

## Metal-assisted Reactions. Part 17.<sup>1</sup> Ring-opening and Dimerization of Cyclic Ethers by Titanium Halides

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Reaction of  $\text{TiCl}_4$  or  $\text{TiBr}_4$  with a variety of cyclic ethers gives, predominantly, products resulting from simple ring-opening or from ring-opening with simultaneous condensation to dimeric species. The variations in yields of these two kinds of products might be correlated qualitatively with an initial formation of the complex  $\text{TiX}_4 \cdot 2\text{E}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ;  $\text{E} = \text{cyclic ether}$ ) in which the ethers were held in a *cis* or *trans* relationship. Although such a correlation might suggest that  $\text{TiCl}_4$  but not  $\text{TiBr}_4$  exerts a template effect on the condensation, stereochemical considerations of the reaction products indicate otherwise.  $\text{TiCl}_3$  and  $\text{VCl}_3$  do not give similar results and  $\text{TiF}_4$  gives no reaction.

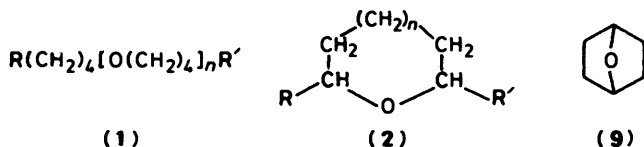
The organic chemistry of  $\text{TiCl}_4$  is dominated by its capacity as a powerful Lewis acid and dehydrating agent. Titanium halides form numerous complexes with electron-donating ligands,<sup>2</sup> including cyclic ethers.<sup>3</sup> Many of these complexes are solids of known structure as, for example, with tetrahydrofuran (THF) which can form the octahedral six co-ordinate  $\text{TiCl}_4 \cdot 2\text{THF}$  in which the THF rings are *cis* to each other.<sup>3</sup> Reaction of THF has been reported with a variety of inorganic acid chlorides such as  $\text{POCl}_3$ ,  $\text{SOCl}_2$ , and  $\text{SiCl}_4$  together with catalysts such as  $\text{Zn}$ ,  $\text{ZnCl}_2$ , and  $\text{H}_2\text{SO}_4$ .<sup>4</sup> The reaction of THF with  $\text{BCl}_3$  has also been examined.<sup>5</sup> These reactions give open chain oligomers of THF ( $1; \text{R}, \text{R}' = \text{OH}, \text{Cl}, \text{Br}, \text{SO}_3\text{Ph}; n \geq 0$ ) in which the degree of polymerisation depends greatly on the reaction conditions. Interestingly, oligomerisation of THF by  $\text{TiCl}_4$  has been examined in the presence of promoters such as epichlorohydrin or acetyl chloride; simple ring-opening and not oligomerisation was observed in the absence of the promoters.<sup>6</sup> We have examined the ring-opening of a variety of cyclic ethers, including THF, by  $\text{TiF}_4$ ,  $\text{TiCl}_4$ ,  $\text{TiBr}_4$ ,  $\text{TiCl}_3$ , and  $\text{VCl}_3$  and found that, in the absence of promoters, the reaction consists of ring-opening and limited oligomerisation (mostly dimerisation).

and the bicyclic ether (9), were treated in excess with  $\text{TiCl}_4$  at room temperature or under reflux. In some instances, other halides ( $\text{TiBr}_4$ ,  $\text{TiF}_4$ ,  $\text{TiCl}_3$ , and  $\text{VCl}_3$ ) were used. For some reactions, the temperature was increased by heating in sealed tubes whereas, for others, the temperature needed to be reduced considerably below room temperature to control the violence of the reaction. The products of reaction were isolated either by direct distillation from the reaction mixture (non-hydrolytically) or by addition of water followed by extraction of organic material. The composition of product mixtures was determined by g.c. and g.c.-m.s. and structures of products were confirmed by  $^1\text{H}$  n.m.r. spectroscopy and mass spectrometry.

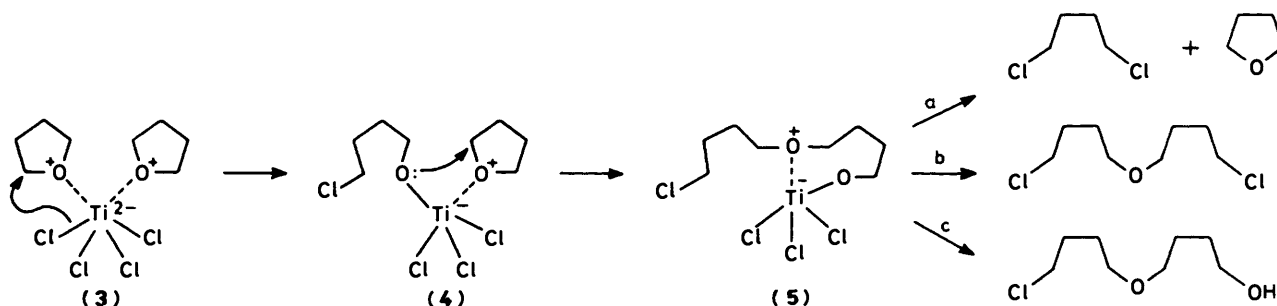
### Results and Discussion

(a) *Non-hydrolytic Work-up*.—After refluxing an excess of THF with  $\text{TiCl}_4$ , the reaction mixture was evaporated to remove THF and leave a black, sticky solid. Extraction of this solid with organic solvents and t.l.c. analysis indicated that there were no extractable organic residues. However, when the solid was heated to 110–125 °C for one hour, an oil was obtained which, on distillation, gave 1,4-dichlorobutane and 1,9-dichloro-5-oxanonane (1;  $\text{R} = \text{R}' = \text{Cl}$ ;  $n = 1$ ), together with a buff-coloured residue. On analysis, the residue was found to contain very little carbon and, with water, it reacted readily to evolve  $\text{HCl}$ ; this residue was thought to be  $\text{TiOCl}_2$ .

Thus, reaction of  $\text{TiCl}_4$  with THF appears to give products resulting from simple ring-opening (1,4-dichlorobutane) or ring-opening with dimerization (1,9-dichloro-5-oxanonane; Scheme 1). Initial attack by chlorine can lead to a ring-opened product (4; Scheme 1) in which the oxygen of one THF molecule which is co-ordinately bound to titanium becomes covalently bonded to



*Method*.—Most of the cyclic ethers (2;  $\text{R}, \text{R}' = \text{H}, \text{Me}, \text{OMe}, \text{CH}_2\text{OMe}$ ;  $n = 0, 1, 2$ ), as well as 1,4-dioxane, 1,3-dioxolane, 2,3-dihydrofuran, 2,5-dihydrofuran, 1,3,5-trioxane,



Scheme 1.

titanium. At this stage, attack by the covalently bound oxygen on a second THF molecule (originally held in a *cis* arrangement with the first) could lead to further ring-opening with dimerisation to give the intermediate (5). On heating, the complex (5) could give either 1,4-dichlorobutane (path a; Scheme 1) or 1,9-dichloro-5-oxanonane (path b; Scheme 1). The reaction described in Scheme 1 supposes that  $\text{TiCl}_4$  acts as a sort of template in holding the two THF groups in a *cis* relationship to each other. For the analogous complex,  $\text{TiBr}_4 \cdot 2\text{THF}$ , it is thought<sup>7</sup> that the THF rings may be held *trans* to each other. When  $\text{TiBr}_4$  was refluxed with an excess of THF, the major product was 1,4-dibromobutane, resulting from simple ring-opening. Very little of the dimeric material (1;  $\text{R} = \text{R}' = \text{Br}$ ;  $n = 1$ ) was formed, in accord with a 'template' mechanism in which a *cis* arrangement of ligands around the titanium would be necessary for a good yield of dimeric product (but see later).

