Dealkylation of Chelating Ethers by Reaction with WCl_4Y (Y = O, S, Se, or NC_2Cl_5)

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Cleavage of an alkyl–oxygen bond occurs when WCl_4Y (Y = O, S, Se, or NC_2Cl_5) reacts with $ROCH_2CH_2OR$ (R = alkyl) or 1,2-dialkoxybenzene. The products of the reaction are an alkyl chloride and a tungsten alkoxide of the type $[WCl_3Y(OCH_2CH_2OR)]$ or $[WCl_3Y(OC_6H_4OR\text{-}2)]$. The stages through which the reaction of $MeOCH_2CH_2OMe$ with WCl_4O passes have been fully investigated and the nature of the final product has been verified by the formation of a number of alkoxides of the type $[WCl_3O(OCH_2CH_2OR)]$ from the reaction of WCl_4O with $ROCH_2CH_2OH$.

CONSIDERABLE interest has been shown in the n.m.r. spectra of the co-ordination compounds formed by the reaction of bidentate ligands of the type $RECH_2CH_2ER$ (R = alkyl, E = S or Se) with metal carbonyls[1,2] and halides.[3] From the n.m.r. spectra, evidence was obtained for inversion of the terminal alkyl groups attached to the ligand sulphur atoms[3] and for conformational changes within the chelate ring.[1,2]

Bidentate ligands of the type $RECH_2CH_2ER$ (E = O S, or Se) usually form chelates when co-ordinating to Lewis acids but two examples are known[4,5] in which ligands of this type form bridges. From the reaction of WCl_4Se with $MeOCH_2CH_2OMe$ an unexpected product, namely $[WCl_3Se(OCH_2CH_2OMe)]$, was obtained.[6] Cleavage of ethers is usually only reported to take place under fairly vigorous reaction conditions; accordingly we have fully investigated the reaction of WCl_4Y (Y = O, S, Se, or NC_2Cl_5) with $ROCH_2CH_2OR$ (R = alkyl or Ph) to ascertain if carbon–oxygen bond cleavage readily occurs in all these systems. The reactions were monitored by n.m.r. spectroscopy. Complex spectra were obtained which could not be attributed to the occurrence of any of the well documented fluxional processes[1-3] but rather to the presence of a number of different species in solution and the ultimate formation (when R = alkyl) of a *O*-demethylated product.

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were obtained with a Varian T60 spectrometer. Resonances are quoted relative to tetramethylsilane. All the reagents were rigorously dried with either molecular sieves or potassium mirrors and were distilled in an all-glass vacuum line. If the reaction time exceeded 4 h the reactions were carried out in vacuum-sealed ampoules. For reaction times of <4 h evacuated flasks attached to the vacuum line were used. The products of all the reactions were isolated using the vacuum line. Analytical data for the products are given in Table 1.

Reaction of WCl_4O *with* 1,2-*Bis(methoxy)ethane*.—(*i*) *Preliminary experiments*. Equimolar quantities of $MeOCH_2CH_2OMe$ and WCl_4O were dissolved in chloroform and allowed to react for 1 h at room temperature, before the solvent, any excess of ligand, and volatile products were removed under reduced pressure. The orange-yellow product was washed with n-pentane to remove any traces of ligand occluded in the solid. The reaction was repeated

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[1] G. Hunter and R. G. Massey, *J.C.S. Dalton*, 1976, 207 and refs. therein.

[2] R. J. Cross, I. G. Dalgleish, G. J. Smith, and R. Wardle, *J.C.S. Dalton*, 1972, 992.

[3] E. W. Abel, R. P. Bush, F. J. Hopton, and C. R. Jenkins, *Chem. Comm.*, 1966, 58.

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[5] M. G. B. Drew and M. J. Riedl, *J.C.S. Dalton*, 1973, 52.

[6] D. Britnell, M. G. B. Drew, G. W. A. Fowles, and D. A. Rice, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 415.

a number of times with reaction times varying between 2 and 3 h. The products were analysed and examined by n.m.r. spectroscopy. Similar reactions were carried out with WCl_4Y (Y = S, Se, or NC_2Cl_5).

