Pergamon

Tetrahedron, Vol. 52, No. 5, pp. 1797-1810, 1996

0040-4020/96 $15.00 + 0.00

0040-4020(95)01014-9

Polychlorinated Materials as a Source of Polyanionic Synthons

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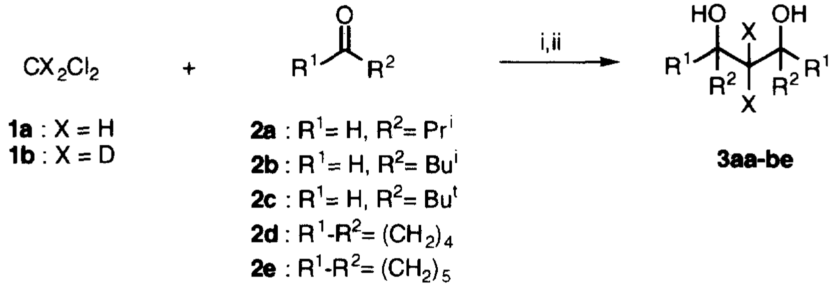
Abstract: The reaction of dichloromethane (**1a**) or dichlorodideuteriomethane (**1b**) with an excess of lithium powder (1:7 molar ratio) and a catalytic amount of DTBB (5 mol %) in the presence of a carbonyl compound **2** (1:2 molar ratio) in THF at -40°C yields, after hydrolysis, the corresponding 1,3-diols **3** in moderate yields. The process is applied to other *gem*-dichlorinated materials such as 7,7-dichloro[4.1.0]heptane (**4**), 1,1-dichlorotetramethylcyclopropane (**7**) and dichloromethyl methyl ether (**10**), using pivalaldehyde as electrophile. Starting from 1,1,1-trichlorinated compounds or tetrachloromethane (**14**) and using chlorotrimethylsilane as electrophile at temperatures ranging between -80 and -90°C, the corresponding polysilylated compounds **15-17** are prepared applying the mentioned methodology.

INTRODUCTION

The use of organolithium reagents in synthetic organic chemistry represents one of the most powerful methodologies, above all in carbon-carbon bond formation reactions[1]. When the organolithium intermediate contains two lithium atoms at the same carbon atom[2] the corresponding species are, in general, rare and very unstable. Thus, for instance, the preparation of dilithiomethane[3,4], the simplest *gem*-dichloroalkane, has been carried out by pyrolysis of methyllithium[5] or by a mercury-lithium transmetallation process[6]. The direct replacement of halogen (bromine[7] or chlorine[8]) with lithium, which is the most commonly used method for the synthesis of organolithium compounds is not applicable, in general[9a], to the synthesis of *gem*-dilithiated molecules: the α-elimination of lithium halide after the first chlorine-lithium exchange gives a carbene, this process being faster than the second lithiation[7-9]. On the other hand, and continuing our interest on lithiation processes at low temperatures[10], we have recently developed a new arene-catalysed lithiation procedure[11], which permits the preparation of very reactive oxygenated or nitrogenated functionalised organolithium compounds[12] starting from chlorinated materials[13] or saturated heterocycles[14]. Using this methodology new ways for organolithium compounds have been found starting from non-halogenated materials[15]. In addition, some 1,n-dilithiated (n>1) synthons have been prepared from the corresponding dichlorinated precursors and reacted with electrophiles under Barbier-type reaction conditions[16]. In the present paper we report the application of the above mentioned methodology for the transformation of *gem*-dichloro compounds[17] or more chlorinated molecules into the corresponding polyfunctionalised compounds by *in situ* reaction with electrophilic reagents[18].

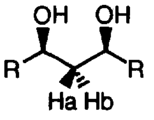
RESULTS AND DISCUSSION

The reaction of dichloromethane (**1a**) with an excess of litthium powder (1:7 molar ratio) and a catalytic amount of 4,4'-di-*tert*-butylbiphenyl (DTBB; 5 mol %) in the presence of a carbonyl compound **2** [Pr^{i}CHO, Bu^{i}CHO, Bu^{t}CHO, $(CH_2)_4CO$, $(CH_2)_5CO$; 1:2 molar ratio] in tetrahydrofuran at -40°C led, after hydrolysis with water, to the corresponding 1,3-diols **3aa-ae** (Scheme 1 and Table 1, entries 1-5). All reactions gave a small amount (<15%) of the corresponding pinacol except in the case of using isopentanal (**2b**) in which a 31% of pinacol was isolated; separation of products **3** and pinacols was carried out by careful flash chromatography. When cyclopentanone (**2d**) or cyclohexanone (**2e**) were used as electrophiles 1-methylcyclopentanol or 1-methylcyclohexanol were detected by GLC in 15 and 25% yield, respectively. When dichlorodideuteriomethane (**1b**) was used as starting material, instead of dichloromethane (**1a**), the corresponding dideuteriated 1,3-diols **3ba-be** were isolated under the same reaction conditions, the process having, as expected, the same characteristics in both cases (Scheme 1 and Table 1, entries 6-10).

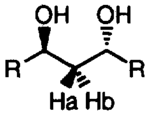


Scheme 1. *Reagents and conditions*: i, Li powder (1:7 molar ratio), DTBB cat. (5 mol %), THF, -40°C; ii, H_2O.

Once diastereoisomers **3aa-ac** were separated by flash chromatography, their stereochemistry was assigned unequivocally on the basis of NMR data taking into accout symmetry considerations. Thus, whilst in the *anti* compounds (C_2 symmetry) protons H_a and H_b are chemically but not magnetically equivalents (homotopic), showing the same chemical shifts, in the case of the *syn* products (plan of symmetry) $\delta_a \neq \delta_b$ with a geminal coupling constant of 14-15 Hz (see experimental), so both protons are diastereotopic. For dideuteriated diols **3ba-bc** the stereochemistry was assigned by analogy with the corresponding non-deuteriated congeners **3aa-ac**.



syn-**3aa-ac**



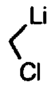
anti-**3aa-ac**

Table 1. Preparation of Diols **3**

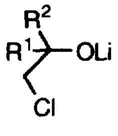
Entry	Starting material	Carbonyl compound	Product[a] no.	X	R^1	R^2	yield (%)[b]	*anti/syn* ratio[c] [mp (°C)][d]
1	**1a**	**2a**	**3aa**	H	H	Pr^i	52	5 [79-80]/2 [oil]
2	**1a**	**2b**	**3ab**	H	H	Bu^i	35	3 [111-112]/2 [oil]
3	**1a**	**2c**	**3ac**	H	H	Bu^t	61	3 [-[e]]/2 [98-102]
4	**1a**	**2d**	**3ad**	H	-$(CH_2)_4$-		27	[80-82]
5	**1a**	**2e**	**3ae**	H	-$(CH_2)_5$-		25	[100-101]
6	**1b**	**2a**	**3ba**	D	H	Pr^i	57	5 [79]/2 [oil]
7	**1b**	**2b**	**3bb**	D	H	Bu^i	45[f]	3 [110-111]/2 [oil]
8	**1b**	**2c**	**3bc**	D	H	Bu^t	61	3 [-[e]]/2 [98-100]
9	**1b**	**2d**	**3bd**	D	-$(CH_2)_4$-		32	[80-81]
10	**1b**	**2e**	**3be**	D	-$(CH_2)_5$-		25	[101]

[a] All isolated products **3** were $\geq$95% pure (GLC and 300 MHz ^{1}H NMR). [b] Isolated yield of pure compounds **3** after flash chromatography (silica gel, hexane/ethyl acetate). [c] Diastereoisomers ratio after isolation of each component by flash chromatography; the stereochemistry was deduced from NMR data (see text). [d] From chloroform. [e] Sublimates; in closed capillary mp $\approx$150°C (see ref 18). [f] This reaction was peformed in THF at -78°C (compare to entry 2).