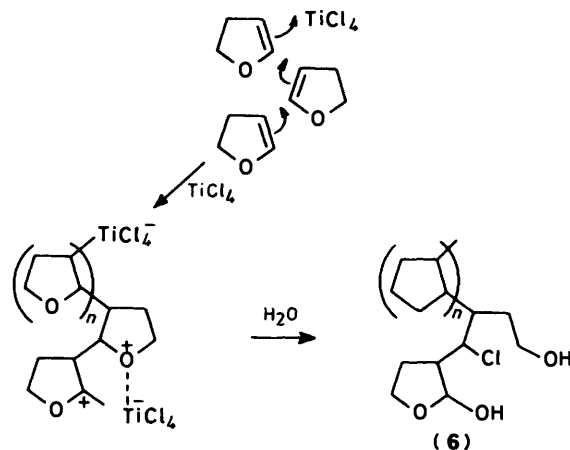
For 2,5-dimethyltetrahydrofuran, reaction with  $\text{TiCl}_4$  occurred even at room temperature, the initial yellow complex rapidly turning almost black. On work-up, a good yield of a diastereoisomeric mixture of 2,10-dichloro-5,7-dimethyl-6-oxaundecane was obtained. Thus, at room temperature, facile opening of the ring in 2,5-dimethyltetrahydrofuran and dimerisation occurred. Reaction of 2,5-dimethyltetrahydrofuran with  $\text{SOCl}_2\text{-H}_2\text{SO}_4$  has been found<sup>8</sup> to give only 2,5-dichlorohexane, the product of simple ring-opening. Reaction of 2-methyltetrahydrofuran with  $\text{TiCl}_4$  also occurred at room temperature and gave dimeric products (see later section on hydrolytic work-up).

The larger ring of tetrahydropyran (2;  $\text{R} = \text{R}' = \text{H}$ ;  $n = 1$ ) (THP) required longer reaction with  $\text{TiCl}_4$  for opening and dimerisation to give 1,11-dichloro-6-oxaundecane, and the reaction of oxepane (2;  $\text{R} = \text{R}' = \text{H}$ ;  $n = 2$ ) to give 1,13-dichloro-7-oxatridecane was slower still. Earlier attempts to ring-open THP with  $\text{POCl}_3\text{-H}_2\text{SO}_4$  or  $\text{BCl}_3$  gave only small yields of chloro compounds because of dehydrochlorination and other side reactions.<sup>4,5,9</sup>

For all of the cyclic ethers (2;  $n = 0, 1, 2$ ), ring-opening became progressively more difficult with increased ring size, but the major products resulted in each case from either simple ring-opening or opening with dimerization. The results from ring-opening of unsaturated cyclic ethers showed that simple dimerization did not occur. Thus,  $\text{TiCl}_4$  with 2,5-dihydrofuran yielded only 1,4-dichlorobut-2-ene as a mixture of *Z*- and *E*-isomers. Ring-opening of 2,5-dihydrofuran would be expected to lead to *Z*-1,4-dichlorobut-2-ene and, indeed, this is the product observed on reaction of the ether with aqueous  $\text{HCl}$ . Inversion of the geometry about double bonds through the catalytic action of  $\text{TiCl}_4$  has been observed previously.<sup>10</sup> Reaction of  $\text{TiCl}_4$  with 2,3-dihydrofuran was highly exothermic and gave a white powdery solid even at  $-78^\circ\text{C}$ ; repetition of the reaction in an inert solvent gave a polymeric solid, having strong  $\text{OH}$  absorption at  $3420\text{ cm}^{-1}$  and intense absorption at  $1055\text{ cm}^{-1}$  ( $\text{C-O-C}$  stretch). The  $^1\text{H}$  n.m.r. spectrum of the solid showed two broad unresolved multiplets at  $\delta$  3.8, and 1.9, and a broad singlet ( $\text{OH}$ ) at  $\delta$  2.5; there was no evidence for olefinic protons. A possible structural type (6) for the polymer would result from polymerisation followed by some ring-opening (Scheme 2; compare easy ring-opening of 2-substituted tetrahydrofurans).

With more oxygen atoms in the ring system, poorly defined complex products or simple break-down were observed. 2,5-Dimethoxytetrahydrofuran reacted vigorously with  $\text{TiCl}_4$  to give thick, black, tarry materials. Reaction of 1,3-dioxolane with  $\text{TiCl}_4$  gave a thick, yellow gelatinous mass and 1,3,5-trioxane gave formaldehyde.

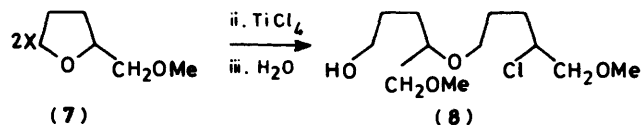
(b) *Hydrolytic Work-up*.—Scheme 1 implies that, before the final thermal release of the dichloro ether (1;  $\text{R} = \text{R}' = \text{Cl}$ ;  $n =$



Scheme 2.

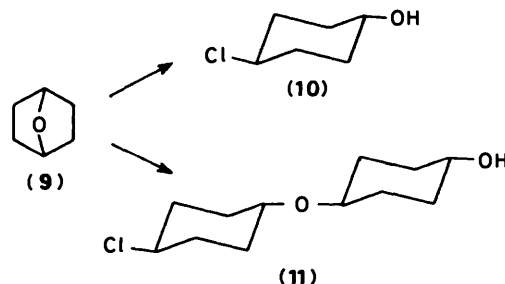
1), a titanium complex (5) is present in which ring-opening and dimerisation has occurred. Addition of water to this complex should result in the release of the chloro alcohol (1;  $\text{R} = \text{Cl}$ ,  $\text{R}' = \text{OH}$ ;  $n = 1$ ) by hydrolysis of the  $\text{Ti-O}$  bond. Therefore, on aqueous work-up, the cyclic ethers which gave dichloro compounds on thermal (non-hydrolytic) work-up should give the corresponding chloro alcohols. In general, this expected correspondence was observed. Aqueous work-up of the products of reaction of  $\text{TiCl}_4$  with THF, 2-methylTHF, 2,5-dimethylTHF, THP, 4-methylTHP and oxepane gave dimeric chloro alcohols (*cf* Scheme 1, path c), as described in the Experimental section.