(*ii*) *Isolation of* $[(WCl_4O)_2(MeOCH_2CH_2OMe)]$. 1,2-Bis(methoxy)ethane was added to a frozen solution of WCl_4O (30 g) in chloroform (mol ratio $MeOCH_2CH_2OMe : WCl_4O = 1 : 2$). The flask was allowed to warm sufficiently for a homogeneous solution to form, and this was rapidly stirred for 10 min, the mixture quickly filtered, and the filtrate pumped free from solvent.

(*iii*) *Isolation of* $[WCl_4Y(MeOCH_2CH_2OMe)]$ (Y = O *or* NC_2Cl_5). A slight molar excess of $MeOCH_2CH_2OMe$ (1 cm^3) was distilled on to a suspension of WCl_4O (3.1 g) in CCl_4 (60 cm^3) which was then stirred for 6 h at room temperature. The yellow precipitate that formed was isolated and washed with CCl_4 {to remove any $[WCl_3O(OCH_2CH_2OMe)]$ that was formed}. By the same procedure, $[WCl_4(NC_2Cl_5)(MeOCH_2CH_2OMe)]$ was isolated as a yellow solid. It has two resonances in its n.m.r. spectrum (in $CDCl_3$) in the ratio 3 : 2 at τ 5.70 and 5.79.

TABLE 1

Analytical data [a] (%)

Compound	W	Cl	C	H
$[(WCl_4O)_2(MeOCH_2CH_2OMe)]$	47.5 (47.6)	36.2 (36.7)		
$[WCl_4(NC_2Cl_5)(MeOCH_2CH_2OMe)]$	30.1 (29.1)	33.9 (33.7) [b]		
$[WCl_4O(MeOCH_2CH_2OMe)]$	42.0 (42.6)	32.5 (32.8)	11.3 (11.1)	2.3 (2.3)
$[WCl_3O(OCH_2CH_2OMe)]$	48.4 (48.2) [c] 48.3 [d]	27.7 (27.9) [c] 27.6 [d]		
$[WCl_3O(OC_6H_4OMe\text{-}2)]$	43.0 (42.8)	24.5 (24.8)	20.0 (19.6)	1.8 (2.6)
$[WCl_3O(OC_6H_4OEt\text{-}2)]$	41.4 (41.5)	23.5 (24.0)	21.5 (21.7)	2.2 (2.0)
$[WCl_3O(SCH_2CH_2SMe)]$ [d]	46.2 (46.3)	26.5 (26.8)		
$[WCl_3O(OCH_2CH_2OEt)]$ [e]	46.6 (46.5)	28.5 (29.0)		
$[WCl_3O(OCH_2CH_2SEt)]$ [d]	44.9 (44.7)	25.5 (25.9)		
$[WCl_3O(OCH_2CH_2OPh)]$ [e]	41.7 (41.5)	23.6 (24.0)	22.1 (21.7)	2.2 (2.0)
$[TaCl_4(OCH_2CH_2OMe)]$	45.7 (45.5)	35.3 (35.7)	8.7 (9.0)	2.0 (1.8)

[a] Calculated values for postulated formulations are given in parentheses. [b] The four chlorine atoms on tungsten and the two on the carbon atom adjacent to nitrogen were determined. [c] From $MeOCH_2CH_2OMe$. [d] From $RSCH_2CH_2OH$. [e] From $ROCH_2CH_2OH$.

(*iv*) *Isolation of* $[WCl_3O(OCH_2CH_2OMe)]$ *from the reaction of* $MeOCH_2CH_2OMe$ *with* WCl_4O. A slight molar excess of $MeOCH_2CH_2OMe$ ($MeOCH_2CH_2OMe : WCl_4O = 1.2 : 1$) was distilled on to a solution of WCl_4O (2.0 g) in benzene (50 cm^3). After 2 d the benzene was removed under reduced pressure and the yellow solid that was deposited was washed with cold n-pentane.

(*v*) *Reaction of* $ROCH_2CH_2OR$ (R = Et, Pr^n, *or* Ph) *with* WCl_4O. The ethers $ROCH_2CH_2OR$ (R = Et or Pr^n) were allowed to react with solutions of WCl_4O (3.0 g, 1 : 1 mol ratio) in benzene and chloroform. The reactions were repeated a number of times with variation in the reaction time. Monitoring by ^1H n.m.r. spectroscopy indicated that the reactions went through similar stages to those observed in the analogous reactions with $MeOCH_2CH_2OMe$. On allowing the reaction to proceed for 4 d the final products (as shown by ^1H n.m.r. spectroscopy) were $[WCl_3O(OCH_2CH_2OR)]$ (R = Et or Pr^n). From the reaction of $PhOCH_2CH_2OPh$ with WCl_4Y (Y = O or S) (1 : 1 mol ratio) only $[(WCl_4Y)_2(PhOCH_2CH_2OPh)]$ was obtained, even when the reaction mixture was heated under reflux for 4 d.