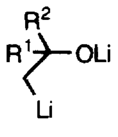
From a mechanistic point of view, and taking dichloromethan as example, we think that after the first lithiation a carbenoide of the type **I** is obtained[19], which in the presence of the carbonyl compound **2** undergoes mainly a rapid condensation (instead of the corresponding α-elimination reaction) to give a chlorohydrine salt of the type **II**[20]. The further lithiation of intermediate **II** affords a very reactive β-alkoxide organolithium species **III**[21], which in the presence of the electrophile yields the dialkoxide **IV** and, after hydrolysis, the obtained products **3**. The transformation **III**→**IV** is a crucial step due to the great instability of intermediate **III**: in absence of the electrophile it decomposes, even at -78°C, to give either proton abstraction[22] (yielding, for instance, the above mentioned 1-methylcycloalkanols as by products when cycloalkanones **2d** and **2e** were used as electrophiles) or β-elimination (giving olefins)[23]. The extrem instability of species **I** and **III** can explain the modest yields obtained for 1,3-diols **3**.



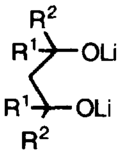
I



II

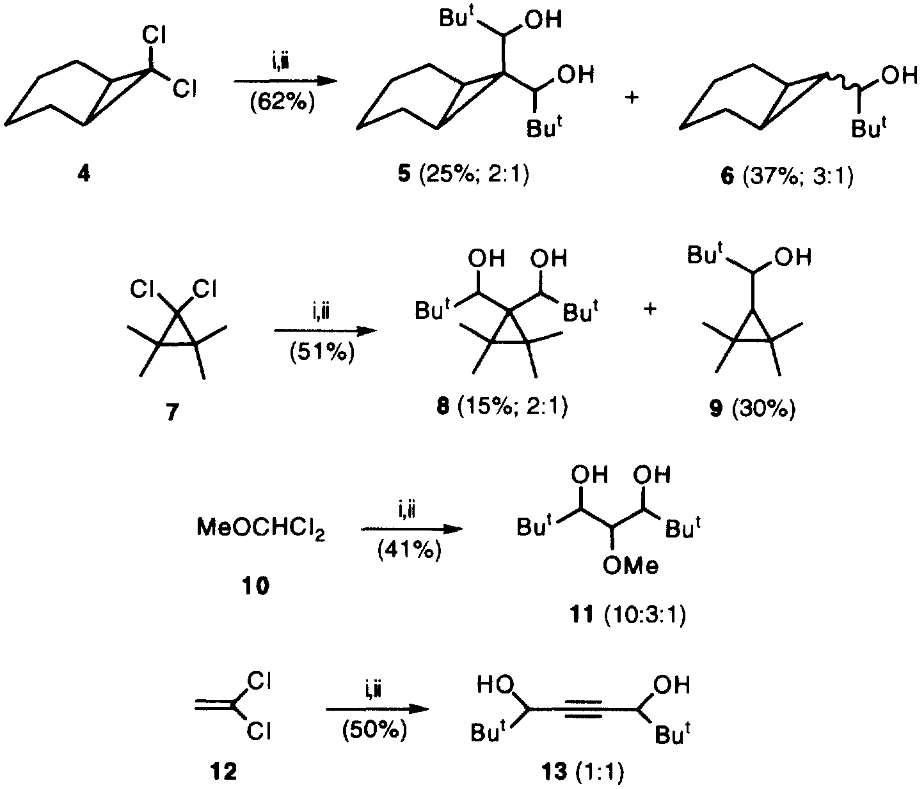


III



IV

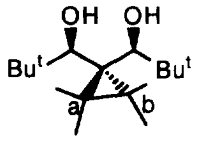
The use of more substituted *gem*-dichlorinated starting materials was studied in order to know the scope of the reaction shown in Scheme 1. In general, in spite of the global yields are comparable as for diols **3**, we observed important amounts of by-products resulting from a proton abstraction of intermediates of the type **III**: as expected, the substitution at the carbanionic centre increases the instability of the corresponding intermediate. Thus, for instance, starting from dichlorinated cyclopropanes **4** and **7** and using pivalaldehyde as electrophile, together with the expected 1,3-diols **5** and **8**, the corresponding alcohols **6** and **9** were also, respectively obtained (Scheme 2).



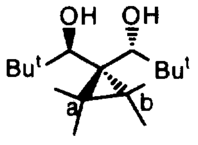
Scheme 2. *Reagents and conditions*: i, Bu^{t}CHO, Li powder (1:7 molar ratio), DTBB cat. (5 mol %), THF, -40°C; ii, H_2O.

The stereochemistry of diastereoisomeric 1,3-diols **8** was deduced by ^{13}C NMR considering (as for diols **3**) symmetry properties: whilst for the *anti* isomer both cyclopropanic carbon atoms Ca and Cb are homotopic giving one only signal, in the corresponding *syn* derivative the same carbon atoms are diastereotopic giving two different signals (see below).

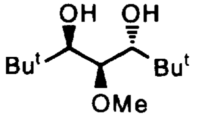
It is also possible to use functionalised *gem*-dichlorinated starting materials such as dichloromethyl methyl ether (**10**). Under the same reaction conditions as above and with pivalaldehyde as electrophile compound **11** was isolated as a mixture of diastereoisomers (Scheme 2), the major one having the relative *syn,anti* configuration. This stereochemistry is in agreement with the appearance of two different singlets in ^1H NMR for the *tert*-butyl groups: for the other possible diastereoisomers (1,3-*syn* stereochemistry) both signals should be only one.