The cyclic ether (7), with  $\text{TiCl}_4$ , ring-opened and dimerised to give the chloro alcohol (8), with no evidence for demethylation occurring (Scheme 3). The bicyclic ether (9) was used to

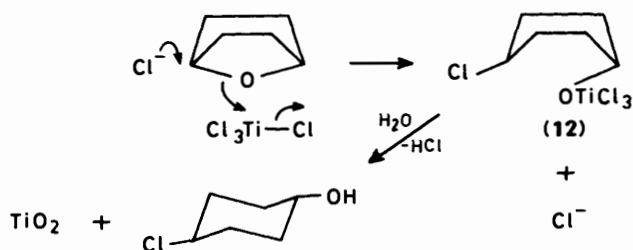


Scheme 3.

investigate the stereochemical aspects of the dimerisation. On reaction with  $\text{TiCl}_4$ , the ether (9) gave the chloro alcohols (10) and (11) (Scheme 4), the conformations of which were examined by  $^1\text{H}$  n.m.r. and are as shown (Scheme 4). Analysis of the  $^1\text{H}$  n.m.r. spectra of the chloro alcohols (10) and (11) is given below.

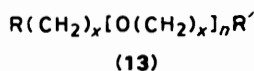


Scheme 4.



For the chloro alcohol (10), the chloro and hydroxy substituents have a *trans* relationship, implying an  $S_N2$  type ring-opening (Scheme 5). The incoming chlorine could arise by inter- or intra-molecular transfer of the Cl from  $TiCl_4$  or from traces of  $Cl^-$  in solution (Scheme 5). The template effect required in Scheme 1 implies intramolecular attack of Cl from the same side as the departing oxygen during ring-opening. Alkyl substitution at the carbon ( $\alpha$ -carbon) adjacent to the oxygen of the cyclic ethers would make attack from the rear by chlorine more difficult in an  $S_N2$  type reaction, but would favour a reaction of the  $S_N1$  type in which a carbonium ion centre is involved. As alkyl substitution was found to greatly accelerate the rate of ring-opening and dimerisation, the process probably involves an  $S_N1$  type reaction; the formation of a carbonium ion centre at the  $\alpha$ -carbon atom would be facilitated through co-ordination of the ether oxygen to  $TiCl_4$ . Molecular models (Dreiding) indicate that intramolecular attack from behind the departing oxygen ( $S_N2$ ) is geometrically improbable. Finally, the rapid hydrolysis of any titanium-bonded species [e.g., structure (5) in Scheme 1 or structure (12) in Scheme 5] would involve attack by water at titanium rather than inversion of configuration by nucleophilic displacement at carbon. These considerations lead to the conclusion that, despite an apparent template effect as considered in Scheme 1, the ring-opening reaction probably proceeds intermolecularly and that there is no template effect. Similarly, the dimeric chloro alcohol (11) (Scheme 4) arises through nucleophilic displacement ( $S_N2$ ) of a second cyclic ether molecule (9) by the initially formed titanium species (12) (Scheme 5). Therefore, the dimerisation step also appears to be intermolecular. If the intermolecular mechanism is correct, it could be expected that the reaction should proceed further to give trimers, tetramers, and so on. However, once bonded to one oxygen and three chlorines (12) (Scheme 5), titanium is not such a powerful Lewis acid as when bonded to four chlorines ( $TiCl_4$ ). For example, the compounds  $Ti(OR)_4$ , in which R is alkyl or phenyl, are very weak Lewis acids. Failure to observe significant quantities of oligomers in the reaction of  $TiCl_4$  with cyclic ethers may therefore be due to the reduced reactivity of mixed oxychloro titanium species such as that in structure (12) (Scheme 5). Significantly, in the reaction of  $TiCl_4$  with THF, some trimer (1; R = Cl, R' = OH;  $n = 2$ ) and tetramer (1; R = Cl, R' = OH;  $n = 3$ ) were isolated. G.c.-m.s. of other crude reaction products from cyclic ethers and  $TiCl_4$  revealed the presence of small quantities of oligomers as well as the major dimeric product (see the Experimental section).

Reaction of 1,4-dioxane with  $TiCl_4$  gave, on aqueous work-up, two products arising from ring-opening (13; R = Cl, R' = OH;  $x = 2$ ;  $n = 1$ ) and dimerisation (13; R = Cl, R' = OH;  $x = 2$ ;  $n = 3$ ). Non-hydrolytic reaction gave the corresponding dichloro compounds (13; R = R' = Cl;  $x = 2$ ;  $n = 1, 2, 3$ ).



With THF,  $TiCl_3$  forms a complex,  $TiCl_3 \cdot 3THF$ , which on heating disproportionates to give  $TiCl_3 \cdot THF$ .<sup>11</sup> On refluxing THF with  $TiCl_3$ , very low yields of the dichloro compound (1; R = R' = Cl;  $n = 1$ ) and 1,4-dichlorobutane were obtained.  $VCl_3 \cdot 3THF$ ,<sup>11</sup> which is almost insoluble in an excess of THF, gave no ring-opened products;  $TiF_4$  gave no ring-opened nor dimeric products.

*Analysis of  $^1H$  N.M.R. Spectra of the Chloro Alcohols (10) and (11).*—The  $^1H$  n.m.r. spectrum of the chloro alcohol (10) was measured at 360 MHz. Irradiation of the various resonances are depicted in Figure 1 in which the full lines represent strong coupling (ca. 15 Hz) and the dotted lines represent weak coupling (ca. 2–6 Hz). For example, irradiation of 2-H

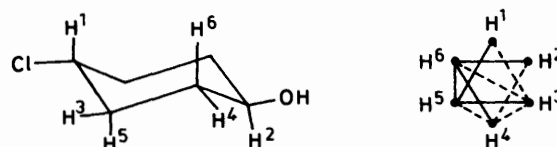


Figure 1.

removed a 15 Hz coupling from 6-H and *vice-versa* but the effect on 4-H was only to remove fine coupling. The predominantly axial nature of the resonances at 1-H, 2-H is indicated by their large width at half-height (ca. 20 Hz), far in excess of that normally observed for equatorial protons.<sup>12</sup> Assignment of 1-H as being adjacent to Cl, and 2-H adjacent to OH can be made by reference to many earlier examples.<sup>13</sup> Actual resonances are given in the Experimental section.

For the chloro alcohol (11), the  $^1H$  resonances could be divided into two non-interacting sets corresponding to the two halves of the molecule. Figure 2 shows the large and small couplings observed on irradiation. Even at 360 MHz, the

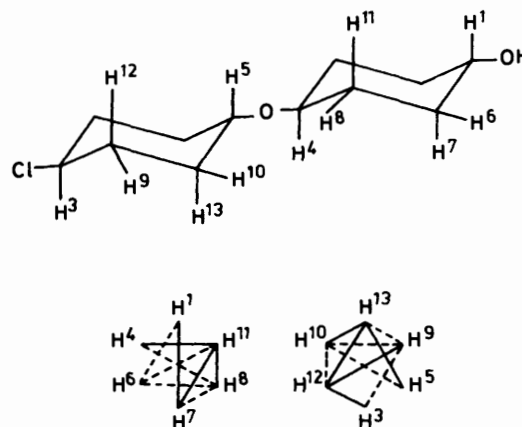


Figure 2.

spectrum of the chloro alcohol (11) was complex, with many overlapping multiplets. Addition of 0.1 equiv. of the shift reagent,  $Eu(fod)_3$ , spread out the spectrum sufficiently for all the multiplets to be separated. The irradiation experiments were carried out on this 'shifted' spectrum.