(*vi*) *Reaction of* WCl_4O *with* 1,2-*bis*(*methoxy*)*benzene and* 1,2-*bis*(*ethoxy*)*benzene*. Equimolar quantities of 1,2-bis(alkoxy)benzene (alkyl = Me or Et) and WCl_4O (3.0 g) were allowed to react in CCl_4 (60 cm^3) at 40 °C for 3 d. The deep purple reaction mixture was allowed to cool to room temperature and the solvent removed *in vacuo* when a purple-brown powder was deposited. Analysis of the products showed them to be $[WCl_3O(OC_6H_4OR\text{-}2)]$ (R = Me or Et). From the reaction in which R = Et it was shown by mass spectrometry that EtCl was formed. Ethyl chloride was also formed when 1,2-bis(ethoxy)benzene and WCl_4O were heated to 100 °C in the absence of solvent.

(*vii*) *Formation of* $[WCl_3O(OCH_2CH_2ER)]$ (E = S, R = Me *or* Et; E = O, R = Me, Et, *or* Ph) *and* $[WCl_3O(OC_6H_4OR\text{-}2)]$ (R = Me *or* Et). An equimolar amount of $RECH_2CH_2OH$ or 2-alkoxyphenol was added to WCl_4O (3.0 g) suspended in $CHCl_3$ (30 cm^3). After 24 h the solution (which was yellow-orange for $RECH_2CH_2OH$ and purple for a phenol) was filtered and the filtrate pumped to dryness.

(*viii*) *Reaction of* $TaCl_5$ *with* $MeOCH_2CH_2OMe$ *to yield* $[TaCl_4(OCH_2CH_2OMe)]$. Equimolar quantities of $MeOCH_2CH_2OMe$ and $TaCl_5$ were allowed to react in CCl_4 solution at room temperature for 3 d. On removal under reduced pressure of the solvent a white solid was deposited which was washed with n-pentane and pumped *in vacuo*.

DISCUSSION

The n.m.r. spectrum of the product obtained by allowing $MeOCH_2CH_2OMe$ to react with WCl_4O (1 : 1 mol ratio) varies with the reaction time. After 2 h the product has a n.m.r. spectrum (in $CDCl_3$) consisting of four singlets A (τ 5.98), B (5.50), C (5.70), and D (5.90) (Figure 1). Increasing the reaction time to 4 h yields a

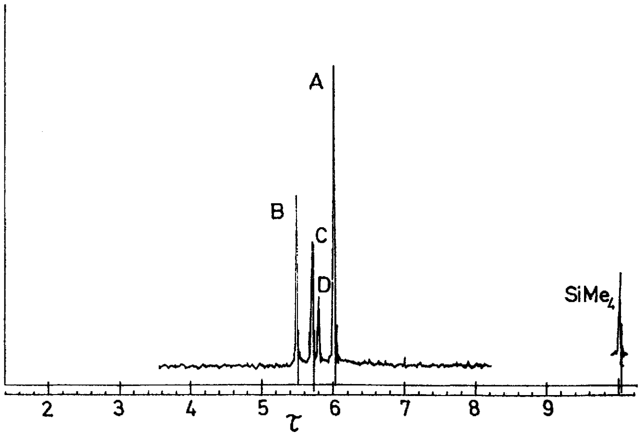

FIGURE 1 Variation in the n.m.r. spectra of the product of the reaction between WCl_4O and $MeOCH_2CH_2OMe$ after 2 h (in $CDCl_3$)

compound with a spectrum still consisting of four resonances but the ratio of A : C has increased while in both spectra the ratio of A : B and C : D is 3 : 2. Thus the products obtained have two environments for $MeOCH_2CH_2OMe$ and there is a slow change from one environment to another. The n.m.r. spectrum (in C_6D_6) of the product obtained after 12 h is illustrated in Figure 2. Comparison of Figures 1 and 2 reveals that as expected the positions of the resonances A—D are altered with change in solvent and in particular resonance D is well clear of any other resonances in C_6D_6 solution. Also in Figure 2 are three new resonances labelled E, G, and H. After 1 d the isolated species has an n.m.r. spectrum containing no A and B resonance, although C and D are still present, and in addition there are resonances E [τ 6.06(s)], F [4.78(t)], and G [4.39(t)]. Finally, after a reaction time of 2 d a product is obtained containing only resonances E—G (Figure 3).

