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Syntheses and Reactions of Metal Organics. VII. Reactions of *n*-Butoxytitanium Chlorides with Saturated Cyclic Ethers

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The reactions of *n*-butoxytitanium chloride, $TiCl_n(O^nBu)_{4-n}$ ($n=0,1,2,3,4$), with 1,4-dioxane, tetrahydrofuran, and tetrahydropyran have been studied. No adducts have been isolated when $n=0,1$, but the compounds $TiCl_2(O^nBu)_2 \cdot O(CH_2CH_2)_2O$, $TiCl_2(O^nBu)_2 \cdot C_4H_8O$, $TiCl_2(O^nBu)_2 \cdot C_5H_{10}O$, $TiCl_3(O^nBu) \cdot O(CH_2CH_2)_2O$, $TiCl_3(O^nBu) \cdot 2C_4H_8O$, $TiCl_3(O^nBu) \cdot 2C_5H_{10}O$, $TiCl_4 \cdot O(CH_2CH_2)_2O$, $TiCl_4 \cdot 2C_4H_8O$ and $TiCl_4 \cdot 2C_5H_{10}O$ have been isolated when $n=2,3,4$. Possible structures for these adducts were discussed on the basis of elemental analysis, IR spectra, NMR spectra, and molecular weights. The adducts undergo hydrolysis very quickly with moisture.

Tin and titanium tetrachlorides have been shown to readily form stable, solid adducts with various ethers, but not silicon and germanium tetrachlorides.[1-4] Formation of tin tetrachloride adducts was understood to result from Lewis acid-base reactions in which the metal atom expanded its valence shell by accepting a pair of electrons from an oxygen atom of each of two molecules of ether to form compounds of the type $MCl_4 \cdot 2R_2O$. Failure of silicon and germanium tetrachlorides to form such compounds was attributed to the fact that the size of the chlorine atom causes four of these atoms to fill the coordination sphere of the silicon and germanium atoms so completely as to prevent any reaction with the ether. The effect of the replacement of the chlorine atoms in titanium tetrachloride by larger halogens was studied as regards the tendency for titanium tetrahalides to react with 1,4-dioxane, tetrahydrofuran, and tetrahydropyran. It was shown that the adducts $TiBr_4 \cdot O(CH_2CH_2)_2O$, $TiBr_4 \cdot 2C_4H_8O$, and $TiBr_4 \cdot 2C_5H_{10}O$ have been isolated, but not the pure adduct of titanium tetraiodide with any ether.[4] The formulas were proposed only on the basis of elemental analysis.

It was shown that the reactions of alkoxy- and phenoxy-titanium chlorides with amides and other compounds involve the carbonyl group. The present investigation revealed that the effect of the alkoxy groups replaced the chlorine atoms of titanium tetrachloride in the reaction with ethers. We used saturated cyclic ethers which are more basic than aliphatic ethers.[5] Possible structures for these adducts were discussed on the basis of elemental analysis, IR spectra, NMR spectra, and molecular weights.

Experimental

All the experiments were carried out in a dry atmosphere or nitrogen.

Materials. Titanium tetrachloride (I) was purified by the method of Clabaugh *et al.*[6] Mono-*n*-butoxytitanium trichloride (II), di-*n*-butoxytitanium dichloride (III), tri-*n*-butoxytitanium monochloride (IV), and tetra-*n*-butyltitanate (V) were prepared by the methods of Bradley *et al.*[7,8] and Jennings *et al.*[9]).

1,4-Dioxane (DO) was purified by the method of Fieser.[10] Tetrahydrofuran (THF) and tetrahydropyran (THP) were dried over calcium chloride, and fractionated from over sodium in a dry nitrogen atmosphere using a 30 cm Widmer distilling column. A constant boiling middle fraction was retained. Boiling point data: DO, 100.3—100.5°C; THF, 65.2—65.5°C; THP, 87.5—88.0°C. To avoid the presence of peroxides, the ethers were purified immediately before use.

Apparatus. All-glass apparatus fitted with standard interchangeable joints was used and special precautions were taken to exclude moisture.

Instruments. The IR spectra were measured in a nujol or a liquid film with a Japan Spectroscopic Co. DS-403G Spectrophotometer. The NMR spectra were measured with a Varian A-60 Spectrometer in a solution of carbon tetrachloride with tetramethylsilane as an internal standard. The molecular weights were determined by the cryoscopic method in benzene.

