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ORGANOTIN AND -MERCURY ROUTES TO ENONES, DIENONES AND SPIROACETALS

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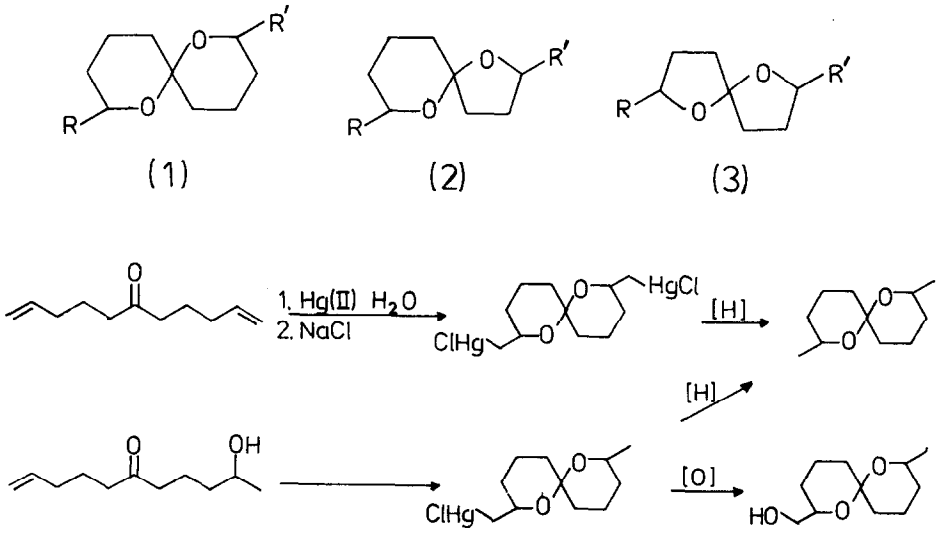
ABSTRACT: Conjugate addition of trimethyltinlithium to cyclohex-2-enone followed by enolate trapping with alkylating agents provide *trans*-2-alkyl-3-trimethylstannylcyclohexanones, which on reaction with Grignard reagents derived from 4-bromo-1-butene or 5-bromo-1-pentene afford tertiary γ-stannylcyclohexanols in a highly diastereoselective fashion. Trimethylstannyl-triggered ring fragmentation (by lead tetraacetate in benzene) leads efficiently to dienones, which on hydroxymercuration, cyclisation and reduction provide a range of 1,6-dioxaspiro[4.5]decanes and 1,7-dioxaspiro[5.5]undecanes, some of which are of insect origin. Epoxidation of these dienones, followed by acid catalysed hydrolysis and cyclisation leads to hydroxy substituted spiroacetals. Syntheses of 6-oxononan-1-ol (a glandular component of the fruit flies, D. halfordiae and D. occipitalis) and *E*-6-nonene-2-one, which is transformed readily into *exo* or *endo*-brevicomin, are also presented. Some dialkyl substituted [4.5]- and [5.5] spiroacetals have been acquired also by free radical addition reactions etc., utilising organomercury chemistry.

INTRODUCTION: A number of relatively simple spiroacetals[1] and hydroxylated derivatives of the types (1, 2, 3) have been identified as rectal glandular components in several Dacus species ("fruit-flies"),[2] and we reported briefly that suitable dienones, when subjected to hydroxymercuration underwent efficient intramolecular cyclisation to provide mercury-bearing spiroacetals.[3] Reductive (or oxidative) removal of mercury then afforded the dialkyl spiroacetals in good to excellent yields.[3] Hydroxyenones also participated well in this type of sequence,[3] shown below in Scheme 1.



Scheme 1

A number of procedures for acquiring various dienones were employed[3] and these were based largely on double alkylation reactions e.g. of diethyl 3-oxoglutarate or β-keto esters. The recurring presence of 2-alkyl-8-methyl-1,7-dioxaspiro[5.5]undecanes (1) and 2-alkyl-7-methyl-1,7-dioxaspiro[4.5]decanes (2) in some insect species,[4] suggested that suitable

fragmentation of the cyclohexyl ring system could be a versatile source of unsaturated C_6 fragments incorporated in suitable dienones, for subsequent transformation to spiroacetals. At about this time, several reports[5] described the oxidative fragmentation of γ-hydroxystannanes and applications of this chemistry are described in the present report, together with some mercury-based reactions leading to similar spiroacetal systems.

RESULTS AND DISCUSSION: Reaction of cyclohex-2-enone with $(CH_3)_3SnLi$ (THF; -78°) followed by aqueous work-up affords 3-trimethylstannylcyclohexanone.[6] However, treatment at the enolate stage with alkylating agents e.g. CH_3I, CH_3CH_2Br or $BrCH_2CO_2Et$ afforded the 2-alkyl-3-stannylcyclohexanone[6] essentially exclusively as the *trans*-diastereomer, based on the relatively large values of $^3J_{Sn-C=O}$ (62 Hz) and $^3J_{Sn-C\beta}$ (67 Hz).[7] Reaction of these 3-stannylketones with the Grignard reagents derived from 4-bromo-1-butene and 5-bromo-1-pentene, afforded in high yield, the unsaturated tertiary alcohols, essentially as one diastereomer on the basis of the single set of ^{13}C nmr signals. 3-Trimethylstannylcyclohexanone, itself, appeared to provide only one diastereomeric tertiary alcohol with the same Grignard reagents as well as with n-propylmagnesium bromide (see later). Consideration of ^{13}C chemical shifts suggests the diastereomers shown below in Scheme 2. (Products resulting from alkylation with ethyl bromoacetate are not considered further here).

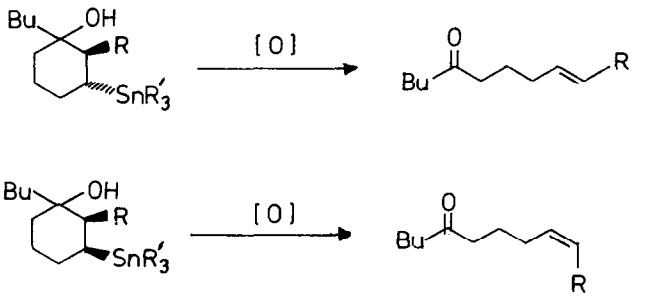
$R' = -(CH_2)_2-CH=CH_2$ $-(CH_2)_3-CH=CH_2$

(4) R= H (5) (8) (9)

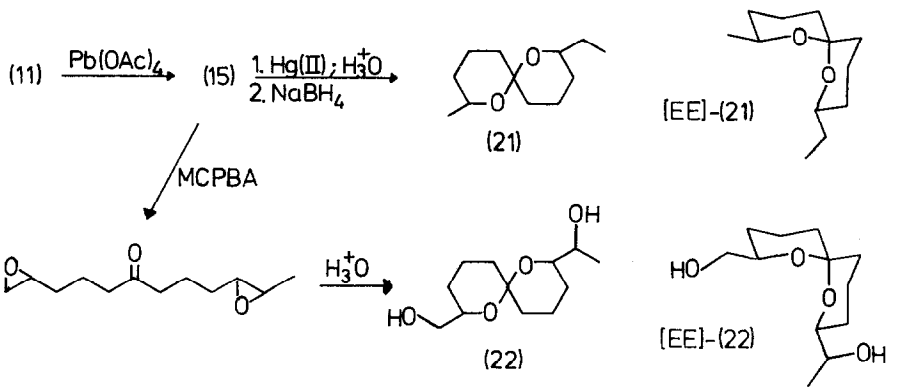
R= CH_3 (6) (10) (11)

Scheme 2

Oxidative 1,4-fragmentation of γ-stannyl alchols with $Pb(OAc)_4$ or iodosylbenzene proceeds stereospecifically to yield the corresponding (*E*) and (*Z*)-ketoalkenes as shown below.[5] Application of this reaction to the tertiary alchols (8-11) generally proceeded in a satisfactory manner.



