Reactivity of Neopentyl-Like Compounds in the Synthesis of Branched Polyethers

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Two singly branched symmetrical hexaethers have been synthesized, starting from 2-bromomethyl-2-methyl-1,3-dibromopropane, in a surprisingly efficient one-pot nucleophilic substitution reaction. It is proposed that the expected adverse neopentyl effect is compensated by favourable neighbouring-group participation involving a 'bromonium'-like four-membered-ring transition state.

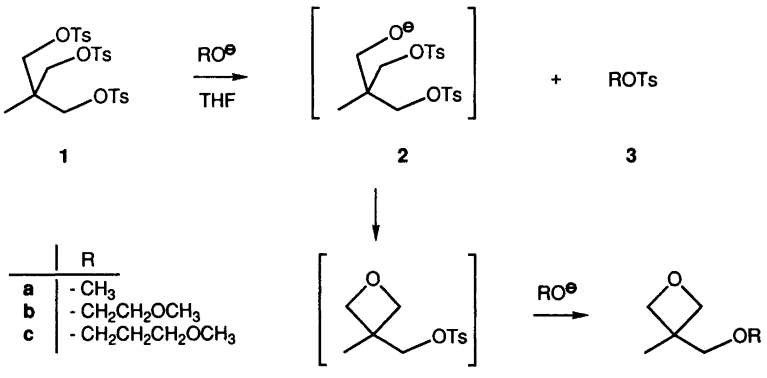
The corresponding trichloride also reacted cleanly, although much more slowly, while the tritosylate gave an oxetane derivative.

In the preceding paper we described the synthesis of branched polyether ligands from 2-hydroxymethyl-2-methyl-1,3-propanediol and various alkyl iodides or tosylates. Our choice of the triol as the alkoxide component in the Williamson synthesis was dictated by the well known and thoroughly studied adverse neopentyl effect,[1–5] as manifested not only in the low reactivity of neopentyl halides, but also in the difficulty of their preparation from the alcohol using PBr_3 or $SOCl_2$.[6] If these difficulties are of steric origin,[1–5] one would expect them to increase in related molecules carrying further substituents in the methyl groups. Nevertheless, the literature abounds in examples of chlorides, bromides, tosylates and acetates from both 2,2-dimethyl-1,3-propanediol, 2-hydroxymethyl-2-methyl-1,3-propanediol, and 2,2-bis(hydroxymethyl)-1,3-propanediol.[7–11] Normal reactivity is also observed in their subsequent nucleophilic substitution reactions.[7,8,12,13] Surprisingly, we have been unable to find any comment on this apparent contradiction, or any attempt to explain it.

We now confirm the absence of a neopentyl effect by reporting the successful alternative preparation of symmetrical branched polyether ligands from 2-bromomethyl-2-methyl-1,3-dibrompropane and the appropriate alkoxides, and we propose that the rate-retarding neopentyl effect is compensated by rate-enhancing neighbouring-group participation.

In addition, we have observed a series of methoxylated by-products and intermediates in the case of 3-methoxypropanol (but not with 2-methoxyethanol) when its alkoxide is used with an excess of the same alcohol as the solvent. Presumably, this is due to base-catalysed ether exchange giving rise to methanol and its alkoxide.

Reactions with 2-methyl-1,3-bis(tosyloxy)-2-tosyloxymethylpropane. The highest reactivity was expected when the tosyloxy group was used as the leaving group. 2-Hydroxymethyl-2-methyl-1,3-propanediol was therefore first converted into the tritosylate **1** in high yield following a standard procedure.[7] Reaction with the appropriate alkoxides (Scheme 1) in refluxing THF did not, however, furnish the desired tris-alkoxy ligands, and in all cases only the oxetane derivative **5** and the tosylate **3** of the alcohol used were



Scheme 1.

obtained. Clearly, nucleophilic attack had occurred on sulfur instead of carbon, resulting in transfer of the tosyl group, followed by cyclization of the resulting alkoxide **2** to give the oxetane **4**, which subsequently underwent substitution to the final oxetane **5**.