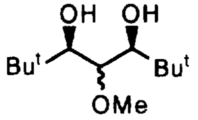
syn-**8**



anti-**8**



syn,anti-**11**

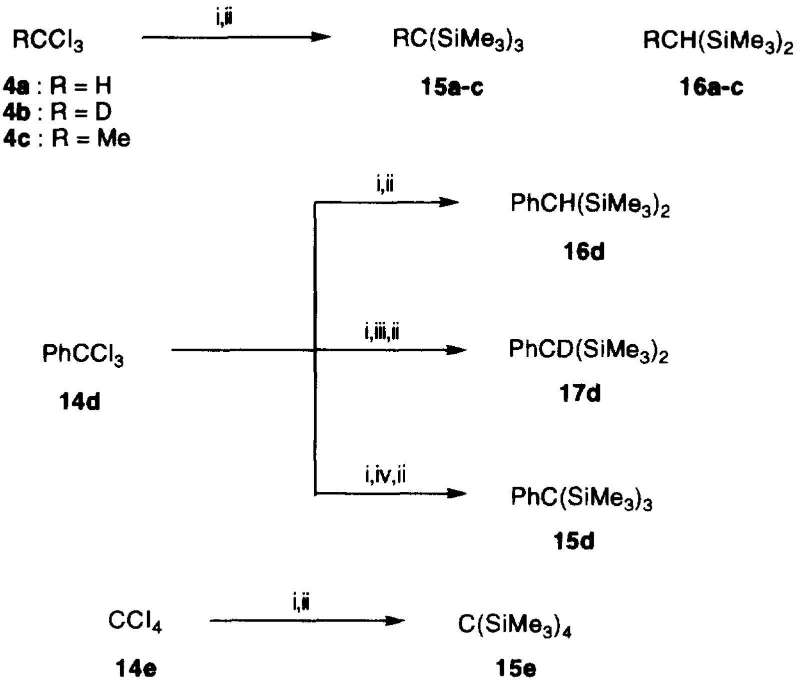


1,3-*syn*-**11**

The methodology shown in Scheme 1 was also applied to the *gem*-dichloroolefin **12**; in this case a mixture of diastereoisomers **13** was obtained as the only reaction products, when pivalaldehyde was used as testing electrophile (Scheme 2). An explanation to this behaviour could be that after the first lithiation an intermediate of the type **I** is formed, which undergoes α-elimination and the corresponding carbene suffers rearrangement (1,2-hydrogen shift) to give acetylene[24]. The final lithium promoted dideprotonation of this material followed by reaction with the electrophile present in the reaction medium affords the obtained acetylenic diol **13**.

Finally, we extended the former study with dichloro compounds to more chlorinated materials. We used chlorotrimethylsilane as electrophile in order to simplify the structure of the reaction products, so persilylated compounds were obtained[25]. The only difference with the protocol shown in Schemes 1 and 2 is that the temperature in the present case has to be kept between -90 and -80°C in order to avoid the indesirable lack of persilylation. Thus, starting from trichloro compounds **14a-c**, trisilylated products **15a-c** were isolated, slightly contaminated (<11%) with the corresponding disilylated compounds **16a-c** (GLC-MS) (Scheme 3 and Table 2, entries 1-3). The use of α,α,α-trichlorotoluene (**14d**) under the same reaction conditions yielded product **16d**, as the only reaction product (Scheme 3 and Table 2, entry 5). In order to obtain mainly the trisilylated derivative **15d** was necessary to allow the temperature to rise to 0°C before the hydrolysis step (Scheme 3 and Table 2, entry 4). We suppose that steric hindrance is responsible of this behaviour: the big size of the phenyl group difficults the incorporation of the third silylated group at low temperature[27]. This hypothesis was confirmed by carrying out the deuteriolysis with deuterium oxide at low temperature after the corresponding silylation, so deuteriated product **17d** was the only isolated reaction product: the small size of deuterium allows its incorporation at low temperature to the corresponding carbanion (Scheme 3 and Table 2, entry 6). Finally, we performed the same reaction with carbon tetrachloride[28]: four silyl groups were incorporated to the carbon atom even at low temperature and only a small amount of the corresponding trisilylated derivative **15a** was detected by tandem GLC-MS (Scheme 3 and Table 2, entry 7). This last result would mean that, at least in this reaction, the steric hindrance of phenyl group is bigger than that of the trimethylsilyl one[27].

Concerning a possible mechanism for the preparation of persilylated compounds, we believe that the reaction takes place through successive lithiation-condensation with the electrophile steps.



Scheme 3. *Reagents and conditions*: i, Me$_3$SiCl, Li powder (1:20 molar ratio), DTBB cat. (5 mol %), THF, -90 to -80°C; ii, H$_2$O; iii, D$_2$O; iv, -80 to 0°C.

Table 2. Preparation of Compounds **15-17**

Entry	Starting material	Product[a]			
		No.	R	Yield (%)[b]	R_f[c]
1	**14a**	**15a**	H	93 (<5)	0.63
2	**14b**	**15b**	D	92[d] (<5)	0.63
3	**14c**	**15c**	Me	64 (11)	0.65
4	**14d**	**15d**[e]	Ph	51 (19)	0.56
5	**14d**	**16d**[e]	-	98	0.57
6	**14d**	**17d**[e]	-	98[d]	0.57
7	**14e**	**15e**	Me$_3$Si	80 (9)[f]	0.61

[a] All products **15-17** were pure (≥94% from GLC and 300 MHz ^{1}H NMR). [b] Isolated yield after flash chromatography (silica gel, hexane) or recrystallisation, based on the chlorinated starting material **14**; in parenthesis GLC yields for the corresponding by-product **16**, characterised by tandem GLC-MS. [c] Silica gel, hexane. [d] >98% deuterium from MS and 300 MHz ^{1}H NMR. [e] See text. [f] GLC yield of compound **15a**.

As a conclusion, we think that the methodology described in this paper, DTBB-catalysed lithiation at low temperature under Barbier-type reaction conditions, allows the introduction of as many electrophilic fragments as chlorine atoms are present in the polychlorinated starting material.

EXPERIMENTAL PART

General.- For general information, see ref 16g. Starting dichlorinated materials **4**[29] and **7**[30] were prepared according to the literature procedures. The other starting materials as well as the electrophiles were commercially available and were used as received.

DTBB-Catalysed Lithiation of Polychlorinated Compounds **1**, **4**, **7**, **10**, **12** *and* **14** *Under Barbier-Type Reaction Conditions. Isolation of Products* **3**, **5**, **6**, **8**, **9**, **11**, **13** *and* **15-17**. *General Procedure.*- To a blue suspension of lithium powder (*ca.* 100 mg, 14 mmol) and DTBB (26 mg, 0.1 mmol, 5 mol %) in THF (5 ml) was slowly added a solution of the corresponding dichlorinated material (2 mmol) and the corresponding carbonyl compound (4 mmol) in THF (5 ml) during *ca.* 45 min at -40°C. For trichlorinated starting materials (**14a-db**) and carbon tetrachloride (**14e**) the **14**:lithium powder:chlorotrimethylsilane ratio was *ca.* 1:20:3 or 4, the reaction temperature ranging between -90 and -80°C and the reaction time being about 2 h. After the addition the reaction mixture was stirred for 10 additional min at the same temperature in each case[31]. Then, it was hydrolysed with water (4 ml), neutralised with 2 N hydrochloric acid and extracted with diethyl ether (2x10 ml). The organic layer was dried with anhydrous Na_2SO_4, evaporated (15 Torr) and the resulting residue was purified by flash chromatography (silica gel, hexane/ethyl acetate) to give the expected title compounds. Yields and some physical data (mp or R_f values) are included in Tables 1 and 2, as well as in Scheme 2; other physical, spectroscopic and analytical data, as well as literature references for known compounds follows.