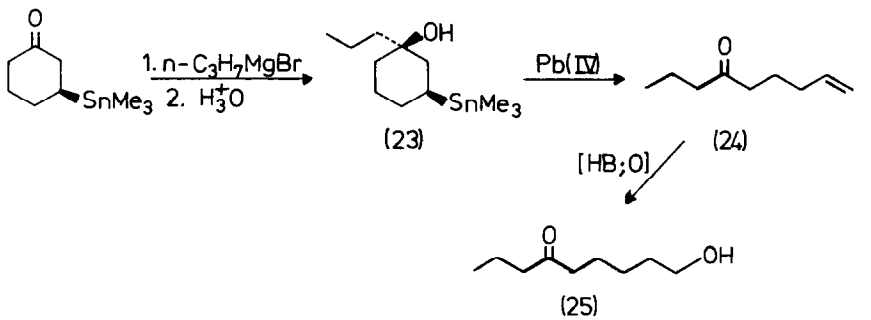
For example, treatment of tertiary alcohol (11) with $Pb(OAc)_4$ in benzene[5(a)] afforded 6-oxo-1,10-dodecadiene, and the dienone formations are summarised below (Table 1). These dienones were subjected to hydroxymercuration-cyclisation and biphasic $NaBH_4$ reduction to provide diastereomeric mixtures of dialkyl spiroacetals.[3] For those cases in which an internal olefin was present, the non-regiospecificity of oxymercuration and cyclisation led to six membered ring formation only, with no detectable amount of the alternative, less favourable seven membered ring. These dienones were also converted to the bisepoxides in the usual way (with *m*-chloroperbenzoic acid) and on acidic hydrolysis/cyclisation led efficiently to bis-hydroxy derivatives of various spiroacetal systems. One example of these sequences is shown below (Scheme 3) leading to E,E-(21), an unusual even carbon-numbered spiroacetal detected in some Dacus species.[2(b)] The results are summarised in Table 1.



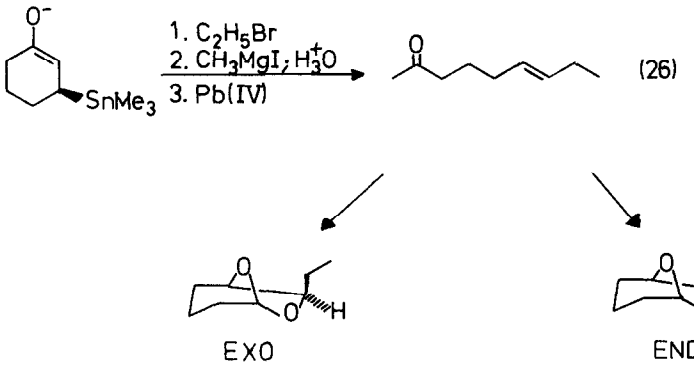
Scheme 3

These spiroacetal systems were fully characterised by ^1H and ^{13}C nmr measurements and mass spectra. In the case of (20), the isomeric diol (20a) was detected by gc-ms ((20) shows a prominent ion for M^+-CH_2OH whereas (20a) does not) and thermal/acid interconversion (gc conditions?) of these isomers is anticipated to be facile.[2(c),9]

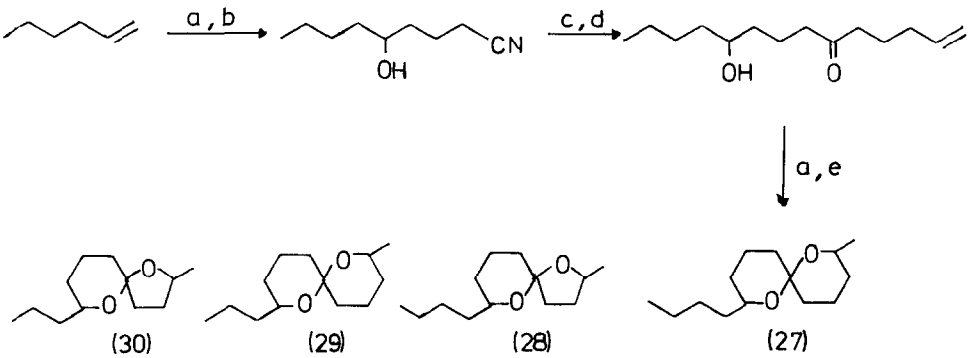
A significant component of the rectal gland secretion of the fruit-flies, D. occipitalis and D. halfordiae[2(b)] is 6-oxononan-1-ol, (25) and access to this compound was achieved as shown below.



Trapping of the enolate with ethyl bromide (to afford the *trans*-diastereomer), treatment with methylmagnesium iodide etc., followed by oxidative cleavage, provided the *E*-olefinic ketone (26), the immediate precursor of both *exo* and *endo*-brevicomin, as shown below.[10]



In a related study, a number of dialkyl spiroacetal systems have been acquired by organomercury-based free radical additions to acrylonitrile and α,β-enones. This general type of chemistry has been elegantly developed by Giese and co-workers.[11] For example, treatment of the hydroxymercurial derived from 1-hexene with sodium borohydride in the presence of acrylonitrile provides the δ-hydroxynitrile, which on reaction with pent-4-enylmagnesium bromide and hydrolysis, affords the corresponding δ-hydroxy ketoolefin as shown below. Hydroxymercuration and reduction efficiently provides (27), 2-n-butyl-8-methyl-1,7-dioxaspiro[5.5]undecane, an unusual even carbon-numbered spiroacetal identified as a glandular component of the fruit-fly species Dacus latifrons, found in South-East Asia and Hawaii.[2(a)]



a= $Hg(II), H_2O$; b= $NaBH_4$,  ; c=  ; d= H_3^+O ; e= $NaBH_4$.

In a similar way, (28) was obtained by employing but-3-enylmagnesium bromide. Initial hydroxymercuration of 1-pentene, provided the n-propyl derivatives (29) and (30). In some cases, the δ-hydroxynitrile was protected as the tetrahydropyranyl ether prior to reaction with the Grignard reagent, but the use of slightly more than two equivalents of the latter reagent with the unprotected hydroxynitrile proved satisfactory.