Using the PRXBLD program,<sup>14</sup> a minimum energy conformation for structure (11) was obtained and hence the coordinates for all the hydrogens (1-H to 13-H). By assuming that the shift reagent resided predominantly at the hydroxy group,

distances ( $\bar{R}_i$ ) from each hydrogen ( $H_i$ ) to the shift reagent were calculated. The induced shifts ( $\Delta\nu_i$ ) for the hydrogens were obtained from the difference between the 360 MHz spectra before and after addition of shift reagent. A graph of  $\log \Delta\nu_i$  against  $\log \bar{R}_i$  was linear with slope  $-2.5$  compared with a theoretical slope<sup>15</sup> of  $-3$ . This close correspondence between the observed and theoretical slopes indicates that the conformation and assignment of protons in the chloro alcohol (11) are as required by Figure 2.

### Conclusion

The reaction of  $TiCl_4$  with a variety of cyclic ethers afforded either dichloro compounds (13;  $R = R' = Cl$ ) or the chloro alcohols (13;  $R = Cl, R' = OH$ ) depending on the method of work-up. Predominantly, either simple ring-opened compounds (13;  $n = 0$ ) or dimers (13;  $n = 1$ ) were obtained and the results, taken with the probable *cis/trans* nature of the initial complexes between the ethers and  $TiCl_4$  or  $TiBr_4$ , initially suggested an intramolecular template effect might be operative. However, the stereochemistry of formation of the chloro alcohols (10) and (11), the formation of small quantities of oligomers, and consideration of molecular models indicates that an intermolecular mechanism was acting and that a template effect is illusory. Failure of significant polymerisation beyond the dimerisation stage can be attributed to the reduced activity of intermediate oxytitanium compounds compared with  $TiCl_4$ . For cyclic ethers, the ease of the ring-opening and dimerisation decreased with increased ring size and increased with aliphatic substitution  $\alpha$ - to the ether linkage.

### Experimental

Compounds were identified and their purity determined by three or more of the following: b.p. (or m.p.), m.s., g.c.-m.s., g.c., i.r.,  $^1H$  n.m.r.,  $^{13}C$  n.m.r., t.l.c., and elemental analysis. Mass spectra were recorded on an AEI MS902 or MS12 mass spectrometer at 70 eV; g.c.-m.s. was performed on a VG Micromass 7070 at 70 eV.  $^1H$  n.m.r. spectra were recorded on a Perkin-Elmer R34 (220 MHz) or a Bruker 360 MHz spectrometer, using  $CDCl_3$  as the solvent;  $^{13}C$  n.m.r. spectra were obtained at 90 MHz. Analytical g.c. was carried out in packed or capillary columns with Ultrabond 20M as the stationary phase. T.l.c. was effected on silica gel with  $CH_2Cl_2$  as the liquid phase.

$TiCl_4$ ,  $TiF_4$ ,  $TiCl_3$ , and  $VCl_3$  were commercial samples (Aldrich) and were used without further purification.  $TiBr_4$  was prepared by a reported method.<sup>16</sup> The cyclic ethers (Aldrich) were dried over  $LiAlH_4$  or  $CaH_2$  and distilled immediately before use.

**Reaction of  $TiCl_4$  with an Excess of THF.**— $TiCl_4$  (30 g, 17.5 ml) was added dropwise with stirring to THF (200 ml) cooled to 0 °C. A vigorous reaction occurred to give the bright yellow insoluble complex,  $TiCl_4 \cdot 2THF$ . When all of the  $TiCl_4$  had been added, the mixture was refluxed for 2 h to yield a black solution. The excess of THF was removed on a rotary evaporator to leave a thick, black oily residue (A) which was worked up either hydrolytically or non-hydrolytically:

(a) *Non-hydrolytic work-up.* The residue (A) was heated at 110–125 °C for 1 h under reduced pressure (10 mmHg) to give a yellow distillate which was taken up in ether, washed with water, and dried. Evaporation of the solvent left a residue which was fractionally distilled to give: (i) 1,4-dichlorobutane (4.1 g), b.p. 22 °C/1.5 mmHg and (ii) 1,9-dichloro-5-oxanonane (1;  $R = R' = Cl; n = 1$ ) (17.1 g, 55% yield based on  $TiCl_4$ ), b.p. 79–82 °C/0.7 mmHg (lit.,<sup>4</sup> b.p. 84–86 °C/0.5 mmHg);  $\delta_H$  3.57 (4 H, t,  $J$  6.3 Hz,  $2 \times CH_2Cl$ ), 3.43 (4 H, t,  $J$  6.3 Hz,  $2 \times OCH_2$ ), 1.85

(4 H, m,  $2 \times CH_2$ ), and 1.70 (4 H, m,  $2 \times CH_2$ );  $m/z$  202, 200, and 198 ( $M^+$ ; 2 Cl).

(b) *Hydrolytic work-up.* The residue (A) was stirred with water (3 ml) and ether for 15 min, after which time more water was added and the ether extracts were dried ( $MgSO_4$ ) and evaporated to leave an oil (36 g). Fractional distillation of this oil gave: (i) 9-chloro-5-oxanonan-1-ol (1;  $R = Cl, R' = OH; n = 1$ ) (9 g), b.p. 91–95 °C/0.012 mmHg (lit.,<sup>5</sup> b.p. 90 °C/0.15 mmHg);  $\delta_H$  3.62 (2 H, t,  $J$  6 Hz,  $CH_2Cl$ ), 3.55 (2 H, t,  $J$  6.5 Hz,  $CH_2OH$ ), 3.45 (4 H, m,  $2 \times OCH_2$ ), 2.48 (1 H, s, OH), 1.85 (2 H, m,  $CH_2$ ), and 1.75–1.64 (6 H, m,  $3 \times CH_2$ );  $m/z$  181 ( $MH^+$ ) (Found: C, 53.1; H, 10.0. Calc. for  $C_8H_{17}ClO_2$ : C, 53.2; H, 9.5%), (ii) 14-chloro-5,10-dioxatetradecan-1-ol (1;  $R = Cl, R' = OH; n = 2$ ) (10.5 g), b.p. 140–146 °C/0.012 mmHg (lit.,<sup>17</sup> b.p. 136 °C/0.01 mmHg);  $\delta_H$  3.61 (2 H, t,  $J$  6 Hz,  $CH_2Cl$ ), 3.54 (2 H, t,  $J$  6.6 Hz,  $CH_2OH$ ), 3.41 (8 H, m,  $4 \times OCH_2$ ), 2.62 (1 H, s, OH), 1.84 (2 H, m,  $CH_2$ ), and 1.72–1.59 (10 H, m,  $5 \times CH_2$ );  $m/z$  253 ( $MH^+$ ) (Found: C, 57.0; H, 10.3. Calc. for  $C_{12}H_{25}ClO_3$ : C, 57.0; H, 10.0%), and (iii) 19-chloro-5,10,15-trioxanadecan-1-ol (1;  $R = Cl, R' = OH; n = 3$ ) (5.5 g), b.p. 198–204 °C/0.012 mmHg;  $\delta_H$  3.61 (2 H, t,  $J$  5.9 Hz,  $CH_2Cl$ ), 3.54 (2 H, t,  $J$  6.6 Hz,  $CH_2OH$ ), 3.41 (12 H, m,  $6 \times OCH_2$ ), 2.63 (1 H, s, OH), 1.84 (2 H, m,  $CH_2$ ), and 1.72–1.58 (14 H, m,  $7 \times CH_2$ );  $m/z$  325 ( $MH^+$ ) (Found: C, 59.3; H, 10.7.  $C_{16}H_{33}ClO_4$  requires C, 59.2; H, 10.2%).