(3R, 5R*)-2,6-Dimethyl-3,5-heptanediol* (*anti*-**3aa**)[32]: R_f = 0.37 (hexane/ethyl acetate: 3/2); ν (film) 3300 (OH), 1045, 1005 and 985 cm^{-1} (C-O); δ_H 0.89 (6H, d, J=6.7, $C\mathit{H}_3CHCH_3$), 0.94 (6H, d, J=6.7, $CH_3CHC\mathit{H}_3$), 1.57 (2H, m, CH_2), 1.68 (2H, deformed octet, 2x$CH_3C\mathit{H}CH_3$), 2.42 (2H, br s, 2xOH) and 3.63 (2H, m, 2xHCO); δ_C 18.05 (2C, 2x$\mathit{C}H_3CHCH_3$), 18.65 (2C, 2x$CH_3CH\mathit{C}H_3$), 33.7 (2C, 2x$CH_3\mathit{C}HCH_3$), 36.5 (CH_2) and 74.15 (2C, 2xHCO); *m/z* 142 (M^+-H_2O, 0.2%), 117 (14), 99 (32), 81 (57), 73 (87), 71 (14), 70 (30), 57 (18), 56 (13), 55 (65), 45 (22), 43 (100) and 41 (55) (Found: C, 67.2; H, 12.5. $C_9H_{20}O_2$ requires C, 67.45; H, 12.58).

(3R, 5S*)-2,6-Dimethyl-3,5-heptanediol* (*syn*-**3aa**)[32]: R_f = 0.43 (hexane/ethyl acetate: 3/2); ν (film) 3340 (OH), 1050 and 1010 cm^{-1} (C-O); δ_H 0.92 (12H, d, J=7.0, 2x $C\mathit{H}_3CHC\mathit{H}_3$), 1.41 (1H, dt, J=14.4, 10.2, $CH\mathit{H}$), 1.59 (1H, dt, J=14.4, 1.2, $C\mathit{H}H$), 1.67 (2H, deformed octet, 2x$CH_3C\mathit{H}CH_3$), 2.95 (2H, br s, 2xOH) and 3.62 (2H, ddd, J= 10.2, 5.1, 1.2, 2xHCO); δ_C 17.35 (2C, 2x$\mathit{C}H_3CHCH_3$), 18.35 (2C, 2x$CH_3CH\mathit{C}H_3$), 34.25 (2C, 2x$CH_3\mathit{C}HCH_3$), 35.85 (CH_2) and 78.15 (2C, 2xHCO); *m/z* 117 (M^+-CH_3CHCH_3, 15 %), 99 (24), 81 (42), 73 (44), 71 (13), 70 (15), 57 (22), 56 (19), 55 (67), 45 (26), 43 (100) and 41 (68).

(3R, 5R*)-4,4-Dideuterio-2,6-dimethyl-3,5-heptanediol* (*anti*-**3ba**): R_f= 0.37 (hexane/ethyl acetate: 3/2), mp 79°C; ν (film) 3300 (OH), 1045, 1005 and 985 cm^{-1} (C-O); δ_H 0.89 (6H, d, J=6.7, $C\mathit{H}_3CHCH_3$), 0.94 (6H, d, J=6.7, $CH_3CHC\mathit{H}_3$), 1.68 (2H, deformed octet, 2x$CH_3C\mathit{H}CH_3$), 2.91 (2H, br s, 2xOH) and 3.61 (2H, d, J=6.4, 2xHCO); δ_C 18.1 (2C, 2x$\mathit{C}H_3CHCH_3$), 18.6 (2C, 2x$CH_3CH\mathit{C}H_3$), 33.6 (2C, 2x$CH_3\mathit{C}HCH_3$), 35.7 (1C, quintet, $J_{C\text{-}D}$= 18, CD_2) and 73.9 (2C, 2xHCO); *m/z* 144 (M^+-H_2O, 0.2%), 101 (28), 83 (40), 73 (86), 72 (33), 58 (11), 57 (31), 56 (11), 55 (43), 47 (16), 45 (37), 44 (21), 43 (100), 42 (13) and 41 (51) (Found: C, 66.5; H/D, 12.4. $C_9H_{18}D_2O_2$ requires C, 66.62; H/D[33], 12.42).

(3R, 5S*)-4,4-Dideuterio-2,6-dimethyl-3,5-heptanediol* (*syn*-**3ba**): R_f = 0.43 (hexane/ethyl acetate: 3/2); ν (film) 3340 (OH), 1050 and 1005 cm^{-1} (C-O); δ_H 0.92 (12H, d, J=7.0, 2x$C\mathit{H}_3CHC\mathit{H}_3$), 1.67 (2H, deformed

octet, $2xCH_3C\mathit{H}CH_3$), 3.40 (2H, br s, 2xOH) and 3.60 (2H, d, *J*= 5.1, 2xHCO); δ_C 17.4 (2C, $2x\mathit{C}H_3CHCH_3$), 18.3 (2C, $2xCH_3CH\mathit{C}H_3$), 34.2 (2C, $2xCH_3\mathit{C}HCH_3$), 34.95 (1C, quintet , $J_{C\text{-}D}$= 19, CD_2) and 78.0 (2C, 2xHCO); *m/z* 144 (M^+-H_2O, 0.1%), 119 (20), 101 (39), 83 (62), 73 (76), 72 (34), 58 (11), 57 (37), 56 (13), 55 (38), 47 (13), 45 (36), 44 (29), 43 (100), 42 (13) and 41 (54).

*(4*R**, 6*R**)-2,8-Dimethyl-4,6-nonanediol* (*anti*-**3ab**): R_f = 0.36 (hexane/ethyl acetate: 3/2); ν (film) 3270 (OH), 1150, 1125, 1075 and 1045 cm^{-1} (C-O); δ_H 0.93 (6H, d, *J*=6.6, $C\mathit{H}_3CHCH_3$), 0.93 (6H, d, *J*=6.7, $CH_3CHC\mathit{H}_3$), 1.24 (2H, ddd, *J*=13.7, 8.4, 4.8, CHCH*H*CO), 1.50 (2H, ddd, *J*=13.7, 8.5, 5.8, CHC*H*HCO), 1.58 (2H, m, $COCH_2CO$), 1.75 (2H, deformed septet, $2xCH_3C\mathit{H}CH_3$), 1.85 (2H, br s, 2xOH) and 4.05 (2H, m, 2xHCO); δ_C 22.25 (2C, $2x\mathit{C}H_3CHCH_3$), 23.25 (2C, $2xCH_3CH\mathit{C}H_3$), 24.65 (2C, $2xCH_3\mathit{C}HCH_3$), 43.3 ($CO\mathit{C}H_2CO$), 46.65 (2c, $CH\mathit{C}H_2CO$) and 67.45 (2C, 2xHCO); *m/z* 187 (M^+-1, 0.8%), 131 (15), 113 (10), 95 (89), 87 (33), 85 (14), 84 (45), 71 (10), 69 (100), 57 (31), 56 (36), 55 (12), 45 (29), 44 (14), 43 (90), 42 (12) and 41 (61) (Found: C, 69.8; H, 12.8. $C_{11}H_{24}O_2$ requires C, 70.16; H, 12.85).