Cyclohexene was also employed as the initial alkene, and addition of the 2-hydroxycyclohexyl radical to 1,6-heptadien-3-one (31) for example, proceeded satisfactorily to provide eventually the tricyclic system (32) shown below,

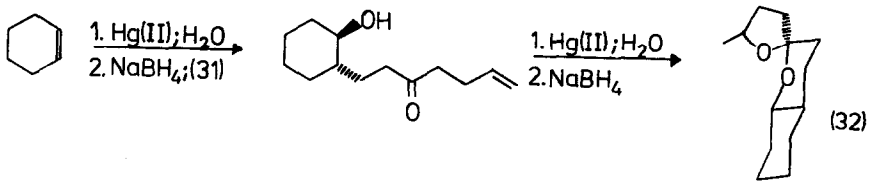
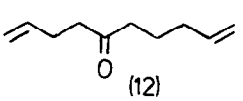
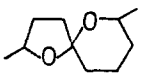
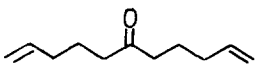
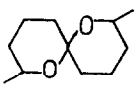
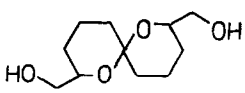
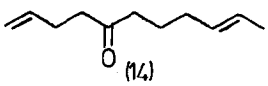
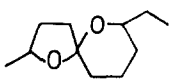
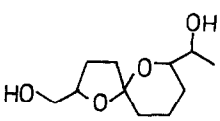
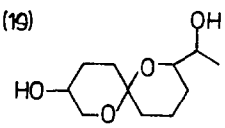
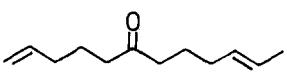
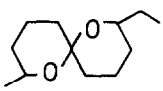
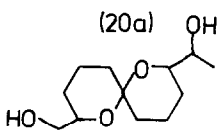


TABLE 1

ALCOHOL	DIENONE	DERIVED SPIROACETALS
(8)	 (12)	 (16)
(9)	 (13)	 (17)  (18)
(10)	 (14)	 (19)  (20)  (20a)
(11)	 (15)	 (21)  (22)

EXPERIMENTAL SECTION

Combined gas chromatography-mass spectrometry was conducted with a Hewlett-Packard model 5992B instrument fitted with OV1 or BP5 capillary columns, whereas gas chromatographic analyses were performed using a Hewlett-Packard 5710A gas chromatograph with OV1 or BP5 capillary columns, or a Varian 3700 gas chromatograph with OV101 capillary column. Preparative gas chromatography was performed with a Shimadzu gas chromatograph Model GC-9A equipped with OV101 and C-20M columns. Mass spectra refer to gc-ms data, except accurate mass determinations which were conducted on a Kratos mass-spectrometer. ^{1}H nmr spectra were recorded at 100 or 400 MHz in the FT mode on JEOL JNM-FX100 or Jeol JNM-GX400 spectrometers respectively. Chemical shifts were referenced to internal tetramethylsilane (0.00 ppm) or residual $CHCl_3$ (7.24 ppm). ^{13}C nmr spectra were recorded at 25.05 MHz or 100 MHz and chemical shifts were referenced to the central peak of the solvent ($CDCl_3$) signal at 77.00 ppm.

Reactions involving organometallic reagents were conducted employing nitrogen or argon atmospheres, and where repetitive procedures were employed, a sample experimental description only is provided.

Trans-2-methyl-3-trimethylstannylcyclohexanone (6): A solution of trimethyltinlithium (*ca* 30 mmol) prepared in anhydrous THF in the normal way, was cooled to -78°C and cyclohex-2-enone (25 mmol), in anhydrous THF, was added dropwise. After stirring at -78° for *ca* 3 hours, an excess of methyl iodide (~100 mmol) was added and the solution allowed to warm to room temperature, followed by quenching with ammonium chloride solution. Extraction with diethyl ether (3 x 75 ml) followed, and the combined organic layers were dried ($MgSO_4$), evaporated and the crude product purified either by conventional vacuum distillation (Kugelrohr) or flash chromatography.

Compound (5) was obtained by adding, at the trimethyltin enolate stage, aqueous NH_4Cl. In this general way the following compounds were acquired.

(5): B.p. 54°C/2 mm. (81%) (Lit.[8,6] 55°C/2 mm). ^{13}C *NMR*. (Values in parentheses are ^{119}Sn-^{13}C coupling constants). 212.4 (58.2), 45.8 (14.5), 42.1, 30.9 (67), 29.4 (13.7), 25.19 (368.5), -11.64 (306). ^{119}Sn *NMR* (rel. $(CH_3)_4Sn$) = +6.53 ppm. *Mass spectrum*: m/z (rel. intensity). 262 (M^+, 0), 247 (M^+-CH_3, 32.9), 245 (25.6), 165 (70.3), 163 (54.3), 135 (48.9), 133 (38.4), 41 (100). ^1H *NMR*: 0.09 ($SnMe_3$, $J_{^{119}Sn-^1H}$ = 51 Hz), 1.5-2.8 (ring protons).

(6): B.p. 80°C/3 mm. (Kugelrohr) (95%). ^{13}C *NMR*: 214.1 (67.5), 48.6, 42.5, 35.5 (380), 32.2 (73), 30.3, 15.8, -10.1 (317). ^{119}Sn *NMR* = + 4.69 ppm. ^1H *NMR* ($CDCl_3$): 0.08 (9H, s, $(CH_3)_3Sn$), 0.97 (3H, d, CH_3), 1.33 (1H, t of d), 1.66 (3H, m), 1.89 (1H, d of q), 2.15-2.38 (3H, m). *Mass spectrum*: 276 (M^+, 0), 261 (M^+-CH_3,13), 165 (99.2), 163 (76), 162 (26.6), 161 (47.4), 135 (51.6), 133 (24.5), 55 (100).

Grignard Addition to 3-Trimethylstannylcyclohexanones: Typical Procedure:

(Compound 10): The Grignard reagent from 4-bromo-1-butene (2.84 g; 20.5 mmol) and magnesium (0.5 g; 20.5 mmol) was prepared in ether (40 ml) and then cooled to 0°C. *Trans*-2-methyl-3-trimethylstannylcyclohexanone (6) (3.76 g; 13.7 mmol) in dry ether (10 ml) was added dropwise to the Grignard solution, and after additon was complete, the reaction mixture was refluxed for one hour and then worked up with saturated aqueous NH_4Cl (50 ml) and extracted with ether (3 x 50 ml). The combined ether extracts were dried ($MgSO_4$), evaporated, and the crude product purified by chromatography (Kieselgel 230-400 mesh: hexane/ethyl acetate (3:1)) to yield

(10) (3.07 g, 67%). ^{13}C *NMR*: 139.0, 114.2, 73.0 (61.2), 41.6 (16.7), 40.34, 36.4, 30.9 (15.9), 28.9, 28.11, 23.8 (71.4), 16.2, -10.19 (306.3). ^{119}Sn *NMR*: + 3.24 ppm. ^1H *NMR*: 0.02 (9H, s, $Sn(CH_3)_3$), 0.85 (3H, d, CH_3), 1.15-2.04 (13H, m), 4.97 (2H, m), 5.81 (1H, m). *Mass Spectrum*: 332 (M^+, 0), 317 (M^+-CH_3, 1.5), 299 (7.1), 297 (6.7), 165 (39.0), 164 (13.2), 163 (30.1), 161 (17.8), 135 (19.6), 111 (17.5), 83 (54.3), 55 (100). Similarly prepared were:

(8): (86% yield). ^{13}C *NMR*: 139.26 (C10), 114.16 (C9), 70.85 (58.7, C1), 43.32 (C6), 41.17 (15.0 Hz, C2), 36.89 (C7), 30.14 (15.0 Hz, C4), 27.38 (C8), 23.71 (66.0 Hz, C5), 18.80, (v. high coupling, C3), -11.97 (307.0 Hz, $SnMe_3$). ^{119}Sn *NMR*: + 2.73 ppm. ^1H *NMR*: 5.79 (1H, m, CH=), 4.93 (2H, m, CH_2=), 1.13-2.09 (14H, complex), 0.04 (9H, s, $J_{^{119}Sn-^1H}$ = 50.8 Hz). *Mass spectrum*: 318 (M^+, 0.0), 303 (M^+-CH_3, 2.7) (285 (M^+-CH_3-H_2O, 10.3), 165 (92.4), 164 (29.7), 163 (68.1), 162 (24.3), 161 (38.9), 135 (47.2), 133 (30.3), 94 (36.2), 55 (100), 41 (92.4).