The fact that the ether R–O–R was not observed, suggests enhanced reactivity of the tosylate intermediate **4** over and above that of the tosylate **3**, indicating a mechanism of primary attack on the oxetane carbon, causing ring opening coupled with recyclization and expulsion of the tosylate group.

Although this reaction thus provides useful intermediates for the synthesis of unsymmetrical polyether ligands (cf. the preceding paper), it failed to give the symmetrical polyether ligands directly.

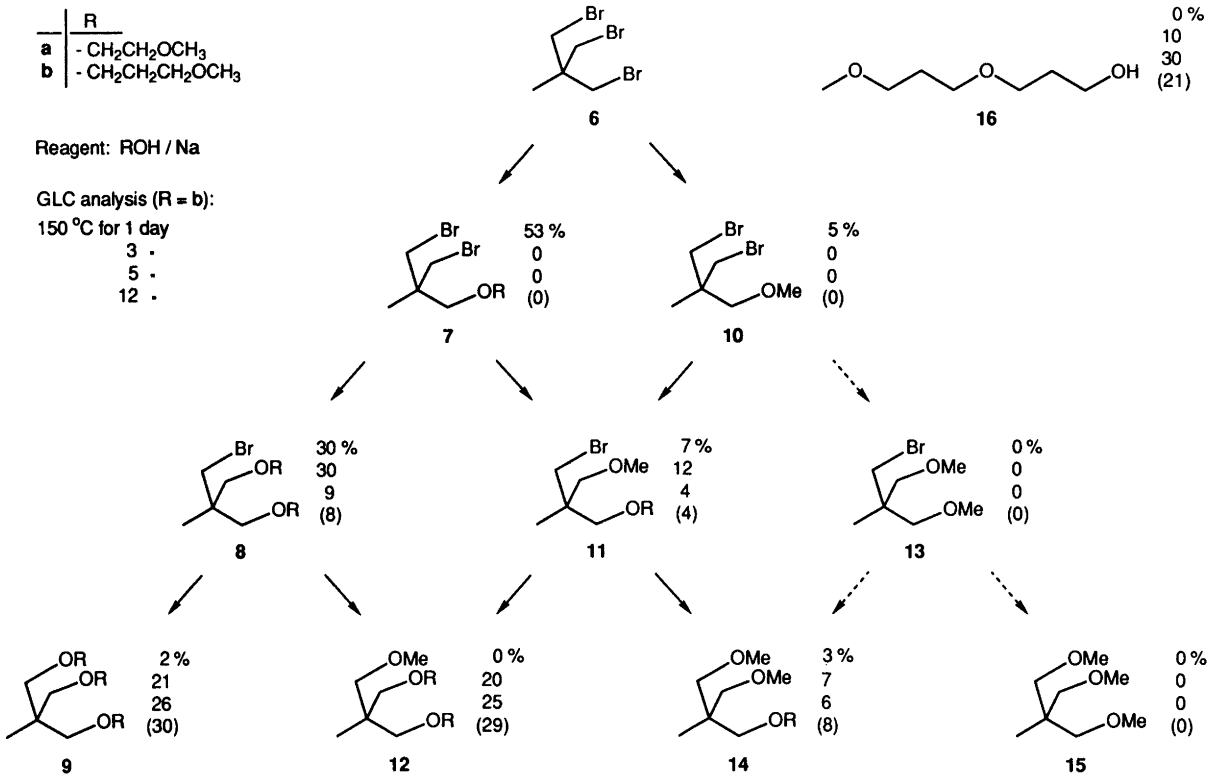
Reactions with 1,3-dichloro-2-chloromethyl-2-methylpropane. Chlorination of 2-hydroxymethyl-2-methyl-1,3-propanediol with $SOCl_2$ in pyridine has been reported to give the trichloride.[11] However, cyclic sulphites are more easily formed from this triol and from 1,3-diols generally. In fact, studies of the mechanism for chlorination of the triol (as well as of pentaerythritol)[14,15] indicate that the chlorinated products are formed exclusively via cyclic sulfites as intermediates. Reaction conditions that lead either to the sulfite or the chloride have not, however, been clearly defined.[16–19] In our hands, using three equivalents of $SOCl_2$ and relatively hard conditions (10 h at 110 °C), the yield of the trichloride was only 23 %.

