.6821. $C_{12}H_{23}O_2I$ + H requires: 327.6821) which showed δ_H: 4.77 (1 H, t, J 4.78 Hz), 3.95-3.7 (4 H, m), 3.12 (2 H, t, J 7.03 Hz), 1.75 (2 H, pent., J 6.8 Hz), 1.58 (2 H, m), 1.4-1.2 (12 H, br, m); δ_C: 104.47, 64.6, 33.77, 33.4, 30.3, 29.3, 29.25, 29.1, 28.34, 23.8, 7.1; υ_{max}: 2925, 2853, 1127, 1035, 944, 720 cm^{-1}.

10-(2-Butylcycloprop-1-enyl)decanal (19)

(i) Butyllithium (2.2 mole eq., 3.5 ml, 1.5 M) was added dropwise to 1,1,2-tribromo-2-butylcyclopropane (8 g, 0.023 mole) stirred in dry ether (50 ml) at -78 °C under nitrogen. The mixture was allowed to reach room temperature for 30 m, then cooled to 0°C when HMPA (2.2. mole eq., 9.13 ml) and then 2-(9-iodononyl)-1,3-dioxacyclopentane (8.56 g, 26 mmole) were added. After stirring for 18 h at room temperature, the reaction was quenched with water (50 ml) and ether (70 ml). The aqueous layer was extracted with ether (2 x 70 ml) and the combined ether layers washed with water (2 x 100 ml), dried and evaporated to give a yellow oil; chromatography on silica eluting with 5:1 petrol and ether gave 9-(2-butylcycloprop-1-enyl)nonyl-1,3-dioxacyclopentane (**26**) (2.87 g, 41 %) (Found: M^++H: 295.2637. $C_{19}H_{34}O_2$+H requires: 295.2637) which showed δ_H: 4.84 (1 H, t, J 4.8 Hz), 4.02 - 3.78 (4 H, m), 2.38 (4 H, m), 1.65 - 1.3 (20 H, m), 0.92 (3 H, t, J 7.27 Hz), 0.77 (2 H, s); δ_c: 109.2, 109.17, 104.57, 64.68, 33.78, 29.4, 29.34, 29.24, 27.23, 25.89, 25.59, 23.9, 22.32, 13.74, 7.25; ν_{max}: 2926, 2256, 1463, 1037 cm^{-1}.

The cyclopropene (**26**) (1.55 g) was added to the stirred solution of 5% HCl (20 ml) and tetrahydrofuran (32 ml) and stirred for 17 h at room temperature. After addition of ether (15 ml) and sat.aq. sodium bicarbonate (5 ml), the aqueous layer was extracted with ether (2 x 10 ml), and the combined ether layers were

dried and evaporated to give a pale yellow oil, which was a mixture of the product and starting material in ratio 2:1. The above procedure was repeated. Chromatography on silica, eluting with 5:1 petrol and ether gave 10-(2-butylcycloprop-1-enyl)-1-decanal (**19**) (0.9 g, 68 %) (Found: M^++H: 251.2374. $C_{17}H_{30}O$+H requires: 251.2374) which showed δ_H: 9.77 (1 H, t, J 1.8 Hz), 2.4 (6 H, m), 1.7-1.5 (6 H, m), 1.4-1.2 (12 H, m), 0.92 (3 H, t, J 7.3 Hz), 0.77 (2 H, s); δ_C: 202.9, 109.36, 109.3, 43.9, 29.55, 29.34, 29.2, 27.36, 26.0, 25.74, 22.47, 22.1, 13.9, 7.4; υ_{max}: 2927, 2855, 1727, 1464, 1008 cm^{-1}.