*(4*R**, 6S*)-2,8-Dimethyl-4,6-nonanediol* (*syn*-**3ab**): R_f = 0.40 (hexane/ethyl acetate: 3/2); ν (film) 3340 (OH), 1150, 1080 and 1060 cm^{-1} (C-O); δ_H 0.92 (6H, d, *J*=6.7, $C\mathit{H}_3CHCH_3$), 0.92 (6H, d, *J*=6.5, $CH_3CHC\mathit{H}_3$), 1.10-1.30, 1.35-1.55 (6H, 2m, $3xCH_2$), 1.75 (2H, deformed septet, $2xCH_3C\mathit{H}CH_3$), 2.45 (2H, br s, 2xOH) and 3.95 (2H, dddd, *J*=9.7, 8.5, 4.6, 2.4, 2xHCO); δ_C 22.15 (2C, $2x\mathit{C}H_3CHCH_3$), 23.3 (2C, $2xCH_3CH\mathit{C}H_3$), 24.25 (2C, $2xCH_3\mathit{C}HCH_3$), 44.0 ($CO\mathit{C}H_2CO$), 47.45 (2c, $CH\mathit{C}H_2CO$) and 71.2 (2C, 2xHCO); *m/z* 155, (M^+-H_2O-CH_3, 1 %), 131 (23), 113 (17), 95 (96), 87 (29), 85 (14), 84 (41), 71 (10), 69 (100), 57 (30), 56 (28), 55 (14), 45 (28), 44 (14), 43 (95), 42 (11) and 41 (64).

*(4*R**, 6*R**)-5,5-Dideuterio-2,8-dimethyl-4,6-nonanediol* (*anti*-**3bb**): R_f = 0.36 (hexane/ethyl acetate: 3/2); ν (film) 3270 (OH), 1150, 1125, 1075 and 1045 cm^{-1} (C-O); δ_H 0.92 (6H, d, *J*=6.4, $C\mathit{H}_3CHCH_3$), 0.93 (6H, d, *J*=6.7, $CH_3CHC\mathit{H}_3$), 1.24 (2H, ddd, *J*=13.7, 8.4, 4.9, 2xCHCH*H*CO), 1.49 (2H, ddd, *J*=13.7, 8.5, 5.8, CHC*H*HCO), 1.74 (2H, deformed septet, $2xCH_3C\mathit{H}CH_3$), 2.51 (2H, br s, 2xOH) and 4.03 (2H, dd, *J*=8.5, 4.9, 2xHCO); δ_C 22.25 (2C, $2x\mathit{C}H_3CHCH_3$), 23.25 (2C, $2xCH_3CH\mathit{C}H_3$), 24.6 (2C, $2xCH_3\mathit{C}HCH_3$), 42.45 (1C, quintet, $J_{C\text{-}D}$= 19, CD_2), 46.6 (2c, $CH\mathit{C}H_2CO$) and 67.25 (2C, 2xHCO); *m/z* 189 (M^+-1, 0.1%), 133 (30), 115 (16), 97 (100), 87 (46), 86 (79), 85 (14), 71 (18), 69 (89), 57 (25), 56 (16), 45 (20), 44 (11), 43 (47) and 41 (30) (Found: C, 68.9; H/D, 12.5. $C_{11}H_{22}D_2O_2$ requires C, 69.42; H/D[33], 12.71).

*(4*R**, 6S*)-5,5-Dideuterio-2,8-dimethyl-4,6-nonanediol* (*syn*-**3bb**): R_f = 0.40 (hexane/ethyl acetate: 3/2); ν (film) 3340 (OH), 1150, 1080 and 1050 cm^{-1} (C-O); δ_H 0.92 (6H, d, *J*=6.7, $C\mathit{H}_3CHCH_3$), 0.92 (6H, d, *J*=6.4, $CH_3CHC\mathit{H}_3$), 1.21 (2H, ddd, *J*=13.7, 8.6, 4.9, 2xCHCH*H*CO), 1.44 (2H, ddd, *J*=13.7, 8.6, 5.8, 2xCHC*H*HCO) 1.75 (2H, deformed septet, $2xCH_3C\mathit{H}CH_3$), 3.25 (2H, br s, 2xOH) and 3.93 (2H, dd, *J*=8.6, 4.9, 2xHCO); δ_C 22.1 (2C, $2x\mathit{C}H_3CHCH_3$), 23.25 (2C, $2xCH_3CH\mathit{C}H_3$), 24.2 (2C, $2xCH_3\mathit{C}HCH_3$), 43.1 (1C, quintet, $J_{C\text{-}D}$= 19, CD_2), 47.35 (2c, $CH\mathit{C}H_2CO$) and 71.0 (2C, 2xHCO); *m/z* 189 (M^+-1, 0.1%), 133 (30), 115 (12), 97 (100), 87 (42), 86 (50), 85 (13), 71 (15), 69 (75), 57 (18), 56 (13), 45 (15), 43 (35) and 41 (24).

*(3*R**, 5*R**)-2,2,6,6-Tetramethyl-3,5-heptanediol* (*anti*-**3ac**): R_f = 0.37 (hexane/ethyl acetate: 3/2); ν(film) 3380, 3285 (OH), 1050 and 1000 cm^{-1} (C-O); δ_H 0.90 [18H, s, $2x(CH_3)_3C$],1.42 (2H, m, CH_2), 1.64 (2H, br s, 2xOH) and 3.52 (2H, m, 2xHCO); δ_C 25.7 (6C, $2x(\mathit{C}H_3)_3C$), 32.6 (CH_2), 34.8 (2C, $2x(CH_3)_3\mathit{C}$) and 76.2 (2C, 2xHCO); *m/z* 188 (M^+, 0.2%), 131 (17), 113 (35), 95 (100), 87 (83), 85 (11), 84 (15), 71 (38), 70 (10), 69 (58), 57 (52), 45 (14), 43 (54) and 41 (45) (Found: C, 69.9; H, 12.8. $C_{11}H_{24}O_2$ requires C, 70.16; H,

12.85).

(3R, 5S*)-2,2,6,6-Tetramethyl-3,5-heptanediol* (*sin*-**3ac**)[34]: R_f = 0.55 (hexane/ethyl acetate: 3/2); ν (film) 3370 (OH), 1090, 1060 and 1010 cm^{-1} (C-O); δ_H 0.90 (18H, s, 2x$(CH_3)_3C$), 1.27 (1H, dt, J=14.4, 10.4, CH*H*), 1.72 (1H, dt, J=14.4, 1.5, C*H*H), 3.41 (2H, br s, 2xOH) and 3.43 (2H, dd, J=10.4, 1.5, 2xHCO); δ_C 25.55 (6C, 2x$(CH_3)_3C$), 30.95 (CH_2), 35.0 (2C, 2x$(CH_3)_3C$) and 81.45 (2C, 2xHCO); *m/z* 188 (M^+, 0.1%), 131 (31), 113 (41), 95 (100), 87 (28), 71 (18), 68 (34), 57 (36), 43 (27) and 41 (35) (Found: C, 70.0; H, 12.8. $C_{11}H_{24}O_2$ requires C, 70.16; H, 12.85).

(3R, 5R*)-4,4-Dideuterio-2,2,6,6-Tetramethyl-3,5-heptanediol* (*anti*-**3bc**): R_f = 0.37 (hexane/ethyl acetate: 3/2); ν (film) 3380, 3285 (OH), 1050 and 1000 cm^{-1} (C-O); δ_H 0.91 (18H, s, 2x$(CH_3)_3C$), 1.63 (2H, br s, 2xOH) and 3.53 (2H, s, 2xHCO); δ_C 25.7 (6C, 2x$(CH_3)_3C$), 31.95 (1C, quintet, $J_{C\text{-}D}$= 19, CD_2), 34.8 (2C, 2x$(CH_3)_3C$) and 76.15 (2C, 2xHCO); *m/z* 189 (M^+-1, 0.1%), 133 (23), 115 (38), 97 (100), 87 (84), 86 (17), 71 (75), 70 (19), 69 (57), 58 (11), 57 (97), 45 (34), 44 (14), 43 (76), 42 (11) and 41 (74) (Found: C, 69.2; H/D, 12.6. $C_{11}H_{22}D_2O_2$ requires C, 69.42; H/D[33], 12.71).