The trichloride reacted cleanly, but very slowly, with the alkoxide of 2-methoxyethanol at reflux, using an excess of 2-methoxyethanol as the solvent. After six days, GLC analysis showed that the ratio between mono-, di- and trisubstituted products was 3:6:1 – less than 10 % of the desired product. No further reactions were therefore attempted.

Reactions with 1,3-dibromo-2-bromomethyl-2-methylpropane. Bromination of 2-hydroxymethyl-2-methyl-1,3-propanediol with PBr_3 is known to proceed in good yield. We followed essentially the procedure of Stetter and Böckmann,[7] isolating the product by steam distillation.

Reaction of this tribromide **6** (Scheme 2) with the alkoxide of 2-methoxyethanol in refluxing THF was slow, and even after 7 days, half of the tribromide could be recovered, the main reaction product being the monoalkylated compound **7a**. Use of 2-methoxyethanol as the solvent to obtain a higher temperature (b.p. 124 °C), led to a single product after only 24 h, and the trisubstituted compound **9a** was obtained in an isolated yield of 78 %.

Reaction of tribromide **6** with the alkoxide of 3-methoxypropanol under similar conditions did not proceed in this simple manner. After being refluxed for one day in 3-methoxypropanol as the solvent (b.p. 150 °C), compound **6** gave a product mixture containing only 2 % of the trisubstituted compound **9b**, with intermediates **7b** and **8b** as the principal components (53 and 30 %, respectively). More serious was the presence of a variety of other com-



Scheme 2.

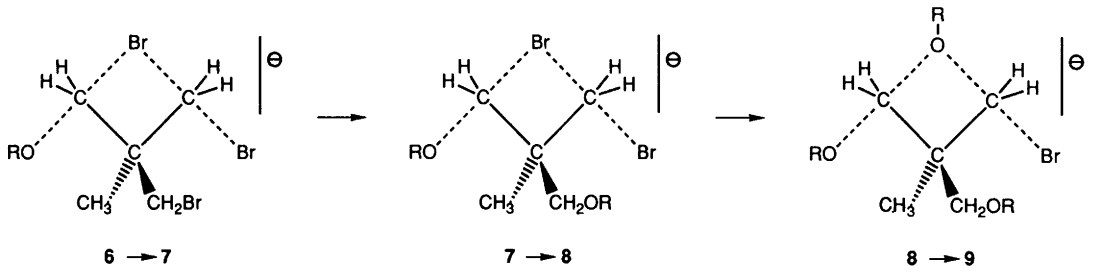


Fig. 1. Proposed transition state for the three successive steps in the nucleophilic substitution of 1,3-dibromo-2-bromomethyl-2-methylpropane.

pounds containing one or two methoxy substituents. Further refluxing showed that the reaction was essentially complete within 5 days. Three main bromine-free by-products were then present: the monomethoxy-bis(3-methoxypropyl) compound **12b**, the dimethoxy-(3-methoxypropyl)-compound **14b**, and a compound identified as 3-(3-methoxypropyloxy)propanol **16**. The change in the GLC-analytical composition of the reaction mixture with reaction time is indicated next to each product in Scheme 2. It is likely that compounds **13** and **15** were present, although they were not detected. Clearly, a displacement of methoxide from 3-methoxypropanol by 3-methoxypropoxide had taken place at this high temperature, so that two alkoxides were competing for the substrate; methoxide in modest quantity to start with, but increasing in importance with time. A parallel increase in the by-product **16** was observed.

The problem did not arise when the reaction was carried out in refluxing DMF (b.p. 153 °C) using 3-methoxypropoxide and no free 3-methoxypropanol. After 15 h no bromine-containing intermediates were present, and the trisubstituted compound **9b** was obtained in 75 % yield (GLC) and the methoxy compound **12b** in 12 %. A reduction product, 2,2-dimethyl-1,3-bis(trimethoxypropyl)propane, due to excess sodium, was present in 13 %.