(ii) Butyllithium (2.2 mole eq., 26.26 ml, 1.25M) was added dropwise to a stirred solution of 1,1,2-tribromo-2-butylcyclopropane (5 g, 0.015 mole) in dry diethyl ether (50 ml) at -78 °C under nitrogen. The mixture was allowed to reach room temperature for 30 m and then cooled to 0 °C when HMPA (2.20 mole eq., 5.71 ml) was added dropwise followed by 1,10-diiododecane (0.9 mole eq., 5.2 g). Stirring was continued for 18 h at room temperature, then the reaction was quenched with water (20 ml) and worked up as above to give a crude product; column chromatography on silica eluting with 5:0.2 petrol and ether gave 10-(2-butylcycloprop-1-enyl)-1-iododecane (**23**, X = I) (2.7 g, 50 %), which showed δ_H: 3.2 (2 H, t, J 7.0 Hz, CH_2I), 2.4 (4 H, br, t, J 6.1 Hz), 1.8 (2 H, m), 1.55 (4 H, m), 1.2-1.5 (14 H, m), 0.9 (3 H, t, J 7.3 Hz), 0.78 (2 H, s). The n.m.r. spectrum showed the presence of a small amount of the corresponding 1-bromo-compound (δ_H: 3.4 (2 H, t, 6.8 Hz, CH_2-Br)).

10-(2-Butylcycloprop-1-enyl)-1-iododecane (**23**, X = I) (0.0041 mole, 1.5 g) was added to anhydrous trimethylamine-N-oxide (10 mole eq., 3.11 g) in dry chloroform (15 ml). The mixture was stirred at 55 °C for 48 h and then quenched with water (15 ml). The organic phase was diluted with chloroform (20 ml) and then washed with water (10 ml) and brine (10 ml), dried and evaporated to afford a crude product; chromatography on silica eluting with 5:1 petrol and ether gave 10-(2-butylcycloprop-1-enyl)-1-decanal (**19**) (0.25 g, 25 %). The ^1H n.m.r. and ^{13}C spectra of this were identical to those above.

8-(2-E-Butenylcycloprop-1-enyl)octan-1-yl acetate (30)

(i) Butyllithium (3.2 mole eq., 13.1 ml, 1.5 M) was added dropwise with stirring to 1,1,2-tribromo-2-(8-hydroxyoctyl)cyclopropane (**15**) (2.5 g, 6.14 mmole) in dry ether (50 ml) at -90 °C under nitrogen. The reaction was allowed to reach room temperature, stirred for 30 m and then cooled to 0 °C. HMPA (2.2. mole eq., 2.35 ml) was added dropwise very slowly followed by *trans*-1-bromo-2-butene (3 mol.eq., 2.48 g). After stirring for 20 h at room temperature, the mixture was treated with water (50 ml) then ether (100 ml), and the aqueous layer was washed with ether (2 x 50 ml). The combined organic layers were washed with water (2 x 50 ml), dried and evaporated to give a brown oil; chromatography on silica eluting with 2:1 petrol and ether afforded *8-(2-E-butenyl-cycloprop-1-enyl)octan-1-ol* (**29**) (0.75 g, 55 %) (Found: M^++H: 223.2061. $C_{15}H_{26}O$ + H requires: 223.2062) which showed δ_H: 5.5 (2 H, m), 3.6 (2 H, t, J 6.6 Hz), 3.06 (2 H, br, m), 2.36 (2 H, tt, J 1.4, 7.1 Hz), 1.65 (3 H, m), 1.56 - 1.35 (5 H, m), 1.38 (8 H, m), 0.79 (2 H, s). This was further purified by bulb to bulb distillation at 40 - 45 °C and 0.06 mm Hg.

(ii) Acetylation of (**29**) at 0 °C as above gave 8-(2-E-butenecycloprop-1-enyl)octan-1-yl acetate (**30**) (65 %) which showed δ_H: 5.5 (2 H, m), 4.01 (2 H, t, J 6.7 Hz), 3.05 (2 H, br, d, J 1.3 Hz), 2.35 (2 H, tt, J 1.4, 7.1 Hz), 2.0 (3 H, s), 1.7 - 1.5 (7 H, m, including the olefinic methyl), 1.4 - 1.3 (8 H, br, s), 0.78 (2 H, s); δ_c: 171.1, 126.7, 126, 110.1, 107.9, 64.5, 29.4, 29.18, 29.1, 28.5, 27.3, 25.95, 25.8, 24.23, 20.8, 17.76, 7.6; ν_{max} : 1870, 1740, 1679 cm^{-1}.

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