(3R, 5S*)-4,4-Dideuterio-2,2,6,6-Tetramethyl-3,5-heptanediol* (*sin*-**3bc**): R_f= 0.55 (hexane/ethyl acetate: 3/2); ν (film) 3370 (OH), 1090, 1060 and 1010 cm^{-1} (C-O); δ_H 0.90 (18H, s, 2x$(CH_3)_3C$), 3.21 (2H, br s, 2xOH) and 3.44 (2H, s, 2xHCO); δ_C 25.55 (6C, 2x$(CH_3)_3C$), 30.5 (1C, quintet, $J_{C\text{-}D}$= 19, CD_2), 35.0 (2C, 2x$(CH_3)_3C$) and 81.55 (2C, 2xHCO); *m/z* 190 (M^+, 0.1%), 133 (22), 115 (31), 97 (100), 87 (50), 71 (53), 69 (41), 57 (71), 45 (22), 44 (13), 43 (65), 42 (10) and 41 (69) (Found: C, 69.8; H/D, 12.8. $C_{11}H_{22}D_2O_2$ requires C, 69.42; H/D[33], 12.71)..

1,1'-Methylenebis(cyclopentanol) (**3ad**): R_f= 0.33 (hexane/ethyl acetate: 3/2); ν (film) 3300 (OH), 1060 and 1020 cm^{-1} (C-O); δ_H 1.50-1.90 (16H, m, 8xring CH_2), 1.96 (2H, s, $COCH_2CO$) and 3.17 (2H, br s, 2xOH); δ_C 23.3 (4C), 41.35 (4C) (8xring CH_2), 48.8 ($COCH_2CO$) and 83.45 (2C, 2xCO); *m/z* 166 (M^+-H_2O, 8%), 109 (17), 85 (100), 84 (12), 83 (11), 82 (71), 71 (11), 67 (95), 57 (16), 56 (20), 55 (73), 43 (22), 42 (10) and 41 (33) (Found: C, 71.6; H, 10.9. $C_{11}H_{20}O_2$ requires C, 71.70; H, 10.94).

1,1'-Dideuteriomethylenebis(cyclopentanol) (**3bd**): R_f= 0.33 (hexane/ethyl acetate: 3/2): ν (film) 3300 (OH), 1060 and 1020 cm^{-1} (C-O); δ_H 1.50-1.90 (16H, m, 8xring CH_2), and 3.32 (2H, br s, 2xOH); δ_C 23.3 (4C), 41.25 (4C) (8xring CH_2), 47.9 (1C, quintet, $J_{C\text{-}D}$= 19, CD_2) and 83.35 (2C, 2xCO); *m/z* 186 (M^+, 0.2%), 168 (17), 139 (11), 125 (10), 110 (17), 96 (16), 86 (10), 85 (100), 84 (91), 83 (20), 73 (16), 68 (11), 67 (89), 57 (20), 56 (31), 55 (71), 43 (15), 42 (10) and 41 (25) (Found: C, 71.0; H/D, 10.6. $C_{11}H_{18}D_2O_2$ requires C, 70.92; H/D[33], 10.82).

1,1'-Methylenebis(cyclohexanol) (**3ae**): R_f= 0.47 (hexane/ethyl acetate: 3/2); ν (Nujol) 3320 (OH), 1165, 1150, 1090 and 980 cm^{-1} (C-O); δ_H 1.20-1.75 (20H, m, 10xring CH_2), 1.65 (2H, s, $COCH_2CO$) and 3.10 (2H, br s, 2xOH); δ_C 22.3 (4C), 25.6 (2C), 40.05 (4C) (10xring CH_2), 49.95 ($COCH_2CO$) and 73.25 (2C, 2xCO); *m/z* 212 (M^+, 2%), 194 (15), 151 (16), 114 (13), 110 (16), 99 (100), 96 (31), 81 (81), 79 (13), 71 (16), 70 (11), 69 (17), 67 (15), 55 (42), 43 (22), 42 (11) and 41 (27) (Found: C, 73.5; H, 11.4. $C_{13}H_{24}O_2$ requires C, 73.54; H, 11.39).

1,1'-Dideuteriomethylenebis(cyclohexanol) (**3be**): R_f = 0.47 (hexane/ethyl acetate: 3/2); ν (nujol) 3320 (OH), 1165, 1150, 1080 and 980 cm^{-1} (C-O); δ_H 1.20-1.75 (20H, m, 10xring CH_2), and 3.06 (2H, br s, 2xOH); δ_C 22.3 (4C), 25.6 (2C), 40.0 (4C) (10xring CH_2), 49.0 (1C, quintet, $J_{C\text{-}D}$= 18, CD_2) and 73.15 (2C, 2xCO); *m/z* 214 (M$^+$, 3%), 196 (12), 153 (15), 116 (19), 110 (21), 100 (10), 99 (100), 98 (58), 97 (12), 83 (20), 81 (65), 73 (12), 70 (15), 69 (20), 55 (35), 43 (14), 42 (10) and 41 (15) (Found: C, 72.8; H/D, 10.9. $C_{13}H_{22}D_2O_2$ requires C, 72.85; H/D[33], 11.28).

1,1'-(Bicyclo[4.1.0]heptane-7,7-diyl)bis-(2,2-dimethyl-1-propanol) (**5**), major diastereomer: R_f= 0.56 (hexane/ethyl acetate: 3/2), sublimates; ν (film) 3340 (OH), 1040 and 1000 cm^{-1} (C-O); δ_H 0.91 (9H, s, $(CH_3)_3C$), 1.11 (9H, s, $(CH_3)_3C$), 0.80-1.40 (5H, m, 2xring CH, 3H of ring CH_2), 1.58-1.70 (3H, m, 3H of ring CH_2), 1.80-2.10 (2H, m, ring CH_2), 2.37 (1H, d, *J*=5.1, OH), 3.07 (1H, d, *J*=5.6, OH), 3.31 (1H, d, *J*=5.6, HCO) and 4.23 (1H, d, *J*=5.1, HCO); δ_C 15.75 (ring CH), 18.65, 21.05, 21.9, 22.15 (4xring CH_2), 22.6 (ring CH), 27.2, 28.3 [2x3C, 2x(CH$_3$)$_3$C], 35.75 [$(CH_3)_3C$], 36.05 (CO*C*CO), 36.15 [$(CH_3)_3C$], 76.95 and 79.65 (2xHCO); *m/z* 267 (M$^+$-1, 0.3%), 235 (M$^+$-H_2O-CH_3, 2%), 193 (53), 175 (29), 147 (11), 135 (11), 133 (16), 121 (11), 119 (21), 109 (24), 107 (29), 105 (19), 95 (37), 93 (23), 91 (21), 83 (33), 81 (29), 79 (31), 77 (16), 71 (11), 69 (33), 67 (33), 57 (96), 55 (39), 53 (14), 43 (43) and 41 (100) (Found: C, 75.9; H, 12.0. $C_{17}H_{32}O_2$ requires C, 76.06; H, 12.02). Minor diastereomer: *m/z* 235 (M$^+$-H_2O-CH_3, 1%), 193 (72), 175 (30), 147 (10), 135 (13), 133 (22), 121 (10), 119 (20), 109 (18), 107 (24), 105 (17), 95 (35), 93 (21), 91 (17), 83 (32), 81 (33), 79 (35), 77 (14), 71 (13), 69 (38), 67 (31), 57 (90), 55 (37), 53 (14), 43 (40) and 41 (100).