The mechanism of nucleophilic substitution in 1,3-dibromo-2-bromomethyl-2-methylpropane. The feature common to di-, tri- and tetra-bromoneopentanes, and lacking in monobromoneopentane (neopentyl bromide), is of course the 1,3-relationship between all bromine atoms. Neighbouring-group participation is well established in solvolysis reactions of compounds containing a substituent with non-bonded electrons in a 1,3-relationship to the leaving group.[1,20–24] For our reaction under S_N2 conditions we propose an analogous, but concerted, transition state, involving the hetero-atom in a four-membered ring arrangement, for each of the three stepwise reactions **6** → **7**, **7** → **8**, and **8** → **9** (Fig. 1). The closing together of the two CH_2-carbon atoms, as they become part of this small ring, relieves the steric problems for both the nucleophile and the leaving group. It is also well established[21,22] in solvolysis reactions that four-membered-ring bromonium intermediates are more easily formed than corresponding oxonium intermediates. The last step (**8** → **9**) should therefore be slower than the first and second steps (Fig. 1). We thus have a simple explanation that accounts for why, when using 3-methoxypropoxide in 3-methoxypropanol as the solvent, dibromo intermediates **7b** and **10b** (Scheme 2) are no longer present after one day, while monobromo intermediates **8b** and **11b** are still present after 12 days.

The final question is why the reaction with 2-methoxyethoxide is so much faster. We have reported[25] that Na^+ is more strongly complexed by ligands **9a**, **12a** and **14a** than by ligands **9b**, **12b** and **14b**, and a similar difference can be expected between the solvents, 2-methoxyethanol and 3-methoxypropanol. This must lead to increased nucleophilic reactivity of 2-methoxyethoxide (cf. the crown-ether effect). Furthermore, this is in agreement with the observed increased reactivity of 3-methoxypropoxide when DMF is used as the solvent. Very little methylation takes place, presumably because the reaction is fast, DMF activating nucleophiles by complexation of the counter-ion.

Experimental

*2-Methyl-1,3-bis(tosyloxy)-2-tosyloxymethylpropane (**1**).* A standard procedure[7] was followed, using 2-hydroxymethyl-2-methyl-1,3-propanediol (18 g, 150 mmol), tosyl chloride (85.8 g, 450 mmol), pyridine (35.6 g, 450 mol) and ethanol-free chloroform (60 ml). The crude product was recrystallized from benzene, yield 70.8 g (81 %), white needles, m.p. 110–111 °C. ^1H NMR (60 MHz, $CDCl_3$): δ 0.90 (3 H, s, CH_3), 2.46 (9 H, s, $ArCH_3$) 3.80 (6 H, s, CH_2), 7.50 (4 H, q, ArH).

*Reactions with 2-methyl-1,3-bis(tosyloxy)-2-tosyloxymethylpropane (**1**). A. With 2-methoxyethanol.* The reaction was run under nitrogen. 2-Methoxyethanol (11.9 g, 156 mmol) was dissolved in dry THF (200 ml). Sodium hydride (3.75 g, 156 mmol) was added, and the mixture was refluxed overnight. The tritosylate **1** (30.4 g, 52.1 mmol) dissolved in dry THF (50 ml) was added, and the reaction mixture was refluxed for 24 h. The mixture was cooled, the solvent was evaporated off, ether was added to the residue, and precipitated sodium tosylate was filtered off. The ether solution

was washed with water and dried ($MgSO_4$), and the ether was evaporated off. The residue was distilled through a Vigreux column to give 3-(2,5-dioxahexyl)-3-methyloxetane (**5**, R = $CH_2CH_2OCH_3$), yield 5.4 g (65 %), b.p. 76–78 °C/10 mmHg. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.30 (3 H, s, CH_3), 3.40 (3 H, s, CH_3O), 3.6–3.8 (6 H, m, CH_2O), 4.40 (4 H, q, *J* 6 Hz, CH_2 ring). MS (CI, isobutane, *m/z* > 100, rel. int. > 5 %): 161 (29), 131 (51).

