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Reactions of Oximes and Diethylhydroxylamine with Titanium Alkoxides

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Alkoxides of titanium react exothermally with oximes and diethylhydroxylamine to give complexes of the formula, $Ti(OR)_{4-x}(L)_x$ [x = 1-4; R = Prⁱ when LH = oxime; R = Et, Prⁱ, and Bu^t when LH = Et₂NOH]. Alcoholysis of some of these give the corresponding t-butoxy-derivatives. I.r. spectra have been recorded and molecular weights determined.

MANY organotitanium compounds which contain Ti-O-C bonds¹ and compounds containing Ti-O-B, Ti-O-P, Ti-O-S linkages have been reported.² Little is known about compounds containing the Ti-O-N bond, although

¹ D. C. Bradley, R. C. Mehrotra, and W. Wardlaw, *J. Chem. Soc.*, 1952, 4204, 5020; D. C. Bradley, R. C. Mehrotra, J. D. Swanwick, and W. Wardlaw, *ibid.*, 1953, 2025; K. C. Pande and R. C. Mehrotra, Z. anorg. Chem., 1957, 290, 87, 95; 1957, 291, 97;
R. C. Mehrotra, J. Indian Chem. Soc., 1961, 38, 509; D. M. Puri, Ph.D. Thesis, Gorakhpur University, Gorakhpur (India), 1962.

² R. Feld, J. Chem. Soc., 1964, 3963.

oxime derivatives of Zn,³ Sn,⁴ Si,⁵, As,⁶, B, Al, Ga, In, and Tl⁷ have been prepared. Boron complexes of

³ (a) D. F. Menard and J. G. Aston, J. Amer. Chem. Soc., 1934, 56, 1601; (b) G. E. Coates and D. Ridley, J. Chem. Soc. (A), 1966, 1064. 4 U.S.P. 3,282,672/1966 (Chem. Abs., 1967, **66**, 28,891).

- ⁵ B. N. Dolgov, Z. I. Sergeeva, N. A. Zubkova, and M. G. Voronkova, *Zhur. obshchei Khim.*, 1960, **30**, 3347.
- ⁶ G. Kamai and R. G. Miftakhova, Zhur. obshchei Khim., 1965,

35, 2001. ⁷ (a) J. R. Jennings and K. Wade, J. Chem. Soc. (A), 1967, 1333; (b) I. Pattison and K. Wade, *ibid.*, 1968, 2618.

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hydroxylamine, R_2BONH_2 and R_2BONHR' are reported to be dimeric through the nitrogen atoms.⁸

Oxime derivatives of titanium and aluminium are reported to be of industrial importance ⁹ and titanium(IV) chloride is reported to react with oximes.¹⁰ Here we report the reactions of some titanium alkoxides with oximes and diethylhydroxylamine.

Titanium alkoxides were treated with various proportions of acetoxime, ethyl methyl ketoxime, and diethylhydroxylamine in anhydrous benzene and the liberated alcohols were azeotroped out; two (ethanol and isopropyl alcohol) of the latter were estimated by an oxidimetric procedure, to check the progress of the reaction:

$$Ti(OPr^{i})_{4} + xR^{1}R^{2}C:NOH \xrightarrow{PhH, reflux}{105-110^{\circ}}$$
$$Ti(OPr^{i})_{4-x}(ON:CR^{1}R^{2})_{x} + xPr^{i}OH$$
$$(R^{1} = Me, R^{2} = Me \text{ and Et}; x = 1-4)$$

$$Ti(OR)_4 + xEt_2NOH \longrightarrow Ti(OR)_{4-x}(ONEt_2)_x + xROH$$

(R = Et, Prⁱ, and Bu^t; $x = 1-4$)

The products varied from solids to viscous liquids; all were moisture sensitive and soluble in common organic solvents. With the exception of the ethoxyderivatives of diethylhydroxylamine, all the products were monomeric in boiling benzene.

The tetra-acetoximate and all the products of diethylhydroxylamine could be distilled under reduced pressure; the mixed isopropoxy-oximates, however, disproportionated yielding volatile titanium tetraisopropoxide.