(9): (79% yield). ^{13}C *NMR*: 138.84 (C11), 114.45 (C10), 70.88 (60.3 Hz, C1), 43.86 (C6), 41.15 (14.5 Hz, C2), 36.83, 34.27, 30.14 (C4), 23.72 (67.1 Hz, C5), 22.22, 18.86 (382.2 Hz, C3), -11.89 (309.8 Hz, $SnMe_3$). ^{119}Sn *NMR*: +2.67 ppm. ^1H *NMR*: 5.82 (1H, M, CH=), 4.91 (2H, m, CH_2=), 1.08-2.01 (16H, m, complex), 0.03 (9H, s, $SnMe_3$, $J_{^{119}Sn-^1H}$ = 50.6 Hz). *Mass Spectrum*: 332 (M^+, 0.4), 317 (M^+-CH_3, 5.1), 299 (M^+-CH_3-H_2O, 22.2), 297 (18.9), 295 (11.0), 167 (24.8), 165 (100), 164 (30.4), 163 (75.0), 162 (24.9), 161 (43.7), 151 (25.7), 149 (30.8), 69 (72.3), 55 (69.5), 41 (69.8).

(11): (88% yield). ^{13}C *NMR*: 138.72 (C11), 114.59 (C10), 73.14 (44.6 HZ, C1), 41.37 (16.0 Hz, C2), 40.88 (C6), 36.57 (C7), 31.00 (15.7 Hz, C4), 28.97 (v. high coupling, C3), 28.85 (C8), 23.83 (71.2 Hz, C5), 23.12 (C9), 16.23 (C12), -10.18 (307.1 Hz, $SnMe_3$). ^{119}Sn *NMR*: + 3.71 ppm. ^1H *NMR*: 5.79 (1H, m, CH=), 4.81 (2H, m, CH_2=), 1.21-2.11 (15H, complex), 0.87 (3H, d, J = 6.7 Hz, CH_3), 0.02 (9H, s, $J_{^{119}Sn-^1H}$ = 50.4 Hz, $SnMe_3$). *Mass spectrum*: 346 (M^+, 0.0), 331 (M^+-CH_3, 4.7), 313 (31.1), 311 (23.2), 309 (16.5), 165 (100), 164 (30.2), 163 (78.1), 161 (41.2), 135 (54.3), 69 (87.5), 55 (94.3).

Oxidative Cleavage of γ-stannyl Alcohols: Typical Procedure[5(a)]

Conversion of (8) *to dienone* (12): To a refluxing suspension of lead tetraacetate (0.28 g; 0.66 mmol) in dry benzene (5 ml) under nitrogen, was added a solution of (8) (0.14 g; 0.44 mmol) in dry benzene (5 ml). The reaction was maintained at reflux for one hour, cooled to room temperature and then poured into a solution of saturated $NaHCO_3$ (50 ml). The resulting solution was filtered (insoluble lead salts) and extracted with ether (3 x 50 ml). The dried ($MgSO_4$) combined extracts were evaporated and the crude product filtered through a pad of silica to provide (12) (deca-1,9-dien-5-one) (0.04 g, 61%), identical with an authentic sample.[12]

Dienones (13) from (9), (14) from (10) and (15) from (11) were obtained in a similar way.

(13): ^{13}C *NMR*: 210.91, 137.99, 115.17, 41.96, 33.12, 22.85. ^1H *NMR*: 6.4 (2H, m, CH=), 5.7 (4H, m, CH_2=), 2.3-3.3 (12H, m). *Mass Spectrum*: 166 (M^+, 0.0), 112 (18.4), 97 (34.8), 84 (26.0), 70 (12.5), 69 (50.3), 58 (38.8), 55 (43.2), 43 (21.6), 41 (100), 39 (40.9).

(14): ^{13}C *NMR*: 210.20 (C5), 137.15 (C1), 130.41 (C9), 125.68 (C10), 115.07 (C2), 42.06 (C4 or C6), 41.81 (C6 or C4) 31.91 (C8), 27.74 (C3), 23.47 (C7), 17.81 (C11). ^1H *NMR*: 5.61 (1H, m, H2),

5.20 (1H, m, H9 or H10), 4.81 (3H, complex, H1 and H9 or H10), 1.11-2.21 (10H, complex), 1.47 (3H, d, J = 6.9 Hz, CH_3). *Mass Spectrum*: 166 (M^+, 0.0), 112 (15.2), 97 (27.9), 84 (29.0), 83 (17.2), 69 (39.4), 55 (81.9), 43 (32.1), 41 (100), 39 (47.1).

(15): *^{13}C NMR*: 211.38 (C6), 137.97 (C1), 130.43 (C10), 125.68 (C11), 115.12 (C2), 42.08 (C5 or C7), 41.91 (C7 or C5), 33.08 (C3 or C9), 31.93 (C9 or C3), 23.55 (C4 or C8), 22.81 (C8 or C4), 17.82 (C12). *^1H NMR*: 5.66 (1H, m, H2), 5.27 (1H, m, H10 or H11), 4.87 (3H, complex, H1 and H10 or H11), 1.05-2.30 (12H, complex), 1.51 (3H, d, J = 6.8 Hz, CH_3). *Mass spectrum*: 180 (M^+, 0.0), 112 (15.9), 97 (28.8), 84 (32.4), 83 (19.8), 69 (40.7), 68 (67.4), 67 (27.4), 58 (33.8), 55 (77.7), 41 (100), 39 (49.3).

Hydroxymercuration-Reduction of Dienones (12-15) to yield Dialkyl-Substituted-[4,5] and -[5,5]spiroacetals. General Procedure:

The dienone (1 mmol) was dissolved in a mixed solvent (20 ml) consisting of 1:1 THF:1% aqueous $HClO_4$, and mercuric acetate (0.72 g; 2.2 mmol) was added. The reaction mixture was stirred at room temperature for thirty minutes, and to the solution was added 10% aqueous NaOH (10 ml), dichloromethane (5 ml) and benzyltriethylammonium chloride (1.6 g) as the phase transfer reagent. The mercury was removed (reductively) by the addition of a solution of sodium borohydride (0.03 g, 0.75 mmol) in 10% aqueous sodium hydroxide (5 ml). The heterogeneous mixture was stirred (30 min), filtered through celite and extracted with ether (3 x 25 ml). The combined extracts were washed with saturated sodium chloride solution, dried ($MgSO_4$) and evaporated to yield the spiroacetals, which were purified by Kugelrohr distillation or preparative gas chromatography. Yields were in excess of 70%, and in some cases, diastereomeric mixtures of spiroacetals were obtained.