Preparation of $TiCl_4 \cdot O(CH_2CH_2)_2O$ (VI). To a stirred solution of I (3.5 g, 0.018 mol) in 30 m*l* of *n*-hexane was added dropwise a solution of DO (4.9 g, 0.054 mol) in 10 m*l* of *n*-hexane, under cooling at 0—5°C. The reaction, highly exothermic, rapidly yielded a yellow solid. After stirring for 1 hr at room temperature for completion of the reaction, the resulting precipitation of VI (5.1 g) was collected by filtration and washed with *n*-hexane and dried in a vacuum at room temperature, decompn.>200°C.

Found: Ti, 17.25; Cl, 50.82; C, 16.81; H, 2.88%. Calcd for $TiCl_4C_4H_8O_2$: Ti, 17.24; Cl, 51.04; C, 17.29; H, 2.90%. IR (nujol) 1044 (ν_{C-O-C}) cm^{-1}.

Preparation of $TiCl_4 \cdot 2C_4H_8O$ (VII) and $TiCl_4 \cdot 2C_5H_{10}O$ (VIII). The procedure for the preparation of VI was adopted. Yellow powder (8.2 g) of VII was collected by the reaction of I (4.7 g, 0.025 mol) with THF (5.4 g, 0.075 mol), mp 118—120°C.

Found: Ti, 14.53; Cl, 42.71; C, 28.59; H, 4.61%. Calcd for $TiCl_4C_8H_{16}O_2$: Ti, 14.34; Cl, 42.47; C, 28.78; H, 4.83%. IR (nujol) 990 (ν_{C-O-C}) cm^{-1}.

Yellow powder (2.9 g) of VIII was collected by the reaction of I (2.0 g, 0.010 mol) with THP (2.8 g, 0.030 mol), mp

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[1] H. H. Sisler, W. J. Wilson, B. J. Gibbins, H. H. Betey, B. Pfahler, and R. Mattair, *J. Amer. Chem. Soc.*, **70**, 3818 (1948).

[2] H. H. Sisler, H. H. Betey, B. Pfahler, and R. Mattair, *ibid.*, **70**, 3821 (1948).

[3] H. H. Sisler, P. M. Hamilton, R. McBeth, and W. Bekebrede, *ibid.*, **75**, 2881 (1953).

[4] H. H. Sisler and R. F. Rolsten, *ibid.*, **79**, 1068 (1957).

[5] H. E. Wirth, P. I. Slick, *J. Phys. Chem.*, **66**, 2277 (1962).

[6] N. S. Clabaugh, R. T. Leslie, and R. Gilchrist, *J. Res. Nat. Bur. Stand.*, **55**, 261 (1955).

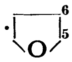
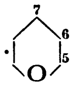
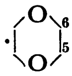
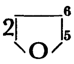
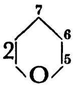
[7] D. C. Bradley, D. C. Hancock, and W. Wardlaw, *J. Chem. Soc.*, **1952**, 2773.

[8] D. C. Bradley, F. M. El-Halim, R. C. Mehrotra, and W. Wardlaw, *ibid.*, **1952**, 4609.

[9] J. S. Jennings, W. Wardlaw, and W. J. Way, *ibid.*, **1936**, 637.

[10] L. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston (1941), Pt. II, p. 368.

TABLE 1. 60MHz-NMR-SPECTRA OF THE ADDUCTS

Adducts	$\tau^{a)}$	Intensity	Proton number	Attribution
$Cl_2Ti(OCH_2{}^1CH_2{}^2CH_2{}^3CH_3{}^4)_2\cdot$ 	4.86—5.52(m) 5.78(*t*, *J*=6.2Hz) 7.80—8.75(m) 9.01(*t*, *J*=6.2Hz)	2 2 6 3	4 4 12 6	H^1 H^5 $H^{2,3,6}$ H^4
$Cl_2Ti(OCH_2{}^1CH_2{}^2CH_2{}^3CH_3{}^4)_2\cdot$ 	4.95—5.67(m) 5.73—6.10(m) 7.75—8.83(m) 9.01(*t*, *J*=6.4Hz)	2 2 7 3	4 4 14 6	H^1 H^5 $H^{2,3,6,7}$ H^4
$Cl_2Ti(OCH_2{}^1CH_2{}^2CH_2{}^3CH_3{}^4)_2\cdot$ 	5.10—5.50(m) 6.22(s) 7.84—8.76(m) 9.01(*t*, *J*=6.0Hz)	2 4 4 3	4 8 8 6	H^1 $H^{5,6}$ $H^{2,3}$ H^4
$Cl_3Ti(OCH_2{}^1CH_2{}^2CH_2{}^3CH_3{}^4)\cdot 2$ 	4.80—5.17(m) 5.71(*t*, *J*=6.9Hz) 7.60—8.80(m) 9.01(*t*, *J*=6.2Hz)	2 8 12 3	2 8 12 3	H^1 H^5 $H^{2,3,6}$ H^4
$Cl_3Ti(OCH_2{}^1CH_2{}^2CH_2{}^3CH_3{}^4)\cdot 2$ 	4.75—5.25(m) 5.48—6.07(m) 7.80—8.80(m) 9.01(*t*, *J*=6.5Hz)	2 8 16 3	2 8 16 3	H^1 H^5 $H^{2,3,6,7}$ H^4