The corresponding t-butoxy-derivatives were prepared by treatment of the mono-, di-, and tri-isopropoxyacetoximates and mono-, di-, and tri-ethoxy diethylaminoxides with t-butyl alcohol in benzene; this also provided a convenient method of analysing the isopropoxy- and ethoxy-contents in the starting materials:

$$\operatorname{Ti}(\operatorname{OPr}^{i})_{4-x}(\operatorname{ON:CMe}_{2})_{x} + 4 - x(\operatorname{But}OH) \xrightarrow{\operatorname{PhH, reflux}}_{(\operatorname{excess})}$$
$$\operatorname{Ti}(\operatorname{OBut})_{4-x}(\operatorname{ON:CMe}_{2})_{x} + 4 - x(\operatorname{Pr}^{i}OH)$$

$$Ti(OEt)_{4-x}(ONEt_2)_x + 4 - x(Bu^tOH) \longrightarrow$$
$$Ti(OBu^t)_{4-x}(ONEt_2)_x + 4 - x(EtOH)$$
$$(x = 1-3)$$

All the t-butoxy-acetoximates are also monomeric in boiling benzene and moisture sensitive. Attempted distillation (90–95°) under reduced pressure gave disproportionation into $Ti(OBu^t)_4$ and $Ti(ON:CMe_2)_4$;

⁸ L. P. Kuhn and M. Inatome, J. Amer. Chem. Soc., 1963, 85, 1206.

⁹ U.S.P. 3,387,010/1968 (Chem. Abs., 1968, 69, 26,779.

¹⁰ J. Charalambous and M. J. Frazer, J. Chem. Soc. (A), 1968, 2361; R. Feld, unpublished data (cf. R. Feld and R. L. Cowe, 'The Organic Chemistry of Titanium,' Butterworths, London, 1965, p. 125.

1965, p. 125.
¹¹ S. Califano and W. Luttke, Z. Phys. Chem., 1956, 6, 83;
J. Fabian, M. Ligrand, and P. Poirier, Bull. Soc. Chim. France, 1956, 1499;
J. F. Brown, jun., J. Amer. Chem. Soc., 1955, 77, 6341.

¹² M. Devies and N. A. Spiers, J. Chem. Soc., 1959, 3971.

only a little (15%) of the monobutoxy-derivative could be distilled $(90-95^{\circ})/0.2-0.4$ mm) accompanied with disproportionation in this case also. The major portion of the dibutoxy-derivative disproportionated into Ti $(OBu^t)_4$ while a portion was distilled at $87-90^{\circ}/0.2-$ 0.4 mm as a viscous liquid which solidified overnight; its analysis corresponded to Ti $(OBu^t)(ON:CMe_2)_3$.

Titanium di-isopropoxy-diacetoximate reacts with acetylacetone as follows:

$$\begin{array}{c} \text{Ti}(\text{OPr}^{i})_{2}(\text{ON:CMe}_{2})_{2} + 2\text{acacH} \longrightarrow\\ \text{Ti}(\text{acac})_{2}(\text{ON:CMe}_{2})_{2} + 2\text{Pr}^{i}\text{OH} \end{array}$$

$$\begin{array}{c} \text{Ti}(\text{OPr}^{i})_{2}(\text{ON:CMe}_{2})_{2} + \text{acacH} \longrightarrow \\ \text{Ti}(\text{OPr}^{i})(\text{acac})(\text{ON:CMe}_{2})_{2} + \text{Pr}^{i}\text{OH} \end{array}$$

The acetylacetonates are soluble in organic solvents and are monomeric in boiling benzene.

Titanium tetrakis-oximates have also been synthesised by the reactions of titanium(IV) chloride with oximes in the presence of triethylamine:

$$TiCl_4 + 4R^1R^2C:NOH + 4Et_3N \xrightarrow{PhH, reflux} Ti(ON:CR^1R^2)_4 + 4Et_3N,HCl$$

$$(R^1 = Me, R^2 = Me \text{ and } Et)$$

I.r. Spectra.—The tentative i.r. assignments (Table 1) have been made on the basis of published data about oximes,¹¹ hydroxylamine,¹² and titanium alkoxides.¹³ Although precautions were taken to avoid contact with atmospheric moisture during sampling, some hydrolysis occurs as evidenced by weak absorptions in the range **3437**—**3280** cm⁻¹.