2,7-Dimethyl-1,6-dioxaspiro[4.5]decane (16) was obtained from (12) in 77% yield as a diastereomeric mixture and was identical with a sample obtained previously.[12] The mass spectra of the three diastereomers were similar. *Mass Spectrum*: 170 (M^+, 5.7), 126 (20.9), 115 (17.4), 101 (100), 100 (20.3), 98 (91.5), 97 (26.2), 83 (32.2), 55 (50), 43 (53.2), 41 (37.9). (The mass spectra of 4,4,10,10-tetradeutero-2,7- dimethyl-1,6-dioxaspiro[4.5]decane was also reported previously).[4]

2,8-Dimethyl-1,7-dioxaspiro[5.5]undecane (17) was obtained from (13) in 70% yield as an (E,E) and (E,Z) diastereomeric mixture and exhibited nmr and mass spectra in agreement with published data, or those of authentic samples.[12,13]

7-Ethyl-2-methyl-1,6-dioxaspiro[4.5]decane (19) was acquired from dienone (14) as an (E,E), (E,Z) mixture in 80% yield, and the mass spectrum was in satisfactory agreement with that reported.[14]

^{13}C NMR (Mixture) (C_6D_6): 106.14, 105.91, 76.58, 73.74, 71.61, 71.22, 39.79, 38.43, 34.21, 34.19, 32.29, 31.90, 31.22, 30.98, 30.02, 29.77, 29.63, 23.53, 21.46, 20.87, 10.43, 10.27.
Mass Spectrum: (E,E): 184 (M^+, 7.3), 169 (M^+-CH_3, 4.2), 155 (M^+-CH_2CH_3, 30.8), 126 (14.1), 111 (32.1), 101 (100), 98 (78.9), 83 (32.9), 55 (54.0), 43 (51.4), 41 (53.5). (E,Z): 184 (M^+, 8.4), 169 (M^+-CH_3, 4.7), 155 (M^+-CH_2CH_3, 29.5), 126 (12.9), 111 (29.3), 101 (100), 98 (68.3), 83 (30.8), 55 (49.7), 43 (44.1), 41 (52.5).

2-Ethyl-7-methyl-1,7-dioxaspiro[5.5]undecane (21) was obtained from dienone (15) in 76% yield as one diastereomer, shown by detailed nmr examination to be the (expected) (E,E). *^{13}C NMR* ($CDCl_3$): 95.9 (C6), 70.25 (C2), 64.97 (C8), 35.51 (C5*), 35.31 (C11*), 32.84 (C9), 30.99 (C3), 29.25 (C12), 21.83 (C14), 18.94 (C4*), 18.86 (C10*), 10.35 (C13). *^1H NMR* (C_6D_6): 3.75 (1H, ddddd, J = 11.4, 6.26, 6,26, 6.26, 2.00, H8), 3.48 (1h, dddd, J = 11.3, 6.26, 6.26, 1.95, H2), 2.01 (1H, qt, J = 13.42, 4.28, H4a or H10a), 2.00 (1H, qt, J = 13.42, 4.28, H4a or H10a), 1.62 (2 x 1H, overlapping d of t, H5e, H11e), 1.50 (2H, obscured d of q, H12), 1.35-1.45 (overlapping equatorial protons, H3e, H4e, H9e, H10e - each d of m), 1.30 (1H, td, J = 13.1, 1.83, H5a or H11a), 1.29 (1H, td, J = 13.27, 1.52, H5a or H11a), 1.14 (3H, d, J = 6.1, H14), 1.10, (2H, overlapping q of d, H3a, H9a), 0.98 (3H, dd, J = 7.63, 7.32, H13). (H14 are C-CH_3 and H12,H13 are ethyl group protons). *Mass Spectrum*: 198 (M^+, 18.2), 169 (M^+-C_2H_5, 15.1), 129 (54.7), 126 (45.1), 115 (100), 114 (22.3), 112 (92.1), 111 (42.1), 97 (53.2), 83 (47.8), 69 (58.6), 55 (75.0), 41 (80.7). Accurate Mass: 198.1632. Calcd. for $C_{12}H_{22}O_2$ = 198.1620.

Bis-Epoxidation of Dienones and Acid Catalysed Hydrolysis-Cyclisation to Bis-Hydroxyspiroacetals. General Procedure:

To 6-oxo-1,10-undecadiene (13) (0.3 g; 1.8 mmol) in dichloromethane (20 ml) was added *m*-chloroperbenzoic acid (0.73 g; 4.0 mmol, 2.2 equiv) in portions. The solution was stirred at room temperature and the reaction progress monitored by gc-ms. Reaction times were of the order of twelve hours. The reaction mixture was washed with saturated sodium bicarbonate solution, and the organic layer was separated, dried ($MgSO_4$), and the solvent removed under vacuum to yield the required bis-epoxide (0.3 g; 90%). The epoxides were not purified before further reaction, in which the bis-epoxide (0.07 g; 0.35 mmol) was dissolved in aqueous tetrahydrofuran (10 ml; 1:1) containing a small crystal of *p*-toluenesulfonic acid. The reaction mixture was stirred at room temperature for two days, neutralised with 0.5M sodium hydroxide solution and extracted with ether (3 x 5 ml). Standard treatment yielded an oil, which sometimes solidified and gc-ms examination confirmed the presence of the hydroxyspiroacetals which were then filtered through a small column (230-400 mesh silica) with hexane to remove non-polar impurities. Elution with ether yielded the hydroxy spiroacetals in pure form with yields in the range 65-80%. Compounds prepared in this way are described below.

E,E-2,8-Bishydroxymethyl-1,7-dioxaspiro[5.5]undecane (*18*): ^{13}C *NMR* ($CDCl_3$): 96.01, 69.72, 66.15, 35.20, 26.34, 18.20. *Mass Spectrum*: *216* (M^+, 3.2), 185 (57, M^+-CH_2OH), 131 (82.1), 121 (41.8), 113 (100), 99 (34.9), 97 (34.9), 67 (75.4), 55 (75.9), 43 (90.7), 41 (89.4). This compound is also described elsewhere.[12]

Compounds (*20*) (*two isomers*) *and* (*20a*) (*two isomers*) were obtained as a mixture and characterised by gc-ms methods. For (20) peaks corresponding to both M^+-CH_2OH and $M^+-CH(CH_3)OH$ was observed, but for (20a), $M^+-CH(CH_3)OH$ was observed but no M^+-CH_2OH peak was present.