a) s, singlet; *t*, triplet; m, multiplet. Internal standard TMS in *ca*. 20% CCl_4 solution.

130—132°C.

Found: Ti, 13.42; Cl, 38.99; C, 33.23; H, 5.61%. Calcd for $TiCl_4C_{10}H_{20}O_2$: Ti, 13.23; Cl, 39.18; C, 33.18; H, 5.57%. IR (nujol) 991 (ν_{C-O-C}) cm^{-1}.

Preparation of $TiCl_3(O^nBu)\cdot O(CH_2CH_2)_2O$ *(IX)*. To a solution of II (4.7 g, 0.020 mol) in 30 m*l* of benzene was added dropwise a solution of DO (7.3 g, 0.080 mol) in 10 m*l* of benzene with stirring at 5—10°C. The reaction was slightly exothermic. A white precipitate was obtained after 25 hr of agitation at room temperature. After filtration, the precipitate was washed with benzene and dried in a vacuum at room temperature, mp 159—160°C.

Found: Ti, 15.28; Cl, 33.50; C, 30.33; H, 5.24%. Calcd for $TiCl_3C_8H_{17}O_3$: Ti, 15.18; Cl, 33.71; C, 30.46; H, 5.43%.

Preparation of $TiCl_3(O^nBu)\cdot 2C_4H_8O$ *(X) and* $TiCl_3(O^nBu)\cdot 2C_5H_{10}O$ *(XI)*. Excess THF (1.9 g, 0.027 mol) in 10 m*l* of benzene was added to II (2.0 g, 0.009 mol) in 30 m*l* of benzene at 15—20°C. The reaction was not exothermic. No solid was obtained after 25 hr of agitation at room temperature. A brown viscous liquid (3.2 g) of X was obtained after the removal of THF and benzene in the mixture in a vacuum at room temperature. The drying in a vacuum was continued 48 hr, at the end of which time the unit was pressurized to one atmosphere with dry nitrogen.

Found: Ti, 12.99; Cl, 28.46; C, 38.77; H, 6.72%, mol wt, 348±20. Calcd for $TiCl_3C_{12}H_{25}O_3$: Ti, 12.89; Cl, 28.62; C, 38.79; H, 6.78%, mol wt, 371.6. IR (liquid film) 1012 (ν_{C-O-C}) cm^{-1}. NMR (Table 1).

Similarly, brown viscous liquid (7.5 g) of XI was obtained by the reaction of II (4.3 g, 0.019 mol) with THP (4.9 g, 0.057 mol) in benzene.

Found: Ti, 11.94; Cl, 26.49; C, 42.05; H, 7.12%, mol wt, 377±21. Calcd for $TiCl_3C_{14}H_{29}O_3$: Ti, 11.99; Cl, 26.61; C, 42.08; H, 7.31%, mol wt, 399.6. IR (liquid film) 1015 (ν_{C-O-C}) cm^{-1}. NMR (Table 1).

Preparation of $TiCl_2(O^nBu)_2\cdot O(CH_2CH_2)_2O$ *(XII)*, $TiCl_2(O{}^nBu)_2\cdot C_4H_8O$ *(XIII) and* $TiCl_2(O^nBu)_2\cdot C_5H_{10}O$ *(XIV)*.
The procedure was the same as that for preparation of X. A brown jelly adduct (6.6 g) of XII was obtained from III (5 g, 0.019 mol) and DO (6.6 g, 0.075 mol) in benzene.

Found: Ti, 13.34; Cl, 19.94; C, 40.73; H, 7.44%, mol wt, 361±22. Calcd for $TiCl_2C_{12}H_{26}O_4$: Ti, 13.56; Cl, 20.08; C, 40.81; H, 7.42%, mol wt, 353.1. NMR (Table 1).