Since titanium(IV) tends to exhibit a higher coordination number,¹⁴ a lowering of 21—50 cm⁻¹ in the C=N stretching frequency in the present oximate derivatives might indicate association through nitrogen.^{36,7a} In diethylhydroxylamine products, Ti-O frequency occurs at 626—658 cm⁻¹ compared to *ca*. 616 cm⁻¹ in the alkoxides and the N-O frequency is shifted to *ca*. 930— 945 cm⁻¹ from that at 912 cm⁻¹ in the free ligand.

EXPERIMENTAL

Titanium alkoxides were prepared as previously described.¹⁵ Acetylacetone was dried over aluminium isopropoxide and fractionated. t-Butyl alcohol was fractionated over sodium t-butoxide. Benzene (B.D.H.) was dried

¹³ C. G. Barraclough, D. C. Bradley, J. Lewis, and I. M. Thomas, J. Chem. Soc., 1961, 2601; D. C. Bradley and A. H. Westlake, personal communication; C. T. Lynch, K. S. Mazdiyasni, J. S. Smith, and W. J. Crawford, Analyt. Chem., 1964, 36, 2332; C. N. R. Rao, 'Chemical Applications of Infrared Spectroscopy,' Academic Press, London and New York, 1963; D. M. Adams, 'Metal-ligand and Related Vibrations,' Edward Arnold, London, 1967.

¹⁴ D. C. Bradley, 'Inorganic Polymers,' eds. F. G. A. Stone and W. A. G. Graham, Academic Press, London and New York, 1962, p. 444; C. N. Caughlan, H. S. Smith, K. Watz, H. Hodgson, and R. W. Growe, J. Amer. Chem. Soc., 1951, **73**, 5652.

¹⁵ D. C. Bradley, D. C. Hancock, and W. Wardlaw, *J. Chem. Soc.*, 1952, 2773; D. C. Bradley, R. C. Mehrotra, and W. Wardlaw, *ibid.*, 1952, 2027; R. C. Mehrotra, *J. Amer. Chem. Soc.*, 1954, **76**, 2266.

TABLE 1

I.r. spectra of products of the reactions of diethylhydroxylamine and oximes with titanium alkoxides

 $Ti(ONEt_2)_4$ *: 3313vw, 2919s(A), 2869s(A), 1452s(B), 1442s(B), 1370s(B), 1349m(B), 1300m(B), 1281w, 1181w, 1174w, 1116w(L), 1074m, 1041m(L), 1011s(G), 941m(E), 921m(H), 821m, 784m, 757s(B), 684w, 672m(F), 624m(F), 604w, 584s(G), 534m, 494m, 469m.

 $\begin{array}{l} Ti(OPr^i)(ONEt_2)_3: \quad 3330-3280vw, \quad 2975s(A), \quad 2930s(A), \\ 2870s(A), \quad 2580w, \quad 1458s(B), \quad 1445s(B), \quad 1370s(B), \quad 1352m(B), \\ 1330m(B), \quad 1312w, \quad 1280w, \quad 1180m, \quad 1160s(C), \quad 1138s(C), \quad 1073m, \\ 1043m(L), \quad 1010m(G), \quad 1000s(G), \quad 930m(E), \quad 914w(H), \quad 843m, \quad 818w, \\ 790m, \quad 775sb, \quad 758m(B), \quad 723w, \quad 653s(F), \quad 613s(F), \quad 600sb(F), \\ 583s(F), \quad 560m(F), \quad 488m, \quad 470m. \end{array}$

 $\rm Ti(OPr^i)_2(ONEt_2)_2\colon$ 3430w, 2980s(A), 2942s(A), 2880s(A), 1455s(B), 1445m(B), 1375s(B), 1350m(B), 1315m(B), 1280w, 1165s(C), 1131s(C), 1073m, 1043m(L), 1004sb(G), 935s(E), 912s(H), 894m, 816w, 793mb, 760w(B), 635—593mb(F), 494w, 463w.