In the following experiments, hydrolytic and non-hydrolytic work-up procedures are similar to those (a) and (b), described above for THF.

**Reaction of  $TiCl_4$  with THP.**— $TiCl_4$  (65 g) was added to an ice-cold solution of THP (850 ml) under  $N_2$  and the mixture was refluxed for 32 h. After evaporation of the excess of THP under reduced pressure, the black oily residue (B) was heated at 135–140 °C/14 mmHg for 2 h to give a distillate. On redistillation, some 1,5-dichloropentane was obtained as well as 1,11-dichloro-6-oxaundecane (29.5 g, 40% based on  $TiCl_4$ ), b.p. 90–95 °C/0.013 mmHg (lit.,<sup>4</sup> b.p. 65–70 °C/ $3 \times 10^{-6}$  mmHg),  $\delta_H$  3.52 (4 H, t,  $J$  6.5 Hz,  $2 \times CH_2Cl$ ), 3.39 (4 H, t,  $J$  6.5 Hz,  $2 \times CH_2O$ ), 1.78 (4 H, m, 5 lines,  $J$  6.5 Hz,  $2 \times CH_2CH_2Cl$ ), 1.58 (4 H, m, 5 lines,  $J$  6.5 Hz,  $2 \times CH_2CH_2O$ ), and 1.50 (4 H, m,  $2 \times CH_2$ );  $m/z$  230, 228, and 226 ( $M^+$ ; 2 Cl) (Found: C, 53.1; H, 8.9. Calc. for  $C_{10}H_{20}Cl_2O$ : C, 52.9; H, 8.9%). Hydrolytic work-up of the residue (B) afforded an oil (22 g) which was fractionally distilled to give: (i) 5-chloropentane-1-ol, b.p. 56–57 °C/0.9 mmHg (8.1 g) and (ii) 11-chloro-6-oxaundecan-1-ol (7.5 g), b.p. 120 °C/0.9 mmHg (lit.,<sup>5</sup> b.p. 110–114 °C/0.3 mmHg),  $\delta_H$  3.63 (2 H, t,  $J$  7 Hz,  $CH_2Cl$ ), 3.55 (2 H, t,  $J$  7 Hz,  $CH_2OH$ ), 3.4 (4 H, t,  $J$  7 Hz,  $2 \times CH_2O$ ), 1.78 (2 H, m,  $J$  7 Hz,  $CH_2CH_2Cl$ ), 1.66 (1 H, s, OH), 1.58 (6 H, m,  $3 \times CH_2$ ), and 1.45 (4 H, m,  $2 \times CH_2$ );  $m/z$  209 ( $MH^+$ ) (Found: C, 57.6; H, 10.4. Calc. for  $C_{10}H_{21}ClO_2$ : C, 57.5; H, 10.1%).

**Reaction of  $TiCl_4$  with 4-Methyltetrahydropyran.**—The experiment was carried out as for tetrahydropyran with an aqueous work-up to give, (i) 1-chloro-3-methylpentan-5-ol (60% yield), b.p. 95–97 °C/13 mmHg and (ii) 11-chloro-3,9-dimethyl-6-oxaundecan-1-ol (38%), b.p. 110 °C/0.025 mmHg,  $\delta_H$  3.33 (2 H, t,  $J$  7 Hz,  $CH_2Cl$ ), 3.28 (2 H, t,  $J$  7 Hz,  $CH_2OH$ ), 3.23 (4 H, t,  $J$  7 Hz,  $2 \times CH_2O$ ), 2.9 (1 H, s, OH), 1.6 (10 H, m,  $5 \times CH_2$ ), and 0.95 (6 H, d,  $J$  6 Hz,  $2 \times Me$ );  $m/z$  237 ( $MH^+$ ) (Found: C, 60.9; H, 10.9.  $C_{12}H_{25}ClO_2$  requires C, 60.9; H, 10.6%).

**Reaction of  $TiCl_4$  with Oxepane (2;  $R = R' = H; n = 2$ ).**—A mixture of  $TiCl_4$  (25.7 g; 15 ml) was stirred with oxepane (50 ml) at 70 °C for 48 h. To the cooled reaction mixture was added ether (200 ml) to precipitate a grey inorganic solid which was filtered off. The filtrate was evaporated to remove the ether and

then heated to 100 °C at 14 mmHg to leave a residue which was fractionally distilled to give; (i) 1,13-dichloro-7-oxatridecane (6.9 g), b.p. 90–92 °C/0.015 mmHg (lit.,<sup>18</sup> b.p. 124 °C/1 mmHg);  $\delta_{\text{H}}$  3.53 (4 H, t,  $J$  6.5 Hz, 2  $\times$  CH<sub>2</sub>Cl), 3.39 (4 H, t,  $J$  6.5 Hz, 2  $\times$  CH<sub>2</sub>O), 1.77 (4 H, m, 5 lines,  $J$  6.5 Hz, 2  $\times$  CH<sub>2</sub>CH<sub>2</sub>Cl), 1.57 (4 H, m, 5 lines,  $J$  6.5 Hz, CH<sub>2</sub>CH<sub>2</sub>O), and 1.49–1.32 (8 H, m, 4  $\times$  CH<sub>2</sub>);  $m/z$  258, 256, and 254 ( $M^+$ ; 2 Cl) (Found: C, 56.4; H, 9.7. Calc. for C<sub>12</sub>H<sub>24</sub>Cl<sub>2</sub>O: C, 56.5; H, 9.4%) and (ii) 1, 20-dichloro-7,14-dioxacosane (2.3 g), b.p. 165 °C/0.006 mmHg,  $\delta_{\text{H}}$  3.53 (4 H, t,  $J$  7 Hz, 2  $\times$  CH<sub>2</sub>Cl), 3.39 (8 H, t,  $J$  7 Hz, 4  $\times$  CH<sub>2</sub>O), 1.77 (4 H, m, 5 lines,  $J$  7 Hz, 2  $\times$  CH<sub>2</sub>CH<sub>2</sub>Cl), 1.58 (8 H, m, 5 lines,  $J$  7 Hz, 4  $\times$  CH<sub>2</sub>CH<sub>2</sub>O), 1.45 (8 H, m, 4  $\times$  CH<sub>2</sub>), and 1.35 (4 H, m, 2  $\times$  CH<sub>2</sub>);  $m/z$  358, 356, and 354 ( $M^+$ ; 2 Cl) (Found: C, 60.8; H, 10.7. C<sub>18</sub>H<sub>36</sub>Cl<sub>2</sub>O<sub>2</sub> requires C, 60.8; H, 10.1%).