1-{(7r)-Bicyclo[4.1.0]hept-7-yl}-2,2-dimethyl-1-propanol (*r*-**6**): R_f= 0.57 (hexane/ethyl acetate: 3/2), oil; ν (film) 3440 (OH), 1040 and 1000 cm^{-1} (C-O); δ_H 0.58 (1H, dt, *J*=9.1, 4.7, HCCO), 0.78 (2H, m, CH_2C*H*C*H*CH_2), 0.93 (9H, s, $(CH_3)_3C$), 1.05-1.30 (4H, m, 2xring CH_2), 1.35 (1H, br s, OH), 1.59 (2H, m, ring CH_2), 1.78 (2H, m, ring CH_2) and 2.48 (1H, d, *J*=9.1, HCO); δ_C 14.15, 17.5 (2xCH_2*C*H), 21.35, 21.55, 22.85, 23.5 (4xring CH_2), 26.05 [3C, (CH$_3$)$_3$C], 26.95 (H*C*HCO), 35.7 [$(CH_3)_3C$] and 84.8 (HCO); *m/z* 182 (M$^+$, 0.3%), 125 (100), 107 (14), 83 (14), 81 (26), 79 (30), 69 (10), 67 (14), 57 (94), 55 (22), 43 (14) and 41 (36).

1-{(7s)-Bicyclo[4.1.0]hept-7-yl}-2,2-dimethyl-1-propanol (*s*-**6**): *m/z* 182 (M$^+$, 0.1%), 125 (49), 107 (11), 83 (12), 81 (20), 79 (33), 69 (13), 67 (15), 57 (100), 55 (26), 53 (10), 43 (19) and 41 (46).

(1R,1'R*)-1,1'-(2,2,3,3-tetramethylcyclopropane-1,1-diyl)bis-(2,2-dimethyl-1-propanol)* (*anti*-**8**): R_f= 0.66 (hexane/ethyl acetate: 3/2), sublimates; ν (film) 3450 (OH), 1180, 1105, 1035 and 985 cm^{-1} (C-O); δ_H 1.12 (18H, s, 2x$(CH_3)_3C$), 1.14 (6H, s, 2xCH_3 of cyclopropyl), 1.17 (6H, s, 2xCH_3 of cyclopropyl), 1.28 (2H, s, 2xOH) and 3.63 (2H, s, 2xHCO); δ_C 19.3 (2C, *C*H$_3$CC*C*H$_3$), 23.3 (2C, *C*H$_3$CC*C*H$_3$), 27.3 (2C, CH$_3$*CC*CH$_3$), 29.65 [6C, 2x(CH$_3$)$_3$C], 36.0 [2C, 2x$(CH_3)_3C$], 36.7 (CO*C*CO) and 79.7 (2C, 2xHCO); *m/z* 237 (M$^+$-H_2O-CH_3, 3%), 195 (17), 135 (15), 121 (18), 109 (19), 107 (10), 97 (13), 95 (13), 85 (11), 83 (18), 81 (14), 71 (14), 69 (33), 67 (17), 59 (20), 57 (100), 55 (25), 43 (51) and 41 (71).

(1R,1'S*)-1,1'-(2,2,3,3-Tetramethylcyclopropane-1,1-diyl)bis-(2,2-dimethyl-1-propanol)* (*syn*-**8**): *m/z* 237 (M$^+$-H_2O-CH_3, 0.5%), 195 (24), 135 (13), 121 (12), 109 (22), 97 (17), 95 (10), 85 (10), 83 (20), 81 (14), 71 (18), 69 (47), 67 (18), 59 (27), 57 (100), 55 (29), 45 (10), 43 (52) and 41 (72).

1-(2,2,3,3-Tetramethylcyclopropyl)-2,2-dimethyl-1-propanol (**9**): R_f = 0.62 (hexane/ethyl acetate: 3/2), oil; ν (film) 3480 (OH), 1140 and 1000 cm^{-1} (C-O); δ_H 0.37 (1H, d, *J*=10.4, C*H*CO), 0.92 (9H, s, $(CH_3)_3C$), 0.98 (3H, s, CH_3 of cyclopropyl), 1.04 (3H, s, CH_3 of cyclopropyl), 1.12 (6H, s, 2xCH_3 of cyclopropyl), 1.60 (1H, br s, OH) and 3.08 (1H, d, *J*=10.4, HCO); δ_C 17.8 (CH_3 of cyclopropyl), 18.3 (CH_3 of cyclopropyl), 21.25 (CH_3*C*CH_3 of cyclopropyl), 23.5 (CH_3 of cyclopropyl), 23.75 (CH_3*C*CH_3 of cyclopropyl), 24.05 (CH_3 of cyclopropyl), 25.75 [3C, (*C*H_3)$_3$C], 34.9 [$(CH_3)_3$*C*], 36.5 (H*C*CO) and 78.0 (HCO); *m/z* 184 (M$^+$, 0.1%), 127 (31), 109 (18), 97 (20), 87 (13), 85 (10), 83 (31), 71 (25), 70 (26), 69 (43), 59 (43), 57 (54), 55 (53), 53 (11), 43 (100) and 41 (83).

(3R, 5R*)-4-Methoxy-2,2,6,6-tetramethyl-3,5-heptanediol* (*anti-syn*-**11**), first (major) diastereomer: R_f = 0.35 (hexane/ethyl acetate: 3/2), oil; ν (film) 3440 (OH), 1100, 1070 and 1010 cm^{-1} (C-O); δ_H 0.95 [9H, s, $(CH_3)_3C$], 0.97 [9H, s, $(CH_3)_3C$], 2.90 (2H, br s, 2xOH), 3.35 (3H, s, OCH_3), 3.43, 3.52 and 3.56 (3x1H, 3s, 2xC*H*OH, C*H*OCH_3); δ_C 26.47 [3C, (*C*H_3)$_3$C], 26.57 [3C, (*C*H_3)$_3$C], 34.25 [(*C*H_3)$_3$C], 35.35 [$(CH_3)_3$*C*], 56.0 (CH_3O), 77.15, 77.5 and 80.6 (2xHCOH, H*C*OCH_3); *m/z* 161 [M$^+$-$(CH_3)_3C$, 0.5%], 114 (16), 99 (100), 87 (16), 74 (18), 69 (15), 57 (42), 45 (16), 43 (16) and 41 (48). Second diastereomer: *m/z* 161 [M$^+$-$(CH_3)_3C$, <0.1%], 114 (13), 99 (100), 87 (10), 74 (11), 69 (11), 57 (34), 45 (12), 43 (15) and 41 (31). Third (minor) diastereomer: *m/z* 161 [M$^+$-$(CH_3)_3C$, 0.4%], 114 (21), 99 (100), 87 (12), 75 (10), 57 (27), 43 (13) and 41 (24).