 $Ti(OBu^t)_2(ONEt_2)_2$: 3437wb, 2966—2889sb(A), 1462s(B), 1373s(B), 1357m(B), 1230m, 1198m(M), 1120m(L), 1075w, 1005sb(G), 938—912sb(E + H), 815m, 780s, 635sb(F), 575m(F), 535m(F).

 $\rm Et_2NOH:$ 3385—3185sb(I), 2975s(A), 2935s(A), 2875s(A), 2840s(A), 1660m, 1625m, 1450s(B), 1375s(B), 1335s(B), 1300m, 1265m, 1215m, 1175m, 1158m, 1130s(L), 1100m, 1072m, 1050s, 1032s, 930vw, 912s(E), 820m, 758s, 718m, 588m, 505m, 480m, 430m.

 $\begin{array}{rl} {\rm Ti}({\rm OPr}^{i})_{3}({\rm ON:CMe}_{2}) \ ^{*}: \ \ 3386-3286{\rm wb}, \ \ 2977-2845{\rm sb}({\rm A}), \\ {\rm 2704w}, \ \ 2604{\rm w}, \ \ 1631{\rm m}({\rm D}), \ \ 1454{\rm s}({\rm B}), \ \ 1368{\rm s}({\rm B}), \ \ 1318{\rm s}, \ \ 1268{\rm m}, \\ {\rm 1162{\rm s}({\rm C}), \ \ 1125{\rm sb}({\rm C}), \ \ 1005-985{\rm sb}({\rm J}), \ \ 938{\rm s}({\rm E}), \ \ 845{\rm s}, \ \ 820{\rm s}, \ \ 714{\rm w}, \\ {\rm 615{\rm s}, \ 600{\rm sh}, \ \ 565{\rm sh}({\rm F}), \ \ 520{\rm sb}({\rm K}), \ \ 435{\rm s}. \end{array}$

 $\rm Ti(OPr!)_2(ON;CMe_2)_2*: 3582-3282wb, 2957s(A), 2861s(A), 1628m(D), 1432s(B), 1357s(B), 1307s, 1265m, 1160s(C), 1120s(C), 1010s(G), 985sb(E), 940s(E), 843s, 818s, 716m, 620-600sb, 560s(F), 515s(K), 435sb.$

 $\rm Ti(OPr^i)(ON:CMe_2)_3*: 3337-3237wb, 2912s(A), 2851s(A), 2712w, 1641m(D), 1455s(B), 1369s(B), 1268m, 1160s(C), 1127s(C), 1100s, 1000s(G), 990s(E), 973sh(E), 945s(E), 857w, 847sh, 815w, 718m, 635s, 618sh, 553s(F), 500s(K), 475s.$

 $\rm Ti(ON;CMe_2)_4\colon$ 3350—3192wb, 2920s(A), 2847s(A), 1638m(D), 1438s(B), 1360s(B), 1263m, 1090s, 1070m, 990sh(E), 972s(E), 945s(E), 856w, 840sh, 815w, 718m, 670s, 635s, 550s(F), 495s(K), 470s.

 $\begin{array}{l} {\rm Ti}({\rm OPr}^i)_3({\rm ON:C(Et)Me})*: \ 3432-3332{\rm wb},\ 2977s({\rm A}),\ 2932s({\rm A}), \\ 2857s({\rm A}),\ 1618m({\rm D}),\ 1441s({\rm B}),\ 1357s({\rm B}),\ 1345s,\ 1307s,\ 1160s({\rm C}), \\ 1125s({\rm C}),\ 1066{\rm w},\ 1005-990{\rm sb}({\rm J}),\ 950{\rm sh}({\rm E}),\ 940m({\rm E}),\ 845{\rm m}, \\ 815{\rm m},\ 625-600{\rm sb},\ 543{\rm sh}({\rm F}),\ 510{\rm sh}({\rm K}). \end{array}$

 $\rm Ti(OPr^{i})_{2}(ON:C(Et)Me)_{2}*: 3380-3230wb, 2930-2855sb(A), 1641m(D), 1455s(B), 1364s(B), 1318m, 1250w, 1233w, 1168s(C), 1136s(C), 1078m, 1008sb(G), 953s(E), 853s, 783s, 628s, 563s(F), 523sh(F), 488sh(K).$