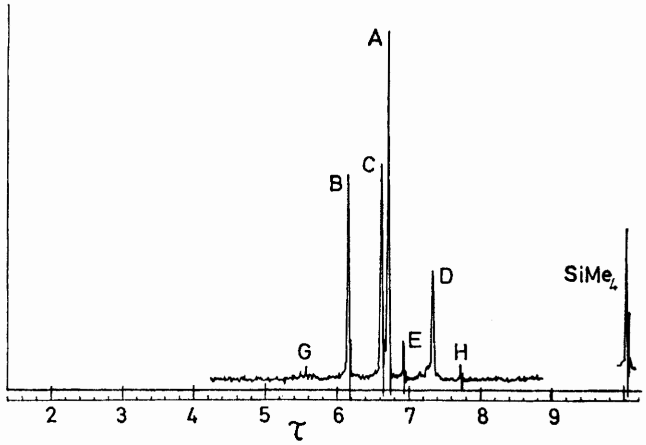

FIGURE 2 Variation in the n.m.r. spectra of the product of the reaction between WCl_4O and $MeOCH_2CH_2OMe$ after 12 h (in C_6D_6 so as to move resonance D away from the other resonances)

By allowing WCl_4O and $MeOCH_2CH_2OMe$ (2 : 1 mol ratio) to react for a very short period an adduct analysing for $[(WCl_4O)_2(MeOCH_2CH_2OMe)]$ was obtained. Its n.m.r. spectrum contains only resonances in identical positions to A and B. With a 1 : 1 mol ratio of the reactants, $[WCl_4O(MeOCH_2CH_2OMe)]$ was obtained, whose n.m.r. spectrum consists of two resonances in identical positions to C and D. Thus the initial variation in the n.m.r. spectra observed when $MeOCH_2CH_2OMe$ is allowed to react with WCl_4O is explained by the rapid formation of $[(WCl_4O)_2(MeOCH_2CH_2OMe)]$ in which the ligand bridges two WCl_4O units {as $MeSCH_2CH_2SMe$ does in $[(WCl_4S)_2(MeSCH_2CH_2SMe)]$ and whose n.m.r. spectrum has the methyl resonance at high field} and the slower formation of $[WCl_4O(MeOCH_2CH_2OMe)]$. Although pure samples of the latter were isolated, we were unable to show whether it is a seven-co-ordinate or an ionic species, since no suitable solvent was found in which the compound was sufficiently soluble for conductivity measurements to be carried out. A range of six-co-ordinate species containing WCl_4Y moieties is known,[4,7-9] but only one seven-co-ordinate crystal structure of a WCl_4O adduct has been reported, namely WCl_4O·pdma [pdma = *o*-phenylenebis(dimethylarsine)],[10] so it appears likely that $[WCl_4O(MeOCH_2CH_2OMe)]$ is ionic with the form $[WCl_3O(MeOCH_2CH_2OMe)]Cl$.

The reaction of the alcohol $MeOCH_2CH_2OH$ with WCl_4O yielded $[WCl_3O(OCH_2CH_2OMe)]$ whose n.m.r. spectrum is identical to that of the product obtained by allowing $MeOCH_2CH_2OMe$ to react with WCl_4O for 2 d (Figure 3). Thus the sequence of reactions can be represented as in (1) thus leading to cleavage of an ether and the formation of an alkyl halide. With the isolation procedure adopted, any alkyl halide was normally removed from the product (see Experimental section); however, resonance H in Figure 2 is assigned to the presence of a trace amount of methyl chloride occluded in the solid product.

The n.m.r. data for all the reported compounds are in Table 2. The assignments of the two triplets in the n.m.r. spectrum of $[WCl_3O(OCH_2CH_2OMe)]$ was made by comparison with the n.m.r. spectrum of $[WCl_3O(OCH_2CH_2SMe)]$; thus the lowest-field triplet is associated with the methylene group α to the alkoxide oxygen atom.