(20) *Isomer 1*: 216 (M^+, 0), 185 (17.6), 171 (30.6), 127 (16.2), 117 (16.7), 85 (23.6), 83 (20.4), 71 (26.4), 55 (44.9), 45 (100).
Isomer 2: 216 (M^+, 0), 185 (27.4), 171 (52.2), 127 (23.5), 99 (29.6), 85 (31.9), 83 (28.3), 71 (35.8), 55 (43.8), 45 (100).
(*20a*) *Isomer 1*: 216 (M^+, 0), 171 (47.2), 142 (38.3), 127 (27.5), 117 (25.7), 109 (19), 99 (24.2), 97 (31.6), 55 (37.9), 45 (97.4).
Isomer 2: 216 (M^+, 0), 171 (40.6), 142 (39.6), 127 (29.9), 117 (15), 109 (18.2), 99 (20.9), 97 (32.1), 55 (36.9), 45 (100).

E,E-2-(1'-hydroxyethyl)-8-hydroxymethyl-1,7-dioxaspiro[5.5]undecane (*22*)
^{13}C *NMR* ($CDCl_3$): 96.22 (C6), 72.70 (C12), 69.75, 69.64 (C2, C8), 66.17 (C14), 35.29, 35.20, (C4,C10), 26.41, 24.07 (C3,C9), 18.21, 18.14, 17.92 (C5, C11, C13). ^1H *NMR*: 3.89 (1H, m, CH-OH), 3.71 (^{1}H, m, CH-OR), 3.52 (1H, m, CH-OR), 3.19 (2H, d, CH_2OH), 1.31-2.09 (14H, complex), 1.09 (3H, d, CH_3). *Mass Spectrum*: 230 (M^+, 1.0), 199 (17.8, M^+-CH_2OH), 185 (64.6, $M^+-CH(CH_3)OH$), 131 (43.8), 121 (57.1), 113 (46.2), 99 (53.7), 71 (50.5), 55 (70.0), 43 (100). *Accurate Mass*: 230.1526. (Calcd. for $C_{12}H_{22}O_4$ = 230.1518).

E,Z-2-(1'-hydroxyethyl)-8-hydroxymethyl-1,7-dioxaspiro[5.5]undecane (*22*) (This was a mixture of the two E,Z-isomers). ^{13}C *NMR* (24 signals for two isomers): 97.86, 97.80 (C6), 73.63, 73.34, 70.81, 69.86, 69.22, 66.16, 66.10, 65.91 (C2,C8,C12,C14), 36.11, 36.03, 32.16, 31.88 (C4,C10), 26.60, 26.35, 26.21, 24.18 (C3,C9), 19.46, 18.98, 18.31, 17.65, 17.52, 17.26 (C5,C11,C13). ^1H *NMR*: 4.02 (2H, m, CH-OH). 3.80 (2 x 1H, m, *CH*-O-R), 3.61 (2 x 1H, m, *CH*-O-R), 3.30 (2 x 2H, d, CH_2OH), 1.3-2.2 (all others, m, complex), 1.15 (2 x 3H, d, CH_3-CH). *Mass Spectrum*: 230 (M^+, 0), 199 (21.2, M^+-CH_2OH), 185 (54.2, $M^+-CH(CH_3)OH$), 131 (30.6), 121 (43.3), 113 (32.1), 99 (41.3), 81 (40.9), 71 (49.3), 55 (71.3), 43 (100). *Accurate Mass*: 230.1529. (Calcd. for $C_{12}H_{22}O_4$ = 230.1518).

γ-Stannyl alcohol (*23*) was obtained as the indicated diastereomer(text) by the addition of n-propylmagnesium bromide to stannylketone (5) in the manner described above. ^{13}C *NMR*: 70.98 (57 Hz, C1), 46.88 (C6), 41.12 (C2), 36.87 (C7), 30.18 (16 Hz, C4), 23.76 (C5), 18.91 (C3 or C8), 16.15 (C8 or C3), 14.73 (C9), -12.00 (309 Hz, $Sn(CH_3)_3$). ^1H *NMR*: δ 1.12-1.85 (m, 14H), 0.89 (t, 3H, J = 7 Hz, CH_3), -0.02 (s, 9H, $Sn(CH_3)_3$). ^{119}Sn *NMR* = +2.52 ppm. *Mass spectrum*: 306 (M^+, 0.9), 291 (M^+-CH_3, 12.5), 289 (9.3), 273 ($M^+-CH_3-H_2O$, 21.1), 271 (16.2), 169 (23.8), 167 (26.1), 165 (96.1), 164 (28.5), 163 (69.4), 162 (23.0), 161 (40.1), 82 (51.6), 71 (100).

6-Oxo-non-1-ene (*24*) formed from (23) on oxidative cleavage with $Pb(OAc)_4$ as described above, in 79% yield. *Mass Spectrum*: 140 (M^+, 2.8), 112 (10.6), 97 (17.9), 86 (16.1), 71 (94.6), 69 (59.3), 58 (91.0), 55 (37.2), 43 (100), 41 (99.2), 39 (39.3). ((24) was also obtained by treating butanoyl chloride with 4-pentenylmagnesium bromide in THF).

6-Oxo-nonan-1-ol (*25*) resulted from a standard hydroboration oxidation sequence on enone (24), and had spectral characteristics in agreement with those previously obtained.[2(b)]

E-6-Nonen-2-one (*26*): Addition of $(CH_3)_3SnLi$ to cyclohex-2-enone followed by trapping with ethyl bromide (at the enolate stage) provided *trans*-2-ethyl-3-trimethylstannylcyclohexanone (68%) characterised by its ^{119}Sn nmr shift (+4.33 ppm), ^{13}C nmr spectrum: 72.17 (59.6 Hz, C1), 40.97, 31.08, 30.85, 29.05, 27.83, 25.13 (16.1 Hz), 23.75 (67.9 hz), 13.95, -10.13 (305.9 Hz, $SnMe_3$) and mass spectrum: 290 (M^+, 2.5), 275 (M^+-CH_3, 27.8), 273 (21.7), 271 (12.7), 261 (21.6), 259 (17.1), 165 (100), 164 (30.4), 163 (75.4), 162 (25.8), 161 (46.0), 135 (32.2), 133 (24.0), 55 (40.9), 41 (32.2). Treatment of this ketone with methylmagnesium iodide etc., provided the tertiary alcohol (85%) which was subjected to oxidative cleavage to provide the enone (26) (in 76% yield) exhibiting spectra in agreement with those reported.[10]

Oxymercuration, Reduction and Conjugate Addition Reactions[11]: A suspension of the alkene (20 mmol) in water-tetrahydrofuran (1:1, 20 ml) was treated with $Hg(OAc)_2$ (6.37 g; 20 mmol) and the mixture allowed to stir for fifteen minutes. Sodium hydroxide (40 ml of 2M), benzyltriethylammonium chloride (1.0 g; 4.4 mmol), acrylonitrile (10.6 g, 200 mmol, 10 equiv.) and dichloromethane (50 ml) were added, and the heterogeneous solution cooled to 0°C. A solution of $NaBH_4$ (0.76 g; 20 mmol) in 2M NaOH (10 ml) was added dropwise, accompanied by vigorous stirring which was maintained for *ca* 30 minutes. The solution was filtered through celite to remove mercury, and the filtrate extracted with CH_2Cl_2 (3 x 30 ml) and the combined extracts dried over $MgSO_4$, and the solvent removed in vacuo, to give the δ-hydroxy nitrile in 40-60% yields.