 $Ti(OPr^i)(ON:C(Et)Me)_3: 3405-3305wb, 2991s(A), 2952s(A), 2894s(A), 1643m(D), 1550w, 1457s(B), 1359s(B), 1248w, 1230w, 1165s(C), 1133s(C), 1008s(G), 987s(E), 948s(E), 783s, 678m, 622s, 553s(F), 490sh(K).$

 $\rm Ti(ON:C(Et)Me)_4:$ 3334wb, 2984s(A), 2950s(A), 2884s(A), 1641m(D), 1535w, 1450s(B), 1359s(B), 1253sh, 1234m, 1123m, 1078m, 993s(E), 953s(E), 786s, 685s, 628s, 563s(F), 518sh(F), 488sh(K).

 $\begin{array}{l} Me_2C:NOH *: \ 3382-3008sb(I), \ 2916s(A), \ 2845s(A), \ 1678m(D), \\ 1458s(B), \ 1416sh(B), \ 1368s(B), \ 1268s, \ 1065sb, \ 970s(E), \ 938s(E), \\ 918s(E), \ 811s, \ 645w, \ 610s, \ 470s. \end{array}$

TABLE 1 (Continued)

A = ν C-H, B = C-H deformation, C=CHMe₂ skeletal. D = ν C=N, E = ν (N-O), F = ν Ti-O, G = ν C-O, H = ν N-O, I = ν O-H, J = ν C-O + ν N-O, K = ν Ti-O + ν Ti-N, L = ν C-N, M = t-butoxy vibrations.

* Scanned in Nujol. vw = Very weak, w = weak, s = strong, m = medium, sh = shoulder, b = broad.

over sodium followed by azeotropic fractionation in the presence of ethanol. Oximes were prepared by standard methods. Diethylhydroxylamine (Pennsalt) was dried by storage over KOH (5-6 h) followed by distillation (77-79°/ca. 40 mm) over KOH and aluminium isopropoxide respectively. Precautions were taken to exclude moisture from the systems. Fractionations were carried out in a column packed with Raschig rings.

Molecular weights were determined in a semi-micro ebulliometer (Gallenkamp) using a thermistor sensing.

Nitrogen was estimated by Kjeldahl procedure. Titanium was estimated gravimetrically as TiO_2 . Ethyl and isopropyl alcohols were estimated by oxidation with N-potassium dichromate in 12.5% sulphuric acid; ¹⁶ in all cases near quantitative yields were obtained.

I.r. spectra of the above derivatives were recorded as neat or in Nujol using KBr optics (Perkin-Elmer 337) in the range of 4000-400 cm⁻¹ (see Table 1). Typical reactions are described below:

Reactions of Titanium Alkoxides with Oximes and Diethylhydroxylamine.—To titanium alkoxides in benzene were added calculated quantities of oxime or hydroxylamine. With the latter reactions, heat was evolved and the solutions turned yellow. The mixture was then heated for ca.5-6 h. The azeotrope was collected followed by benzene. The residual solvent was removed under reduced pressure, ca. $50-60^{\circ}/0.5-1.0$ mm. With the ethoxides and isopropoxides, the reactions could be followed by estimating the alcohols azeotroped out. Results of these reactions are summarised in Table 2.

Interchange Reactions with t-Butyl Alcohol.—To the titanium product in benzene was added t-butyl alcohol and the mixture was heated under reflux for ca. $5\frac{1}{2}$ h. The azeotrope was collected. The residue was distilled under reduced pressure at room temperature and product was finally dried at 50°/0.5 mm. Reactions are summarised in Table 3.

Disproportionation of Mixed Butoxy-acetoximates of Titanium.—Distillation of $Ti(OBu^{t})_{3}(ON:CMe_{2})$ gave $Ti(OBu^{t})_{4}$, b.p. 65—66°/0·4—0·5 mm (Found: Ti, 14·0. $C_{16}H_{36}O_{4}Ti$ requires Ti, 14·1%).