For the hydrolytic work-up, TiCl<sub>4</sub> (10.4 g, 6.0 ml) was stirred with oxepane (30 g) at 60–70 °C for 24 h to give a dark brown solution. Water was added and the mixture was extracted with ether. The ether extracts were dried (MgSO<sub>4</sub>) and the solvent evaporated to yield a residual oil which, on fractional distillation, gave 6-chlorohexan-1-ol and 13-chloro-7-oxatridecane-1-ol (3.4 g), b.p. 110 °C/0.006 mmHg (lit.,<sup>18</sup> b.p. 141 °C/2 mmHg);  $\delta_{\text{H}}$  3.64 (2 H, t,  $J$  7 Hz, CH<sub>2</sub>Cl), 3.52 (2 H, t,  $J$  7 Hz, CH<sub>2</sub>OH), 3.38 (4 H, t,  $J$  7 Hz, 2  $\times$  CH<sub>2</sub>O), 1.77 (2 H, m,  $J$  7 Hz, CH<sub>2</sub>CH<sub>2</sub>Cl), 1.56 (6 H, br m, 3  $\times$  CH<sub>2</sub>), 1.52 (1 H, s, OH), and 1.36 (8 H, br m, 4  $\times$  CH<sub>2</sub>);  $m/z$  237 ( $MH^+$ ) (Found: C, 60.9; H, 10.7. Calc. for C<sub>12</sub>H<sub>25</sub>ClO<sub>2</sub>: C, 60.9; H, 10.6%).

**Reaction of TiCl<sub>4</sub> with 2-Methyltetrahydrofuran.**—TiCl<sub>4</sub> (10 g) was added dropwise, with stirring, to an excess of 2-methyltetrahydrofuran (50 ml) at 0 °C. The initial yellow solution darkened as the TiCl<sub>4</sub> was added. The mixture was stirred at room temperature for 48 h to give a black solution to which water (100 ml) was added. Extraction with diethyl ether and subsequent distillation gave 9-chloro-4-methyl-6-oxadecan-1-ol (4.52 g), b.p. 105 °C/0.03 mmHg [a mixture of diastereoisomers];  $m/z$  209 ( $MH^+$ );  $\delta_{\text{H}}$  4.04 (1 H, m,  $J$  7 Hz, CHCl), 3.62 (2 H, t,  $J$  7 Hz, CH<sub>2</sub>OH), 3.53 (2 H, m,  $J$  7 Hz, OCH<sub>2</sub>), 3.43 (1 H, m,  $J$  7 Hz, OCH), 2.11 (1 H, s, OH), 1.8–1.55 (8 H, m, 4  $\times$  CH<sub>2</sub>), 1.52 (3 H, d,  $J$  7 Hz, Me), and 1.15 (3 H, d,  $J$  7 Hz, Me) (Found: C, 57.1; H, 10.2. C<sub>10</sub>H<sub>21</sub>ClO<sub>2</sub> requires C, 57.5; H, 10.1%).

**Reaction of TiCl<sub>4</sub> with 2,5-Dimethyltetrahydrofuran.**—TiCl<sub>4</sub> (20 g) was added dropwise to a stirred excess of *cis/trans*-2,5-dimethyltetrahydrofuran (50 ml) at 0 °C. The initial yellow solution darkened rapidly and became black after stirring at room temperature for 48 h. Addition of water (100 ml), extraction with ether and evaporation of the solvent gave an oil which was separated by column chromatography on silica gel, with dichloromethane as the eluant, into 3 components: (i) 5-chlorohexan-2-ol (4.2 g), b.p. 40–42 °C/0.4 mmHg; (ii) 2,10-dichloro-5,7-dimethyl-6-oxaundecane (3.8 g), b.p. 110–113 °C/0.2 mmHg;  $\delta_{\text{H}}$  4.04 (2 H, m, 2  $\times$  CHCl), 3.46 (2 H, m, CHOCH), 1.9–1.6 (8 H, br m, 4  $\times$  CH<sub>2</sub>), 1.51 (6 H, d,  $J$  6 Hz, 2  $\times$  Me), 1.13 (3 H, d,  $J$  6 Hz, Me), and 1.09 (3 H, d,  $J$  6 Hz, Me): a mixture of diastereoisomers;  $m/z$  258, 256, and 254 [ $M^+$ ; 2 Cl] (Found: C, 56.8; H, 9.8. C<sub>12</sub>H<sub>24</sub>Cl<sub>2</sub>O requires C, 56.5; H, 9.5%); (iii) a diastereoisomeric mixture of 10-chloro-5,7-dimethyl-6-oxaundecan-2-ol (0.5 g), b.p. 84 °C/0.012 mmHg;  $m/z$  237 ( $MH^+$ );  $\delta_{\text{H}}$  4.03 (1 H, m,  $J$  6 Hz, CHCl), 3.72 (1 H, m, CHOH), 3.49 (2 H, m, CHOCH), 2.60 (1 H, s, OH), 1.9–1.45 (8 H, m, 4  $\times$  CH<sub>2</sub>), 1.5 (3 H, d,  $J$  6 Hz, Me), 1.17 (3 H, d,  $J$  6 Hz, Me), and 1.1 (6 H, d,  $J$  6 Hz, 2  $\times$  Me) (Found: C, 60.7; H, 10.7. C<sub>12</sub>H<sub>25</sub>ClO<sub>2</sub> requires C, 60.9; H, 10.6%).

**Reaction of TiCl<sub>4</sub> with 1-Tetrahydrofuran-2-yl-2-oxapropane (7).**—TiCl<sub>4</sub> (25.9 g) was added dropwise with stirring to 1-

tetrahydrofuran-2-yl-2-oxapropane (90 g) at 0 °C. After the mixture had been stirred for 2 h under N<sub>2</sub> at 70–80 °C, it was allowed to stand for 48 h and then heated again for 3 h at 80 °C. The solution was poured into water and extracted with ether to give, after fractional distillation, (i) 4-chloro-2-oxaheptan-7-ol (5.3 g), b.p. 100–103 °C/12 mmHg;  $m/z$  153 ( $MH^+$ );  $\delta_{\text{H}}$  3.78 (1 H, m,  $J$  8 Hz, CHCl), 3.57 (2 H, m,  $J$  7, 2 Hz, 2 H, CH<sub>2</sub>OH), 3.39 (1 H, dd,  $J$  10, 8 Hz, CHOMe), 3.37 (2 H, s, OMe), 3.24 (H, dd,  $J$  10, 8 Hz, CHOMe), 2.42 (1 H, s, OH), 2.0–1.8 (2 H, m, CH<sub>2</sub>), and 1.65–1.45 (2 H, m, CH<sub>2</sub>), and (ii) 4-chloro-9-methoxymethyl-2,8-dioxadodecane-12-ol (8) (1.5 g), b.p. 140 °C/0.005 mmHg;  $m/z$  269 ( $MH^+$ );  $\delta_{\text{H}}$  3.78 (1 H, m,  $J$  8 Hz, CHCl), 3.63 (1 H, m,  $J$  8 Hz, CHO), 3.54 (2 H, m,  $J$  7, 2 Hz, CH<sub>2</sub>OH), 3.45 (2 H, m, OCH<sub>2</sub>), 3.38 (3 H, s, OMe), 3.35 (3 H, s, OMe), 3.30 (2 H, m, 2  $\times$  CHOMe), 3.25 (2 H, dd,  $J$  8, 2 Hz, 2  $\times$  CHOMe), 2.45 (1 H, s, OH), 1.96–1.75 (2 H, m, CH<sub>2</sub>), 1.75–1.55 (2 H, m, CH<sub>2</sub>), and 1.54–1.40 (4 H, m, 2  $\times$  CH<sub>2</sub>): a mixture of diastereoisomers (Found: C, 53.6; H, 9.4. C<sub>12</sub>H<sub>25</sub>ClO<sub>4</sub> requires C, 53.6; H, 9.3%).