Following a full study of the reaction between $MeOCH_2CH_2OMe$ and WCl_4O, the general nature of the reaction was investigated by allowing $ROCH_2CH_2OR$ to react with WCl_4O. When R = alkyl the reaction followed the path observed with $MeOCH_2CH_2OMe$ and $[WCl_3O(OCH_2CH_2OR)]$ was the ultimate product; however, when R = Ph, an adduct $[(WCl_4O)_2(PhOCH_2CH_2OPh)]$ was obtained. An interesting variation was provided by the reaction of WCl_4O with 1,2-dialkoxybenzene where again cleavage occurred to give chelating

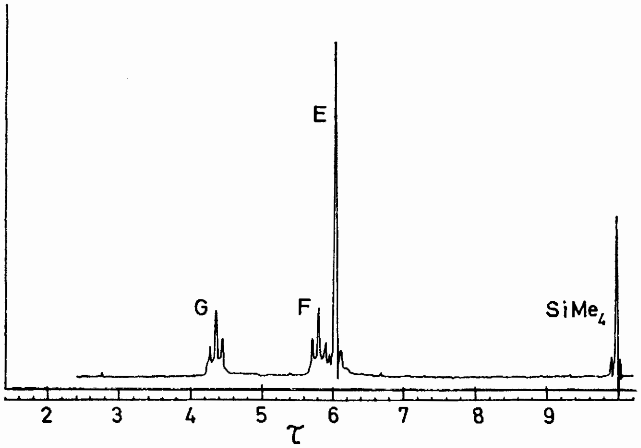

FIGURE 3 Variation in the n.m.r. spectra of the product of the reaction between WCl_4O and $MeOCH_2CH_2OMe$ after 2 d (in $CDCl_3$)

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[7] M. G. B. Drew and R. Mandyczewsky, *J. Chem. Soc.* (*A*), 1970, 2815.

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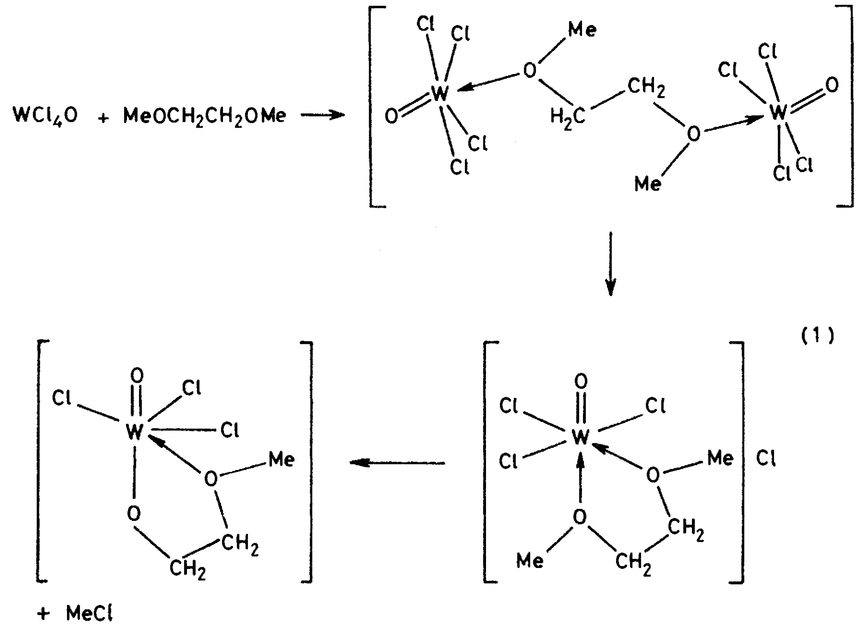
[9] M. G. B. Drew, G. W. A. Fowles, D. A. Rice, and N. Rolfe, *Chem. Comm.*, 1970, 231.

[10] M. G. B. Drew and R. Mandyczewsky, *Chem. Comm.*, 1970, 292.

alkoxyphenoxides $[WCl_3O(OC_6H_4OR\text{-}2)]$. Thus, it would appear that any bidentate ether which can form a five-membered chelate ring can be selectively monodealkylated by allowing it to react with WCl_4O.