The residue was extracted with benzene to yield a solid (Found: Ti, 14.2; N, 16.5. $C_{12}H_{24}N_4O_4Ti$ requires Ti, 14.2; N, 16.7%).

Distillation of Ti(OBu^t)₂(ON:CMe₂)₂ gave first Ti(OBu^t)₄ identified by its b.p. $64-66^{\circ}/0\cdot 4-0\cdot 5$ mm and chemical analysis as Ti(OBu^t)₄ (Found: Ti, 14.2. C₁₆H₃₆O₄Ti requires Ti, 14.1%). The second fraction which distilled out at 87-90°/0.1 mm was identified by its chemical analysis as Ti(OBu^t)(ON:CMe₂)₃ (Found: Ti, 14.3; N, 12.3. C₁₃H₂₇N₃O₄Ti requires Ti, 14.2; N, 12.45%).

¹⁶ D. C. Bradley, F. M. A. Halim, and W. Wardlaw, J. Chem. Soc., 1950, 3450.

TABLE 2

Reactions of titanium alkoxides with diethylhydroxylamine and oximes

	Reactants (g) Ti $(OR)_4$: Et ₂ NOH			Alcohol liberated	Analys	nalysis (%)	
	(1)(4) $R = Et;$			(g)	Found	Found	M
Compd	. $(5)-(8) R = Pr^{i};$	Molar		Found	(calc.)	(calc.)	Found
no.	(9)—(11) $R = Bu^{t}$	ratio	Products; b.p.; % yield; nature *	(calc.)	Ti	N	(calc.)
(1)	3.39 : 1.33	1:1	Ti(OEt) ₃ (ONEt ₂); 110°/1 mm; 83; YVL	0.64	17.65	5.15	400
				(0.68)	(17.7)	(5.15)	(271)
(2)	3.13 ± 2.45	1:2	$Ti(OEt)_2(ONEt_2)_2$; 108°/0.6 mm; 80;	1.26	$15 \cdot 2$	8.85	439
(0)	0 77 4 40	1.0	$\frac{YVL}{T'(OEU(ONE))} = 160000 T = 0.1$	(1.27)	(15.3)	(8.9)	(314)
(3)	3.77:4.43	1:3	$11(OEt)(ONEt_2)_3; 160^{\circ}/0.5 \text{ mm}; 91;$	2.20	13.4	(11.75)	440
(4)	2.50 + 5.47	1 · 4	15 Ti/ONE+) + 150°/0.5 mm + 85 + VBS	(2.28) 2.82	(13.4)	(11.75)	(357)
(*)	5.50.5.47	1.4	$\Pi(OMEt_2)_4$, 150 /0.5 mm, 85, 1155	(2.83)	(12.0)	(14.0)	(400)
(5)	$4.87 \cdot 1.55$	1 · 1	$Ti(OPr^{i})_{o}(ONEt_{o}) \le 110 - 115^{\circ}/1 mm \le 79$	1.05	15.2	4.4	320
(0)	1011100		YVL	$(\hat{1} \cdot \hat{0}\hat{3})$	(15.3)	(4.45)	(313)
(6)	4.22:2.67	1:2	$Ti(OPr^{i})_{o}(ONEt_{o})_{o}; 101-103^{\circ}/0.1 mm;$	1.76	14.0	8.15	345
			90; YVL	(1.78)	(14.0)	(8.2)	(342)