The distillation residue was 2-methoxyethyl tosylate (**3**, R = $CH_2CH_2OCH_3$). ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.40 (3 H, s, $ArCH_3$), 3.23 (3 H, s, CH_3O), 3.46 (2 H, t, CH_2O), 4.30 (2 H, s, CH_2OTs), 7.40 (4 H, q, ArH).

B. With 3-methoxypropanol. The reaction between tritosylate **1** and 3-methoxypropanol proceeded in a similar way, to give the oxetane **5** (R = $CH_2CH_2CH_2OCH_3$) in a yield of 60 %. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.30 (3 H, s, CH_3), 1.85 (2 H, quint., *J* 6 Hz, CH_2), 3.35 (3 H, s, CH_3O), 3.48 (2 H, s, CH_2O), 3.5–3.6 (4 H, m, CH_2O), 4.43 (4 H, q, *J* 6 Hz, CH_2 ring).

The distillation residue was 3-methoxypropyl tosylate (**3**, R = $CH_2CH_2CH_2OCH_3$). ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.84 (2 H, quint., CH_2), 2.38 (3 H, s, $ArCH_3$), 3.15 (3 H, s, CH_3O), 3.30 (2 H, t, CH_2O), 4.20 (2 H, t, CH_2OTs), 7.4 (4 H, q, ArH).

C. With methanol. The reaction between the tritosylate **1** and methanol proceeded in a similar way, to give the oxetane **5** (R = CH_3) in a yield of 70 %. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.30 (3 H, s, CH_3), 3.43 (3 H, s, CH_3), 3.47 (2 H, s, CH_2O), 4.38 (2 H, d, *J* 6 Hz, CH_2 ring). 4.55 (2 H, d, *J* 6 Hz, CH_2 ring).

1,3-Dichloro-2-chloromethyl-2-methylpropane.[11] Thionyl chloride (17.8 g, 150 mmol) was slowly added to a stirred and cooled solution of 2-hydroxymethyl-2-methyl-1,3-propanediol (6.0 g, 50 mmol) and pyridine (15.8 g, 200 mmol) in ethanol-free chloroform (20 ml). The reaction mixture was stirred for 3 days at room temperature and then at 110 °C for 10 h. The solution was cooled, washed with water and dried ($MgSO_4$). The solvent was evaporated off and the residue was distilled through a Vigreux column to give the trichloride, yield 2.0 g (23 %), b.p. 80–82 °C/10 mmHg. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.22 (3 H, s, CH_3), 3.60 (6 H, s, CH_2). MS (CI, isobutane, *m/z* > 100, rel. int. > 7 %): 139 (19, 2 Cl), 125 (41, 2 Cl), 103 (100, Cl).

Further distillation gave the cyclic sulfite *5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxathiane* (isomer mixture), yield 3.8 g, b.p. 82–110 °C/10 mmHg. The isomers were separated by preparative GLC. The main isomer was crystalline, m.p. 41–42 °C after recrystallization from hexane–ethyl acetate. The assignment of configuration was achieved by X-ray structure determination, which showed this to be the *trans*-isomer (M. van Meerssche and J. P. Declercq, Louvain la Neuve, Belgium. Unpublished work). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.93 (3 H, s, CH_3), 3.73 (2 H, d, *J* 12 Hz, H4, H6), 3.84 (2 H, s, CH_2Cl), 4.70 (2 H, d, *J* 12 Hz, H4, H6). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.2, 36.3, 47.9, 62.0.

The *cis*-isomer was a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.38 (3 H, s, CH_3), 3.36 (2 H, s, CH_2Cl), 3.60 (2 H, d, *J* 11 Hz, H4, H6), 4.76 (2 H, d, *J* 11 Hz, H4, H6). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.8, 35.9, 48.5, 64.0.

1,3-Dibromo-2-bromomethyl-2-methylpropane (**6**) was prepared according to a literature procedure,[7] using 2-hydroxymethyl-2-methyl-1,3-propanediol (24.0 g, 200 mmol) and freshly distilled phosphorus tribromide (81.2 g, 300 mmol). Yield 24.7 g (40 %), b.p. 104–105 °C/10 mmH. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.30 (3 H, s, CH_3), 3.52 (6 H, s, CH_2). MS (CI, isobutane, *m/z* > 100, rel. int. > 5 %): 306 (19, 3 Br), 227 (49, 2 Br), 147 (85, Br), 133 (12, Br).