**Reaction of TiCl<sub>4</sub> with 2,5-Dihydrofuran.**—During the dropwise addition of TiCl<sub>4</sub> (10 g) to a stirred excess of 2,5-dihydrofuran (40 ml) at 0 °C, a vigorous reaction occurred to give a dark red solution. As the addition of TiCl<sub>4</sub> continued, the solution became paler and, eventually, a bright yellow solid was precipitated. The mixture was then refluxed for 72 h to give a black solution. Excess of 2,5-dihydrofuran was removed by distillation and the residue was heated under reduced pressure to give a distillate (1.2 g, b.p. 30–40 °C/0.5 mmHg) consisting of a mixture (23 : 77) of (*Z*)- and (*E*)-1,4-dichlorobut-2-ene; a black intractable residue remained. A mixture of 2,5-dihydrofuran (4.0 g) and concentrated HCl (20 ml) was heated to about 90 °C for 4 h. The product was extracted with ether and the extracts were dried (MgSO<sub>4</sub>) and evaporated to give (*Z*)-1,4-dichlorobut-2-ene (4.2 g), b.p. 30 °C/0.5 mmHg.

**Reaction of TiCl<sub>4</sub> with 2,3-Dihydrofuran.**—Reaction between TiCl<sub>4</sub> (10 g) and 2,3-dihydrofuran (40 ml) was uncontrollably violent even at –78 °C. Accordingly, TiCl<sub>4</sub> (10 g) was added dropwise to a stirred solution of 2,3-dihydrofuran (8 g) in CH<sub>2</sub>Cl<sub>2</sub> (200 ml) at 0 °C. The reaction mixture was refluxed for 72 h, concentrated under reduced pressure and the residue was treated with water (100 ml). Extraction with ether gave a light brown, powdery solid polymer (1.4 g);  $\nu_{\text{max}}$ . 3 420 (OH) and 1 055 (C–O–C) cm<sup>–1</sup>;  $\delta_{\text{H}}$  3.8 (vbr, unresolved), 2.5 (br, OH, exchanges with D<sub>2</sub>O), and 1.9 (vbr, unresolved) (Found: C, 65.5; H, 8.5%).

**Reaction of TiCl<sub>4</sub> with 1,3,5-Trioxane.**—TiCl<sub>4</sub> (20 g) was added dropwise to a stirred solution of trioxane (20 g) in CCl<sub>4</sub> (200 ml) cooled to 0 °C. The initial yellow precipitate became colourless. The reaction mixture was stirred at room temperature for 18 h, filtered, and the filtrate evaporated under reduced pressure to yield an oil, attempted distillation of which caused the oil to change to a white solid. A positive silver mirror test with ammoniacal silver nitrate, after boiling a sample with dilute HCl for a few minutes, indicated the solid was a polymer of formaldehyde.

**Reaction of TiCl<sub>4</sub> with 1,4-Dioxane.**—(a) TiCl<sub>4</sub> (30 g) was added dropwise to a stirred excess of 1,4-dioxane (100 ml) at 20 °C. Following a vigorous reaction, a bright yellow solid separated. The mixture was heated in a sealed tube at 160 °C for 5 days. The resulting black mixture was concentrated under reduced pressure to yield a dark oil which was washed with water and extracted with CHCl<sub>3</sub>. Evaporation of the chloroform extracts afforded a brown oil which was chromatographed on silica gel, with CH<sub>2</sub>Cl<sub>2</sub> as the eluant, to give, (i) 1,5-dichloro-

3-oxapentane (7.8 g), b.p. 67–69 °C/17 mmHg (lit.,<sup>19</sup> b.p. 177 °C/760 mmHg), (ii) 1,8-dichloro-3,6-dioxaoctane (2.8 g), b.p. 76–78 °C/1.2 mmHg;  $\delta_{\text{H}}$  3.70 (12 H, m);  $m/z$  139 and 137 ( $M^+ - \text{CH}_2\text{Cl}$ ) (no  $M^+$  observed) (Found: C, 38.8; H, 6.4.  $\text{C}_6\text{H}_{12}\text{Cl}_2\text{O}_2$  requires C, 38.5; H, 6.5%), and (iii) 1,11-dichloro-3,6,9-trioxaundecane (2.1 g), b.p. 98–100 °C/0.2 mmHg;  $\delta_{\text{H}}$  3.70 (16 H, m);  $m/z$  183 and 181 ( $M^+ - \text{CH}_2\text{Cl}$ ) [no  $M^+$  observed] (Found: C, 41.2; H, 6.8.  $\text{C}_8\text{H}_{16}\text{Cl}_2\text{O}_3$  requires C, 41.6; H, 7.0%).

(b)  $\text{TiCl}_4$  (10 g) in an excess of 1,4-dioxane (40 ml) was refluxed for 3 weeks. The resulting black reaction mixture was worked up as in (a) above to give 1,5-dichloro-3-oxapentane (0.69 g), 1,8-dichloro-3,6-dioxaoctane (0.07 g), and 1,11-dichloro-3,6,9-trioxaundecane (1.55 g).

(c)  $\text{TiCl}_4$  (26 g) was added to dry 1,4-dioxane (100 ml) at 20 °C and the mixture was heated under reflux for one week. Water (ca. 100 ml) was added and the organic products were extracted with diethyl ether. Evaporation of the ether extracts yielded an oil (250 mg) which was chromatographed on silica gel, with  $\text{CH}_2\text{Cl}_2$  as the eluant, to give, (i) 5-chloro-3-oxapentanol (55 mg);  $m/z$  124 ( $M^+$ ); (ii) 11-chloro-3,6,9-trioxaundecan-1-ol (150 mg), b.p. 150 °C/0.005 mmHg,  $m/z$  213 ( $M^+$ );  $\delta_{\text{H}}$  3.75 (2 H, t,  $J$  7.2 Hz,  $\text{CH}_2\text{Cl}$ ), 3.72 (2 H, t,  $J$  7.2 Hz,  $\text{CH}_2\text{OH}$ ), 3.67 (8 H, s,  $2 \times \text{OCH}_2\text{CH}_2\text{O}$ ), 3.63 (2 H, t,  $J$  7.2 Hz,  $\text{OCH}_2\text{CH}_2\text{Cl}$ ), 3.61 (2 H, t,  $J$  7.2 Hz,  $\text{OCH}_2\text{CH}_2\text{OH}$ ), and 1.85 (1 H, s, OH) (Found: C, 45.0; H, 8.1.  $\text{C}_8\text{H}_{17}\text{ClO}_4$  requires C, 45.2; H, 8.0%).