Compounds related to WCl_4O are those of formulation WCl_4Y ($Y = S$, Se,[11] or NC_2Cl_5 [12]). The reaction of any of these with the chelating ethers resulted in reactions exactly like those observed with WCl_4O; however, only with WCl_4O was it possible to isolate pure samples of both of the first two stages namely $[(WCl_4Y)_2(MeOCH_2CH_2OMe)]$ and $[WCl_4Y(MeOCH_2CH_2OMe)]$. Indeed the reactions with $WCl_4(NC_2Cl_5)$ had the advantage that the products were more soluble in $CDCl_3$ (the solvent used for the measurement of n.m.r. spectra) than the analogous WCl_4O compounds. Finally, experiments were carried out to ascertain whether the presence of the W=Y group ($Y = O$, S, Se, or NC_2Cl_5) was essential for the dealkylation to proceed. Tantalum(V) chloride was allowed to react with $MeOCH_2CH_2OMe$ and the final product was $[TaCl_4(OCH_2CH_2OMe)]$, thus showing the wider applicability of the reaction.



(1)

Table 2

Hydrogen-1 n.m.r. spectra [a]

Compound	Chemical shift (τ)			
$[(WCl_4O)_2(MeOCH_2CH_2OMe)]$	5.98 (s, 3, Me)	5.50 (s, 2, CH_2)		
$[WCl_4(NC_2Cl_5)(MeOCH_2CH_2OMe)]$	5.79 (s, 2, CH_2)	5.70 (s, 3, Me)		
$[WCl_4O(MeOCH_2CH_2OMe)]$	5.90 (s, 2, CH_2)	5.72 (s, 3, Me)		
$[WCl_3O(OCH_2CH_2OMe)]$	6.06 (s, 3, Me)	4.78 (t, 2, $CH_2\beta$)	4.39 (t, 2, $CH_2\alpha$)	
$[WCl_3O(OCH_2CH_2SMe)]$	7.47 (s, 3, Me)	6.80 (t, 2, $CH_2\beta$)	4.06 (t, 2, $CH_2\alpha$)	
$[WCl_3O(OCH_2CH_2OEt)]$	8.52 (t, 3, Me)	5.74 (t, 2, $CH_2\beta$)	5.61 (q, 2, CH_2)	4.34 (t, 2, $CH_2\alpha$)
$[WCl_3O(OCH_2CH_2SEt)]$	8.56 (t, 3, Me)	7.01 (q, 2, CH_2)	6.82 (t, 2, $CH_2\beta$)	4.04 (t, 2, $CH_2\alpha$)
$[WCl_3O(OCH_2CH_2OPh)]$	5.26 (t, 2, $CH_2\beta$)	4.26 (t, 2, $CH_2\alpha$)	2.67 (s, 5, aromatic H)	
$[WCl_3O(OC_6H_4OMe\text{-}2)]$ [b]	5.56 (s, 3, Me)	2.9 (m, 4, aromatic H)		
$[WCl_3O(OC_6H_4OEt\text{-}2)]$ [b]	8.40 (t, 3, Me)	5.05 (q, 2, CH_2)	2.9 (m, 4, aromatic H)	
$[TaCl_4(OCH_2CH_2OMe)]$	5.84 (s, 3, Me)	5.56 (t, 2, CH_2)	4.67 (t, 2, CH_2)	
$[(WCl_4S)_2(MeSCH_2CH_2SMe)]$	7.62 (s, 3, Me)	6.96 (s, 2, CH_2)		

[a] All the spectra were measured in $CDCl_3$ solution; peak positions relative to $SiMe_4$. $CH_2\alpha$ denotes a methylene group adjacent to an alkoxide oxygen atom. [b] Prepared in CCl_4 and the progress of the reaction monitored by n.m.r. spectroscopy in CCl_4 solutions.

Cleavage of an alkyl–oxygen bond appears to be favoured if there is the possibility of a seven-co-ordinate (or sterically crowded) intermediate being formed, and this statement has been substantiated by experiments in which titanium(IV) chloride was allowed to react with the tridentate ether $MeC(CH_2OMe)_3$ where MeCl and $[TiCl_3\{OCH_2C(Me)(CH_2OMe)_2\}]$ were formed.[13]

[8/422 *Received*, 8*th March*, 1978]

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