5-Hydroxynonanenitrile from 1-hexene and acrylonitrile. ^{13}C *NMR*: 119.74, 70.83, 37.24, 35.81, 27.61, 21.71, 18.70, 17.06, 13.09. ^1H *NMR*: 3.9 (1H, m, C*H*OH), 2.37 (2H, t, CH_2CN), 1.20-2.03 (11H, m), 0.93 (3H, t, J = 6.9 Hz, CH_3). *Mass Spectrum*: 155 (M^+, 0), 154 (M^+-H, 0.8), 127 (6.9), 98 (31.8), 87 (25.3), 70 (13.7), 69 (73.8), 57 (20.6), 55 (37.7). Accurate Mass ((M-1) peak): 154.1242 (Calcd. for $C_9H_{17}NO$ = 154.1232).

5-Hydroxyoctanenitrile from 1-pentene and acrylonitrile. ^{13}C *NMR*: 119.68, 70.39, 39.59, 35.77,

21.61, 18.56, 16.96, 13.82. *^{1}H NMR*: 1.25-1.90 (9H, m), 0.89 (3H, t, J = 6.8 Hz, CH_3), 2.35 (2H, t, J = 7 Hz, CH_2CN), 3.69 (1H, m, CH-*OH*). *Mass Spectrum*: 141 (M^+, 0), 140 (M^+-H, 1.1), 113 (7.5), 98 (28.4), 73 (37.1), 69 (26.1), 57 (19.6), 55 (86.5), 54 (22.6). Accurate Mass (M-1) peak: 140.1072. (Calcd. for $C_8H_{15}NO$ = 140.1075).

The tetrahydropyranylethers of the above hydroxy nitriles were prepared in the normal way from dihydropyran in ether using either HCl or pyridinium p-toluenesulfonate as catalyst.

Grignard Additions to Hydroxy (and Protected) Hydroxy Nitriles: The following is illustrative. To the Grignard reagent from 4-bromo-1-butene (0.87 g; 6.5 mmol) and magnesium (0.16 g, 6.5 mmol) in dry tetrahydrofuran (15 ml) was added dropwise at 0°C, a solution of the protected nitrile (1.02 g, 4.3 mmol) in dry tetrahydrofuran (15 ml). After addition was complete, the reaction mixture was refluxed for at least one hour before a standard work-up procedure. This yielded the protected hydroxyenones as yellowish oils in moderate to good yields (60-80%), and generally further purification was not conducted prior to Hg(II) cyclisation and reduction to provide the spiroacetal product. However, in the case of the addition of *4-pentenylmagnesium bromide to 5-hydroxyoctanenitrile*, the resulting hydroxyenone, *10-hydroxytridec-1-en-6-one* was characterised spectroscopically. *^{13}C NMR*: 211.16, 137.91, 115.14, 71.06, 42.59, 41.83, 39.59, 36.79, 33.03, 22.77, 19.65, 18.76, 14.01. *^{1}H NMR*: 0.88 (3H, t), 1.25-1.45 (6H, m), 1.63-1.65 (4H, m), 2.00 (2H, m), 2.37-2.39 (4H, m), 3.53 (1H, m), 4.95 (2H, m), 5.73 (1H, m). *Mass spectrum*: 212 (M^+, 0), 194 (M^+-H_2O, 7.7), 140 (24.3), 97 (41.1), 83 (19.6), 82 (25.6), 69 (22.4), 67 (24.0), 55 (93.0).

(E,E)-2-n-Butyl-8-methyl-1,7-dioxaspiro[5.5]undecane (27): 5-Hydroxynonanenitrile described above was converted to a diastereomeric mixture of the tetrahydropyranylethers in the normal way. (Mass spectrum: 239 (M^+, 0), 138 (M^+-OTHP, 27.9) 101 (13.1), 85 (100)). Subsequent treatment with the Grignard reagent from 5-bromo-1-pentene in the manner described provided 10-hydroxytetradec-1-en-6-one (as the THP ether) (80%), as a diastereomeric mixture, characterised by its mass spectrum. (Mass Spectrum: 310 (M^+,0), 209 (M^+-OTHP, 11.2), 169 (9.6), 97 (19.3), 85 (100)). This protected hydroxyenone (0.42 g, 1.35 mmol) was dissolved in 1:1 aqueous THF (1% $HClO_4$) (15 ml) to which was added mercuric acetate (0.52 g, 1.63 mmol). After stirring for *ca* 24 hours, NaOH solution (2M, 10 ml), dichloromethane (15 ml), benzyltriethylammonium chloride (0.2 g) and sodiumborohydride (0.05 g) were added. Standard work-up provided the spiroacetal as a diastereomeric mixture (0.27 g, 88%), with the (E,E) greatly predominating.[2(a)] [EE:2EZ = 25:1]. The title compound (E,E)-(27) was separated from the two E,Z-diastereomers by preparative gas chromatography.

^{13}C NMR (C_6D_6): 95.93 (C6), 69.08 (C2), 65.26 (C8), 36.74 (C12), 36.01*, 35.79* (C5,C11), 33.29 (C9), 31.76 (C3), 28.42 (C13), 23.31 (C14), 22.20 (C16), 19.49* (C4), 19.36* (C10), 14.29 (C15). *^{1}H NMR*: 3.80 (1H, ddddd, J = 11.15, 6.21, 6.21, 6.21, 2.05; H8), 3.62 (1H, dddd, J = 11.14, 6.21, 6.21, 1.98; H2), 2.06 (1H, qt, J = 13.40, 4.28; H4a or H10a), 2.05 (1H, qt, J = 13.40, 4.28, H10a or H4a), 1.53-1.69 (2H, 2 x d of m, H5e, H11e), 1.37-1.46 (4H, m, H3e, H4e, H9e, H10e), 1.27-1.36 (8H, complex m, (some obscured), H5a, H11a, H12, H13, H14), 1.18 (3H, d, J = 6.82 Hz, H16), 1.12 (2H, overlapping qd, H3a, H9a), 0.91 (3H, t, J = 6.90 Hz, H15). *Mass Spectrum*: 226 (M^+, 8.9) 211 (M^+-CH_3, 5.9), 169 (M^+-C_4H_9, 12.2), 157 (18.7), 140 (19.5), 139 (18.9), 115 (86.4), 112 (60.5), 97 (45.6), 69 (39.4), 55 (72.2), 43 (65.2), 41 (100). *Accurate Mass*: Calcd. for $C_{14}H_{26}O_2$ = 226.1894. observed = 226.1913.

(E,Z)- and (Z,E)-2-n-Butyl-8-methyl-1,7-dioxaspiro[5.5]undecane were obtained together by preparative gas chromatography and were characterised spectroscopically. *^{13}C NMR* (C_6D_6): Twenty-eight signals consistent with the two (E,Z) isomers, were observed. 94.80, 94.54 (C_6), 70.00, 67.21, 66.02, 63.53 (carbon adjacent to oxygen) and twenty-two signals between 11.79 and 34.37 ppm. *^{1}H NMR* (C_6D_6): 0.85, 0.93 (t, 2 x CH_3), 1.16, 1.19 (d, 2 x CH_3), 3.20, 3.49, 4.18, 4.37 (all multiplets, H adjacent to oxygen). *Mass spectrum*: 226 (M^+, 11.4) 211 (M^+-CH_3, 8.9) 169 (M^+-C_4H_9, 30.8), 157 (59.0), 156 (23.8), 139 (61.6), 115 (100), 112 (30.8), 97 (71.8), 69 (57.8), 55 (81.4).