Reactions with 1,3-dibromo-2-bromomethyl-2-methylpropane (**6**).

7-(2,5-Dioxahexyl)-7-methyl-2,5,9,12-tetraoxatridecane (**9a**). *Method A.* The reaction was run under nitrogen. Sodium (3.0 g, 130 mmol) was added to 2-methoxyethanol (50 ml) with stirring and cooling. The temperature was allowed to rise to 60 °C and the mixture was stirred until all of the sodium had reacted. The tribromide **6** (6.0 g, 19.4 mmol), dissolved in 2-methoxyethanol (20 ml), was added, and the reaction mixture was refluxed for 24 h. The solvent was distilled off in a simple distillation flask. Ether was added to the residue, precipitated sodium bromide was filtered off and the ether solution was washed with water and dried ($MgSO_4$). The solvent was evaporated off and the crude product was distilled through a Vigreux column. Yield 4.5 g (78 %), b.p. 97–99 °C/0.01 mmHg. ^{1}H NMR (300 MHz, CD_3CN): δ 0.87 (3 H, s, CH_3), 3.26 (6 H, s, CH_2O), 3.29 (9 H, s, CH_3O), 3.43–3.51 (12 H, m, CH_2O). ^{13}C NMR (75 MHz, CD_3CN): δ 17.8, 41.7, 59.0, 71.7, 72.5, 74.4. MS (CI, isobutane, *m/z* > 100, rel. int. > 5 %): 295 (43), 219 (13), 163 (24), 143 (100), 129 (25).

Method B. The experimental procedure was similar to that described above, using dry THF as the solvent and a large excess (100 %) of the alkoxide. The reaction mixture was analysed by GLC–MS. After 7 days at reflux, the main reaction product was the monoalkylated compound **7a**. MS (CI, isobutane, *m/z* > 100, rel. int. > 1 %): 303 (34, 2 Br), 271 (1, 2 Br), 227 (3, 2 Br), 147 (7, Br), 143 (7), 139 (1), 116 (1).

Only traces of the dialkylated compound **8a** were detected. MS (CI, isobutane, *m/z* > 100, rel. int. > 8 %): 299 (78, Br), 293 (12, Br), 143 (100), 129 (19). Half of the tribromide was recovered.

8-(2,6-Dioxaheptyl)-8-methyl-2,6,10,14-tetraoxapentadecane **9b**). *Method A.* The reaction was run under nitrogen. Sodium (2.0 g, 87 mmol) was added to 3-methoxypropanol (30 g), and the mixture was stirred until all of the sodium had reacted. The tribromide **6** (4.00 g, 13 mmol) was added, and the reaction mixture was refluxed for 5 days. The reaction was followed by GLC–MS, and the change in the composition of the reaction mixture with time is shown in

Scheme 2. Unchanged 3-methoxypropanol was distilled off in a columnless distillation flask, ether was added to the residue, and precipitated salts were filtered off. The ether solution was washed with water and dried ($MgSO_4$), and the solvent was evaporated off. The product mixture was distilled through a Vigreux column to give the following fractions: 1, 2.1 g, b.p. 60–90 °C/0.01 mmHg, containing **11b**, **12b**, **14b** and **16**; 2, 0.8 g, b.p. 90–100 °C/0.01 mmHg, containing **8b**, **11b** and **12b**; 3, 1.5 g, b.p. 100–125 °C/0.01 mmHg, containing **8b**, **9b** and **12b** in the relative ratio 1:3:4 (GLC). **9b**, **12b** and **16** were isolated by preparative GLC.

Spectral data:

7b: MS (CI, isobutane, $m/z > 100$, rel. int. > 5 %): 317 (47, 2 Br), 286 (5, 2 Br), 147 (5, Br), 125 (5), 103 (100).

8b: MS (CI, isobutane, $m/z > 100$, rel. int. > 5 %): 327 (99, Br), 237 (25, Br), 157 (63), 143 (5), 125 (27), 103 (56).