**Reaction of  $\text{TiBr}_4$  with THF.**—A solution of  $\text{TiBr}_4$  (13.3 g) in  $\text{CH}_2\text{Cl}_2$  (20 ml) was added dropwise, with stirring, to THF (150 ml) at 0 °C; a dark red solid was formed. The reaction mixture was stirred at room temperature for 18 h to give a red solution. Excess of THF was removed under reduced pressure to yield a viscous, dark red, oily residue which was heated under reduced pressure (0.8 mmHg) to give a brown distillate. This oil was fractionally distilled to afford (i) 1,4-dibromobutane (4.7 g), b.p. 32–34 °C/0.8 mmHg and (ii) 1,9-dibromo-5-oxanonane (1.2 g), b.p. 105 °C/0.8 mmHg (lit.,<sup>20</sup> b.p. 98–104 °C/0.6 mmHg);  $m/z$  290, 288, and 286 ( $M^+$ ; 2Br);  $\delta_{\text{H}}$  3.45 (4 H, t,  $J$  6.5 Hz,  $2 \times \text{CH}_2\text{Br}$ ), 3.42 (4 H, t,  $J$  6.5 Hz,  $2 \times \text{OCH}_2$ ), 1.82 (4 H, m,  $2 \times \text{CH}_2$ ), and 1.69 (4 H, m,  $2 \times \text{CH}_2$ ).

A similar reaction with aqueous work-up afforded only 4-bromobutan-1-ol (75% yield).

**Reaction of  $\text{TiF}_4$  with THF.**—Addition of  $\text{TiF}_4$  (16.1 g) in small portions to THF (150 ml) at 0 °C gave a pale pink solution and a colourless precipitate. The mixture was refluxed for 5 h and excess of THF was removed under reduced pressure, to leave a residue which, when heated under reduced pressure, yielded no organic material. Similarly, on aqueous work-up, no organic material was obtained.

**Reaction of  $\text{TiBr}_4$  with 1,4-Dioxane.**—A solution of  $\text{TiBr}_4$  (5.4 g) in  $\text{CH}_2\text{Cl}_2$  (5 ml) was added dropwise, with stirring, to 1,4-dioxane (40 ml) at room temperature. The mixture was heated under reflux for three weeks and then worked up to give an oil (2.5 g) which contained (g.c.–m.s.): (i) 1,5-dibromo-3-oxapentane (70%);  $m/z$  234, 232, and 230 ( $M^+$ ; 2Br), (ii) 1,8-dibromo-3,6-dioxaoctane (10%);  $m/z$  197 and 195 ( $M^+ - \text{Br}$ ) (no  $M^+$

observed), and (iii) 1,11-dibromo-3,6,9-trioxaundecane (20%);  $m/z$  322, 320, and 318 ( $M^+$ ; 2Br).

**Reaction of  $\text{TiCl}_4$  with 7-Oxabicyclo[2.2.1]Heptane (9).**— $\text{TiCl}_4$  (2 ml) with 7-oxabicyclo[2.2.1]heptane (10 g) was stirred at 30 °C for 18 h, after which time water was added and the thick material was extracted with ether. The ether extracts were dried and evaporated to afford a residue which was fractionally distilled to yield: (i) 4-chlorocyclohexanol (10) (1.4 g), b.p. 40–45 °C/0.0002 mmHg (lit.,<sup>21</sup> b.p. 105 °C/12 mmHg), m.p. 69–70 °C (Found: C, 53.6; H, 8.6. Calc. for  $\text{C}_6\text{H}_{11}\text{ClO}$ : C, 53.5; H, 8.2%) and (ii) 4-chlorocyclohexyl 4-hydroxycyclohexyl ether (11) (0.8 g), b.p. 100–105 °C/0.0002 mmHg, m.p. 89–90 °C (Found: C, 61.9; H, 8.9.  $\text{C}_{12}\text{H}_{21}\text{ClO}_2$  requires C, 61.9; H, 9.0%).

## References

- Part 16, R. A. W. Johnstone and P. J. Price, *Tetrahedron*, 1985, **41**, 2493; see also, P. A. Delaney, Ph.D. Thesis, University of Liverpool, 1983.
- See for examples, R. J. H. Clark, 'The Chemistry of Titanium and Vanadium,' Elsevier, Amsterdam, 1968; R. Feld and P. L. Cowe, 'The Organic Chemistry of Titanium,' Butterworth, London, 1965; D. L. Kepert, 'The Early Transition Metals,' ch. 2, Academic Press, New York, 1972; R. Colton and J. H. Canterford, 'Halides of the First Row Transition Metals,' ch. 2, Wiley, New York, 1969; E. Wertyporoch and B. Altmann, *Z. Phys. Chem., Abt. A*, 1934, **168**, 1; H. J. Emeléus and G. S. Rao, *J. Chem. Soc.*, 1958, 4245.
- P. M. Hamilton, R. McBeth, W. Bekebrede, and H. H. Sisler, *J. Am. Chem. Soc.*, 1953, **75**, 2881; D. Schwartz and P. Reski, *J. Inorg. Nucl. Chem.*, 1965, **27**, 747; R. J. H. Clark, *Spectrochim. Acta*, 1965, **21**, 955; R. J. H. Clark in, 'Comprehensive Inorganic Chemistry,' vol. 3, ed., A. F. Trotman-Dickenson, Pergamon Press, Oxford, 1973, p. 409.
- K. Alexander and L. E. Schniepp, *J. Am. Chem. Soc.*, 1948, **70**, 1839.
- J. D. Edwards, W. Gerrard, and M. F. Lappert, *J. Chem. Soc.*, 1957, 348.
- M. Kucera, A. Zahradnickova, and K. Majerova, *Polymer*, 1976, **17**, 528.
- R. F. Rolsten and H. H. Sisler, *J. Am. Chem. Soc.*, 1957, **79**, 1819.
- W. Reppe et al., *Justus Liebig's Ann. Chem.*, 1955, **596**, 80.
- V. I. Lutkova, N. I. Kutsenko, and M. I. Itkina, *Zhur. Obshchei Khim.*, 1955, **25**, 2102 (*Chem. Abstr.*, 1956, **50**, 8584a).
- A. H. Wilby, Ph.D. Thesis, University of Liverpool, 1981, pp. 66–73.
- R. J. Kern, *J. Inorg. Nucl. Chem.*, 1962, **24**, 1105.
- A. Hassner and C. Heathcock, *J. Org. Chem.*, 1964, **29**, 1350.
- N. C. Franklin and H. Feltkamp, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 774.
- W. T. Wipke, T. M. Dyott, and J. Q. Verbalis, Abstracts, 161st National Meeting, American Chemical Society, Los Angeles, 1971; Molecular Design, Hayward, California.
- C. C. Hinckley, M. R. Kotz, and F. Patil, *J. Am. Chem. Soc.*, 1971, **93**, 2417.
- R. B. Johannesen and C. L. Gordon, *Inorg. Synth.*, 1967, **9**, 46.
- R. Bill, M. Dröscher, and G. Wegner, *Makromol. Chem.*, 1978, **179**, 2993.
- A. Müller and W. Vanc, *Monatsh. Chem.*, 1947, **77**, 259; (*Chem. Abstr.*, 1948, **42**, 5419c).
- O. Kamm and J. H. Waldo, *J. Am. Chem. Soc.*, 1921, **43**, 2223.
- G. Sieber, *Justus Liebig's Ann. Chem.*, 1960, **631**, 180.
- L. Palfray and B. Rothstein, *Compt. Rend. Acad. Sci.*, 1929, **189**, 701.

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