2,2,7,7-Tetramethyl-4-octyn-3,6-diol (**13**)[35]: R_f = 0.30 (hexane/ethyl acetate: 3/2); ν (film) 3240 (OH), 1120, 1040 and 990 cm^{-1} (C-O); δ_H 1.00 [36H, s, 2x(C*H*$_3$)$_3$CCOC≡CCOC(C*H*$_3$)$_3$], 2.02, 2.06 (2x2H, 2s, 2xCHO*H*C≡CCHO*H*), 4.06, 4.10 (2x2H, 2s, 2xC*H*OHC≡CC*H*OH); δ_C 25.3 [12C, 2x(*C*H$_3$)$_3$CCOC≡CCOC(*C*H$_3$)$_3$], 35.85, 35.85 [4C, 2x$(CH_3)_3$*C*COC≡CCO*C*$(CH_3)_3$], 71.35 (4C, 2x*C*OC≡C*C*O) and 85.45 (4C, 2xC≡C); *m/z* 183 [M$^+$-H_2O, 0.2%], 124 (100), 123 (10), 109 (62), 95 (11), 81 (20), 57 (97), 43 (15) and 41 (30) (Found: C, 72.7; H, 11.2. $C_{12}H_{22}O_2$ requires C, 72.68; H, 11.18).

Tetrakis(trimethylsilyl)methane (**15e**)[25d]: R_f = 0.61 (hexane), sublimates ; ν (film) 1260, 855, 832 ($SiCH_3$) and 672 cm^{-1} (C-Si); δ_H 0.23 (36H, s, 12xCH_3); δ_C -1.88 (CSi_4) and 5.30 (12C, 12xCH_3) ; *m/z* 293 (M$^+$-CH_3+4, 1%), 292 (M$^+$-CH_3+3, 4%), 291 (M$^+$-CH_3+2, 17%), 290 (M$^+$-CH_3+1, 29%), 289 (M$^+$-CH_3, 100%), 201 (21) and 73 (42).

Tris(trimethylsilyl)methane (**15a**)[25d]: R_f = 0.57 (hexane) ; ν (film) 1252, 845 ($SiCH_3$), 687 and 676 cm^{-1} (C-Si); δ_H -0.77 (1H, s, CH) and 0.11 (27H, s, 9xCH_3); δ_C 3.30 (9C, 9xCH_3) and 4.00 (CH) ; *m/z* 221 (M$^+$-CH_3+4, 1%), 220 (M$^+$-CH_3+3, 2%), 219 (M$^+$-CH_3+2, 17%), 218 (M$^+$-CH_3+1, 33%), 217 (M$^+$-CH_3, 100%), 129 (35), 73 (38), 59 (12) and 45 (10).

Tris(trimethylsilyl)deuteriomethane (**15b**): R_f = 0.57 (hexane) ; ν (film) 1260, 1251, 844 ($SiCH_3$), 688 and 678 cm^{-1} (C-Si); δ_H 0.12 (27H, s, 9xCH_3); δ_C 3.30 (9C, 9xCH_3) and 3.30 (1C, t, $J_{C\text{-}D}$=25, CD) ; *m/z* 221 (M$^+$-CH_3+3, 2%), 220 (M$^+$-CH_3+2, 13%), 219 (M$^+$-CH_3+1, 24%), 218 (M$^+$-CH_3, 100%), 217 (M$^+$-CH_3, 100%), 130 (55), 73 (79), 59 (21) and 45 (25).

1,1,1-Tris(trimethylsilyl)ethane (**15c**)[25a]: R_f = 0.65 (hexane) ; ν (film) 1264, 1252, 839 ($SiCH_3$) and 675 cm^{-1} (C-Si); δ_H 0.08 [27H, s, 3x$(CH_3)_3Si$] and 1.08 (3H, s, CH_3C); δ_C -1.85 (1C, CH_3*C*), 1.00 [9C, 3x$(CH_3)_3Si$]

and 13.85 (CH_3C); *m/z* 246 (M^+, 1%), 158 (15), 85 (17), 73 (100), 59 (11) and 45 (18).

Phenylbis(trimethylsilyl)methane (**16d**)[25a]: R_f = 0.57 (hexane) ; ν (film) 1598, 1493 (ArC=C), 1250, 844 ($SiCH_3$) 701 and 688 cm^{-1} (ArC-H, C-Si); δ_H 0.03 [18H, s, 2x$(CH_3)_3Si$], 1.49 (1H, s, PhCH), 6.90-6.95 (2H, m, *o*-ArH), 6.97-7.04 (1H, m, *p*-ArH) and 7.13-7.20 (2H, m, *m*-ArH); δ_C 0.20 [6C, 2x$(CH_3)_3Si$], 29.55 (PhCH), 123.3 (2C, ArC), 128.05 (2C, ArC), 128.7 (ArC) and 143.1 (ArC); *m/z* 238 (M^++2, 0.5%), 237 (M^++1, 1%), 236 (M^+, 5%), 149 (15), 148 (83), 135 (13), 74 (11), 73 (100), 59 (11), 45 (20) and 43 (10).

Phenylbis(trimethylsilyl)deuteriomethane (**17d**): R_f = 0.57 (hexane) ; ν (film) 1597, 1493 (ArC=C), 1250, 840 ($SiCH_3$) 701 and 688 cm^{-1} (ArC-H, C-Si); δ_H 0.03 [18H, s, 2x$(CH_3)_3Si$], 6.90-6.95 (2H, m, *o*-ArH), 6.97-7.04 (1H, m, *p*-ArH) and 7.13-7.20 (2H, m, *m*-ArH); δ_C 0.20 [6C, 2x$(CH_3)_3Si$], 29.05 (1C, t, $J_{C\text{-}D}$=17, CD), 123.3 (2C, ArC), 128.05 (2C, ArC), 128.7 (ArC) and 143.1 (ArC); *m/z* 238 (M^++1, 1%), 237 (M^+, 5%), 150 (12), 149 (87), 135 (13), 74 (10), 73 (100), 45 (17) and 43 (10).

Phenyltris(trimethylsilyl)methane (**15d**)[25a]: R_f = 0.56 (hexane) ; ν (film) 1590, 1496 (ArC=C), 1259, 877, 835 ($SiCH_3$) 702, 675 and 617 cm^{-1} (ArC-H, C-Si); δ_H 0.21 [27H, s, 3x$(CH_3)_3Si$], 7.01-7.08 (1H, m, *p*-ArH), 7.15-7.23 (2H, m, *m*-ArH) and 7.31-7.38 (2H, m, *o*-ArH); δ_C 4.20 [9C, 3x$(CH_3)_3Si$], 21.45 (PhC), 123.45 (ArC), 127.45 (2C, ArC), 131.50 (2C, ArC) and 143.2 (ArC); *m/z* 310 (M^++2, 0.6%), 309 (M^++1, 1.3%), 308 (M^+, 4%), 221 (15), 220 (59), 206 (11), 205 (47), 135 (10), 74 (11), 73 (100), 59 (10) and 43 (31).

ACKNOWLEDGEMENTS

This work was supported by DGICYT (nos. PB91-0751 and PB94-1514) from the Ministerio de Educación y Ciencia (MEC) of Spain. A. G. thanks the MEC for a grant.

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(*Received in UK* 6 *October* 1995; *revised* 14 *November* 1995; *accepted* 16 *November* 1995)