2-Methyl-7-n-butyl-1,6-dioxaspiro[4.5]decane (28) was obtained in a similar way from 5-hydroxynonanenitrile (as THP ether) and the Grignard reagent from 4-bromo-1-butene, followed by cyclisation etc. *Mass spectrum*: (E,E-28)[15]: 212 (M^+, 0.4), 197 (6.0), 155 (M^+-C_4H_9, 14.1), 126 (12.2), 111 (13.2), 101 (100), 99 (9.5), 98 (66.4), 83 (19.7), 55 (43.3), 43 (35.7), 41 (40.2). *(E,Z-28)*: 212 (M^+, 0), 197 (M^+-CH_2. 7.1), 153 (10.9), 126 (9.2), 111 (12.4), 101 (100), 99 (9.0), 98 (56.3), 83 (21.8), 55 (50.5), 43 (43.7), 41 (53.3). GC-MS examination also revealed the presence of two diastereomers of *2-hydroxymethyl-7-n-butyl-1,6-dioxaspiro[4.5]decane*, which presumably resulted from oxygen intervention during the $NaBH_4$-mercuration step. *Mass spectrum*: *(E,E)*: 228 (M^+,0), 197 (M^+-CH_2OH, 37.3), 171 (M^+-C_4H_9, 9.3), 117 (100), 114 (96.1), 99 (63.9), 85 (44.7), 83 (39.1), 71 (38.9), 57 (40.7), 55 (75.9), 41 (78.8). *(E,Z)*: 228 (M^+,0), 197 (M^+-CH_2OH, 43.1), 171 (M^+-C_4H_9 ,7.0), 142 (18.4), 117 (99.1), 114 (100), 99 (71.9), 85 (56.6), 83 (39.5), 71 (43.3), 55 (84.8), 41 (85.1).

2-n-Propyl-8-Methyl-1,7-dioxaspiro[5.5]undecane (29): Treatment of 5-hydroxyoctanenitrile described above with the Grignard reagent from 5-bromo-1-pentene, followed by cyclisation and reduction, provided (29) as a mixture of diastereomers in which the (E,E) was very predominant, along with the two possible (E,Z) isomers.

(E,E) *^{13}C NMR (CDCl$_3$)*: 94.77, 75.02, 71.22, 37.30, 33.74, 33.20, 33.11, 27.53, 26.34, 22.85, 20.34, 18.11, 14.09. *^{1}H NMR* ($CDCl_3$): 3.79 (1H, m, H8), 3.51 (1H, m, H2), 1.17-2.05 (16H, complex m), 1.31 (3H, d, H15), 0.89 (3H, t, H14). *Mass Spectrum* :[15] 212 (M^+, 5.9), 197 (M^+-CH_3, 8.1), 169 (M^+-n-C_3H_7, 8.5), 143 (13.9), 140 (20.9), 125 (18.1), 115 (43.3), 112 (36.6), 97 (32.5), 55 (66), 43 (87.4), 42 (43.8), 41 (100).

(E,Z) (Isomer 1): 212 (M^+, 2.8) 197 (M^+-CH_3, 4.9), 169 (M^+-n-C_3H_7, 6.4), 125 (15.2), 115 (92.4), 114 (13.9), 112 (15.2), 97 (40.8), 69 (38.4), 55 (65.6), 43 (72.8), 42 (49.6), 41 (100).

(*E,Z*) (*Isomer 2*): 212 (M^+, 3.9), 197 (M^+-CH_3, 8.4), 169 ($M^+-n-C_3H_7$, 13.4), 143 (35.3), 125 (37.8), 115 (25.0), 112 (15.2), 97 (34.7), 69 (23.9), 55 (75.3), 43 (75.9), 42 (54.3), 41 (100).

Dienone (31) to Tricyclic spiroacetal (32)

1,6-Heptadien-3-one (31) resulted from treatment of acrolein with the Grignard reagent from 4-bromo-1-butene, followed by oxidation of the resulting dienol with pyridinium chlorochromate. The resulting (31) (b.p. 82°, 85 mm Hg) was used immediately without further purification in the reaction with 2-hydroxycyclohexylmercuric acetate and sodium borohydride. The resulting hydroxyenone was not purified, but cyclised in the normal way with Hg(II) and then reduced ($NaBH_4$). The diastereomers of (32) were isolated by preparative gas chromatography. *^{13}C NMR (Mixture)*: 106.13, 105.9 (spiro C), 76.91, 74.14, 73.86, 73.77 (carbon adjacent to oxygen), and twenty signals between 15 and 45 ppm. *^1H NMR*: 1.1-1.3 (d, CH_3 groups), 4.1 (m, H-C-O), 1.0-2.5 (other ring protons). *Mass Spectrum (Isomer 1)*: 210 (M^+, 2.9), 110 (15.3), 101 (100), 99 (12.7), 98 (90.9), 83 (20.0), 81 (15.8), 67 (21.8), 55 (42.7). (*Isomer 2*); 210 (M^+, 3.3), 110 (19.0), 101 (100), 100 (12.8), 98 (83.7), 83 (21.6), 81 (19.5), 67 (22.6), 55 (43.7).

2-Methyl-7-n-butyl-1,6-dioxaspiro[4.5]decane (28) (described above from the nitrile route) was also obtained when 1-hexene was substituted for cyclohexene in the sequence outlined immediately above. *Mass Spectrum* (*E,E*): 212 (M^+, 1.5), 197 (M^+-CH_3, 5.3), 1.55 ($M^+-n-C_4H_9$, 15.5), 126 (14.2), 111 (13.5), 101 (100), 99 (12.0), 98 (87.1), 83 (16.2), 69 (53.6), 41 (55.9). (*E,Z*): 212 (M^+, 1.4), 197 (M^+-CH_3, 7.5), 155 (14.1), 126 (11.7), 111 (11.7), 101 (100), 99 (7.2), 98 (49.3), 83 (13.3), 55 (19.7), 43 (12.6), 41 (11.9). (These mass spectra, should be compared with those given above for (28). Both sets are in satisfactory agreement with a published mass spectrum).[15]

2-Methyl-7-n-propyl-1,6-dioxaspiro[4.5]decane (30) resulted from the above sequence (using conjugate addition to 1,6-heptadien-3-one) when 1-pentene was the initial alkene. A diastereomeric mixture of spiroacetals was again obtained.
Mass Spectrum: (*E,E*): 198 (M^+,2.5), 183 (1.7), 155 (21.3), 126 (16.1), 111 (20.5), 101 (100), 100 (17.3), 99 (16.4), 98 (81.7), 97 (14.3), 83 (36.3), 55 (56.0), 43 (45.0), 41 (38.5). (*E,Z*): 198 (M^+,2.6), 183 (1.8), 155 (20.7), 126 (15.2), 111 (22.1), 101 (100), 100 (19.3),99 (16.6), 98 (77.7), 97 (14.0), 83 (43.8), 55 (61.9), 43 (50.4), 41 (45.9).

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