A brown viscous liquid (2.6 g) of XIII was prepared from III (2.0 g, 0.008 mol) with THF (4.4 g, 0.060 mol) in benzene.

Found: Ti, 14.36; Cl, 21.12; C, 42.66; H, 7.68%, mol wt, 318±25. Calcd for $TiCl_2C_{12}H_{26}O_3$: Ti, 14.21; Cl, 21.03; C, 42.75; H, 7.68%, mol wt, 337.1. IR (liquid film) 1020 (ν_{C-O-C})cm^{-1}. NMR (Table 1).

A brown viscous liquid (2.8 g) of XIV was obtained from III(2.1 g, 0.008 mol) and THP (2.0 g, 0.024 mol) in benzene.

Found: Ti, 13.63; Cl, 20.49; C, 44.19; H, 8.00%, mol wt, 342±30. Calcd for $TiCl_2C_{13}H_{28}O_3$: Ti, 13.46; Cl, 20.19; C, 44.46; H, 8.04%, mol wt, 351.2. IR (liquid film) 1020(ν_{C-O-C}) cm^{-1}. NMR (Table 1).

IV and V did not react with ethers.

Results and Discussion

The reactivity of I—V with acetanilide (Lewis base) and the IR measurement of the adducts of I—IV with the amide showed that the activity of Lewis acid decreased as reported.[11] I>II>III>IV>V. From this fact, it seems probable that no adducts have been isolated from the reaction of ethers with IV and V, which are less active Lewis acids.

The IR spectra of VII, X, and XIII indicated that the ν_{C-O-C} of THF (1068 cm^{-1}) indicate the shift toward the lower wave numbers, 990, 1012, and 1020 cm^{-1} respectively. The negative shifts of the ν_{C-O-C} of THF (1093 cm^{-1}) for VIII, XI, and XIV were observed at 991, 1015, and 1020 cm^{-1} respectively. The shifts indicate the order of the activity of the Lewis acids (I—III). The shifts of the ν_{C-O-C} of DO (1119 cm^{-1}) in IX and XII were not confirmed because of the mixing of their frequencies with that of the alkoxy group ν_{C-O} in alkoxytitanium chlorides, but we found adduct VI at 1044 cm^{-1}.

NMR spectra of adduct XIII indicate that, for ex-

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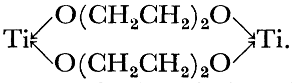
[11] N. Yoshino and T. Yoshino, *Kogyo Kagaku Zasshi*, **71**, 1025 (1968).

ample, the chemical shift of the proton H^5 (τ 5.78) should be lower than that of THF (τ 6.37).[12] Similar lower chemical shifts of the adducts of THF and THP were measured. Thus we conclude that the oxygen atom of THF or THP is coordinated to the titanium atom of each of the alkoxytitanium chlorides.

In the case of the adducts of DO, either two oxygen atoms of DO are coordinated to a titanium atom to form a five-membered-ring chelate, or only one oxygen atom of DO coordinated to a titanium atom, and otherwise two oxygen atoms of DO coordinate to two titanium atoms such as  $\mathrm{Ti}\begin{array}{c}\diagup O(CH_2CH_2)_2O\diagdown\\ \diagdown O(CH_2CH_2)_2O\diagup\end{array}\mathrm{Ti}$. A comparison of the IR spectrum of DO with that of its adduct VI indicates that the ν_{C-O-C} of the latter is shifted to lower values; this indicates that the oxygen atom of DO is involved in coordination. Observation of the NMR spectra of XII indicates that, the intensity of H^1, $H^{2,3}$, $H^{5,6}$, and H^4 is 2 : 4 : 4 : 3, respectively the results indicate that the two oxygen of DO are on even conditions. Since the molecular weight determination of adduct XII gives a monomeric value, one can believe that two oxygen atoms of DO are coordinated to a titanium atom of III to form a chlate ring.

Sisler[3] and his co-workers have shown the molecular weight of the adduct VIII to be monomeric in benzene.

Molecular weight determination of all the liquid adducts and a jelly adduct indicate them to be monomeric in benzene. X and XI filled the coordination number of titanium 6, but XIII and XIV did not. Thus it seems reasonable to assume that the adducts in non-solution state are dimeric, but monomeric in solution.

The adducts undergo rapid hydrolysis with moisture.

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12) F. A. Bovey, "NMR Data Tables for Organic Compounds," Vol. 1, John Wiley & Sons, New York, London, Sydney, p. 73.