10: MS (CI, isobutane, $m/z > 100$, rel. int. > 5 %): 259 (42, 2 Br), 229 (28), 179 (51, Br), 147 (53, Br), 134 (16, Br).

11b: MS (CI, isobutane, $m/z > 100$, rel. int. > 5 %): 269 (100, Br), 179 (29, Br), 157 (21), 145 (11), 125 (13), 103 (47), 101 (10).

14b: MS (CI, isobutane, $m/z > 100$, rel. int. > 5 %): 221 (100), 189 (7), 157 (4), 133 (12), 131 (60), 103 (16), 99 (40).

9b: MS (CI, isobutane, $m/z > 100$, rel. int. > 10 %): 337 (100), 247 (13), 191 (22), 157 (14), 143 (54), 103 (26). ^{1}H NMR (300 MHz, CD_3CN): δ 0.87 (3 H, s, CH_3), 1.74 (6 H, quint., J 6.4 Hz, CH_2), 3.21 (6 H, s, CH_2O), 3.25 (9 H, s, CH_3O), 3.39 (6 H, t, J 6.4 Hz, CH_2O), 3.41 (6 H, t, J 6.4 Hz, CH_2O). ^{13}C NMR (75 MHz, CD_3CN): δ 17.9, 30.7, 41.7, 58.7, 68.9, 70.2, 74.0.

12b: MS (CI, isobutane, $m/z \geq 99$, rel. int. > 7 %): 279 (100), 189 (30), 157 (23), 133 (23), 125 (77), 103 (29), 101 (11), 99 (38). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.92 (3 H, s, CH_3), 1.82 (4 H, quint., J 6.4 Hz, CH_2), 3.23 (2 H, s, CH_2O), 3.26 (4 H, s, CH_2O), 3.31 (3 H, s, CH_3O), 3.33 (6 H, s, CH_3O), 3.45 (4 H, t, J 6.4 Hz, CH_2O), 3.46 (4 H, t, J 6.4 Hz, CH_2O). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.4, 30.0, 40.9, 58.6, 59.3, 68.2, 69.8, 73.5, 75.8.

16: MS (CI, isobutane, $m/z > 100$, rel. int. ≥ 3 %): 149 (59), 133 (3), 122 (24), 121 (10), 117 (7), 107 (8), 105 (100). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.84 (4 H, m, CH_2), 2.43 (1 H, br s, OH), 3.33 (3 H, s, CH_3O), 3.46 (2 H, t, J 6.1 Hz, CH_2O), 3.53 (2 H, t, J 6.3 Hz, CH_2O), 3.62 (2 H, t, J 5.6 Hz, CH_2O), 3.77 (2 H, t, J 5.6 Hz, CH_2OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.0, 32.1, 58.6, 62.2, 68.4, 69.8, 70.3.

Method B. The reaction was run under nitrogen. 3-Methoxypropanol (10.4 g, 115 mmol) was dissolved in dry THF (70 ml), sodium (2.60 g, 113 mmol) was added, and the mixture was stirred until all of the sodium had reacted. The solvent was then changed to DMF. The tribromide **6** (10.5 g, 34.0 mmol) dissolved in dry DMF (10 ml) was added, and the reaction mixture was stirred for 12 h at 125 °C and then refluxed for 3 h. The solution was cooled, ether was added, and precipitated salts were filtered off. The organic phase was washed several times with water and dried ($MgSO_4$) and the ether was evaporated off. The residue was distilled through a Spaltrohr column to give a fraction (2.4 g, b.p. 92–103 °C/0.05 mmHg) containing **12b** and the reduction product 2,2-dimethyl-1,3-bis(trimethoxypropyl) propane, and pure **9b**, yield 7.4 g (65 %), b.p. 103–112 °C/0.05 mmHg. The relative amounts (GLC) of the three components in the product mixture were 12, 13 and 75 %, respectively. Spectral data for **9b** and **12b** are given above. Data for 2,2-dimethyl-1,3-bis(trimethoxypropyl) propane are MS (CI, isobutane, $m/z \geq 100$, rel. int. ≥ 10 %): 249 (100), 159 (54), 103 (33).

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