(7)	5.44:5.13	1:3	$Ti(OPr^{i})(ONEt_{2})_{3}; 140^{\circ}/1.5 \text{ mm.}; 88;$	$3 \cdot 42$	12.8	11.4	385
			YVL	$(3 \cdot 44)$	$(12 \cdot 9)$	(11.3)	(371)
(8)	5.62:7.09	1:4	$Ti(ONEt_2)_4$; 150°/0·5 mm; 90; YBS	4.73	11.95	14.0	410
				(4 ·74)	(12.0)	(14.0)	(400)
(9)	3.50:0.92	1:1	$T_1(OBut)_3(ONEt_2); 112^{\circ}/1 mm; 81;$		13.5	3.9	358
(10)	9 75 - 1 06	1.0	$\frac{YVL}{T_{1}^{2}(OR-t)} = \frac{100810}{1000} \frac{F}{T_{1}^{2}(OR-t)} = \frac{100}{1000} $		(13.5)	(3.95)	(355)
(10)	3.75 : 1.96	1:2	$11(ODu^{0})_{2}(ONEt_{2})_{2}; 108^{-}/0.5 \text{ mm}; 80;$		(12.95)	(7.55)	372
(11)	4.15 . 3.96	1 . 3	$T_{i}(OBut)(ONEt) + 130^{\circ}(1 mm + 80)$		12.45	10.95	390
(11)	410.520	1.5	VVI.		(12.45)	(10.9)	(385)
	$Ti(OPr^{i})$, : RNOH		1,12		(12 10)	(100)	(000)
	(12) (15) D — Mo C:						
	$(12) - (15) R = Me_2C,$ (12) - (10) R = Me(Et)C						
(12)	(12) - (19) R = Me(Et)C 6.65 · 1.71	1 · 1	$Ti(OPri)_{ONCMe_{1}} = 95 WCS$	1.40	16.05	4.6	324
(12)	0.00.111	1.1	m(orr/3(orrosic ₂), , , , , , , , , , , , , , , , , , ,	(1.40)	(16.1)	(4.7)	(297)
(13)	5.57:2.86	1:2	$Ti(OPr^{i})_{o}(ON:CMe_{o})_{o};; 96;$	$2 \cdot 34$	15.6	`9 •0´	324
()			WCS WCS	(2.35)	(15.45)	(9.05)	(310)
(14)	4.12:3.18	1:3	$Ti(OPr^{i})(ON:CMe_{2})_{3}; ; 97;$	2.60	14.65	13.0	396
			WCS	(2.62)	(14.8)	(13 ·0)	(323)
(15)	10.36:10.66	1:4	$Ti(ON:CMe_2)_4$; — ; 98; WCS	8.70	14.3	16.4	342
(10)				(8.76)	(14.25)	(16.7)	(336)
(16)	7-26:2-23	1:1	$11(OPT')_{3}(ON.C(Me)Et);; 96;$	1.52	15.4	4.5	329
(17)	5.01 . 9.65	1.0	$\begin{array}{ccc} Y WS \\ T_{i}(OD_{i}) & (ON^{*}O(M_{O})Et) \\ \end{array}$	(1.03)	(10.4)	(4.5)	(311)
(17)	9.91 9.09	1.4	VWS = 5.00000000000000000000000000000000000	2·40 (2·50)	(14.15)	(8.3)	(338)
(18)	1.80 - 1.66	$1 \cdot 3$	Ti(OPri)(ONC(Me)Ft) 95.	1.14	13.15	11.6	434
(10)	1 00 , 1 00	1.0	YWSS	(1.14)	(13.1)	(11.5)	(365)
(19)	4.75 : 5.83	1:4	$Ti(ON:C(Me)Et)_{4}; - ; 99; YWL$	3.95	12.15	13.95	386
v - 7				(4.0)	(12.2)	(14.3)	(392)

* YVL = Yellow viscous liquid; YS = yellow solid; YBS = yellow-brown solid; WCS = white crystalline solid; YWS = yellowish white semisolid; YWL = yellowish white liquid.

TABLE 3

Interchange with t-butyl alcohol

Alcohol

				Alcohol liberated	Analysis (%)			
		Molar		(g) Found	Found (calc.)	Found (calc.)	M Found	
Reactants	(g)	ratio	Product; b.p.; % yield; nature *	(calc.)	Ti	N	(calc.)	
(1) $Ti(OEt)(ONEt_2)_3$ Bu ^t OH	$2.10 \\ 0.44$	1:1	Ti(OBu ^t)(ONEt ₂) ₃ ; 128-130°/1 mm; 88; VVL	0.32 (0.32)	12.45 (12.45)	10.9 (10.9)	388 (385)	
(2) $Ti(OEt)_2(ONEt_2)_2$ ButOH	2.45 1.15	1:2	$Ti(OBu^{t})_{2}(ONEt_{2})_{2}; 108-110^{\circ}/0.5 \text{ mm};$	(0.36)	12.9 (12.95)	7.55	372 (370)	
(3) $Ti(OEt)_{s}(ONEt_{2})$ Bu ^t OH	1.75 1.43	1:3	$Ti(OBu^{t})_{3}(ONEt_{2}); 110-112^{\circ}/1 mm;$ 90: VVL	0.90 (0.89)	13.5 (13.5)	3.95 (3.95)	360 (355)	
(4) $Ti(OPr^i)(ON:CMe_2)_3$ Bu ^t OH	$3.26 \\ 1.49$	1:1	$\begin{array}{ccc} \text{Ti}(\text{OBu}^{t})(\text{ON:CMe}_{2})_{3}; &; & 98; \\ \text{YWS} \end{array}$	0.59 (0.61)	14.25 (14.25)	12.25 (12.45)	337 (339)	
	(excess)			(* *-)	()	()	(000)	
(5) $\operatorname{Ti}(\operatorname{OPr}^{i})_{2}(\operatorname{ON:CMe}_{2})_{2}$ Bu ^t OH	$1.59 \\ 1.07$	1:2	$Ti(OBu^t)_2(ON:CMe_2)_2;$ — ; YWSS	$0.58 \\ (0.62)$	$14 \cdot 3$ (14 \cdot 15)	$8 \cdot 2 \\ (8 \cdot 3)$	370 (338)	
(6) $Ti(OPr^i)_3(ON:CMe_2)$ Bu ^t OH	(excess) 2.98 4.52	1:3	$Ti(OBu^t)_3(ON:CMe_2);$; YWL	1·80 (1·89)	$14 \cdot 2$ (14 · 15)	$4.35 \\ (4.15)$	$358 \ (339)$	
	(excess)							

* See footnote to Table 2.

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Reaction between Titanium(IV) Chloride and Acetone Oxime in 1: 4 Ratio in the Presence of Triethylamine.—To the oxime (5·17 g) and Et₃N (7·17 g) in benzene (50 ml) at 0·5° was added dropwise with shaking titanium(IV) chloride (3·36 g) in benzene. The mixture was kept at room temperature overnight, filtered, and washed with benzene. Excess of solvent was removed under reduced pressure from the filtrate which was then dried at 60°/1 mm for 2 h to give a white solid (3·10 g) which was crystallised from benzenen-hexane (Found: Ti, 14·25; N, 16·6. $C_{12}H_{24}N_4O_4Ti$ requires Ti, 14·25; N, 16·7%).

Ethyl methyl ketone oximate was similarly prepared (Found: Ti, 12·15; N, 14·0. $C_{20}H_{40}N_4O_4Ti$ requires Ti, 12·2; N, 14·3%).

Reaction between Titanium Di-isopropoxy Bis-acetone Oximate and Acetylacetone.—(a) In 1:1 molar ratio. Acetylacetone (0.85 g) was added to the oximate (2.64 g) in benzene (50 ml) and the mixture was heated under reflux for ca. 6 h; the azeotrope was collected. The residue was distilled under reduced pressure and then dried at $45^{\circ}/0.1$ mm for 2 h to leave an orange red viscous liquid (2.97 g), which solidified with time (Found: Ti, 13.55; N, 7.9%; *M*, 401. $C_{14}H_{26}N_2O_5Ti$ requires Ti, 13.6; N, 8.0%; *M*, 350).

(b) In 1:2 molar ratio. Acetylacetone (1.75 g) was added to the oximate (2.71 g) in benzene (50 ml) and the reaction mixture was heated under reflux for ca. 7 h; the azeotrope was removed at 72° followed by benzene at 80°. The residue was distilled under reduced pressure and the product was dried at 50°/2.5 mm for 2 h to leave a yellow orange solid (3.39 g) (Found: Ti, 12.3; N, 7.15%; M, 374. $C_{16}H_{26}N_2O_6Ti$ requires Ti, 12.25; N, 7.2%; M, 390).

Hydrolysis of Tetrakis-acetoximate of Titanium.—The oximate upon exposure to air was hydrolysed to acetone oxime and titanium oxide dihydrate as evidenced by analysis of the products.

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