REACTIONS OF OXIMES WITH BIS(CYCLOPENTADIENYL) TITANIUM(IV) CHLORIDE

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Summary

The reactions of bis(cyclopentadienyl)titanium(IV) chloride $(C_5H_5)_2$ TiCl₂ with o-hydroxy oximes (OXH₂) in THF/benzene (molar ratio 1:1) in the presence of triethylamine (2 moles) at room temperature lead to the formation of derivatives of the type $(C_5H_5)_2$ Ti(OX), where OXH₂ is 2-hydroxy-5-methyl acetophenone oxime, 2-hydroxy-5-methyl propiophenone oxide, 2-hydroxy-5-methyl butyrophenone oxime, salicylaldoxime or α -benzoin oxime. Reactions of $(C_5H_5)_2$ TiCl₂ with glyoxime (GH_2) and α -benzildioxime (DPGH₂) at various molar ratios and under various conditions always gave $(C_5H_5)_2$ Ti(G) and $(C_5H_5)_2$ Ti(DPG), respectively, whereas with dimethylglyoxime (DMGH₂) under similar conditions $(C_5H_5)_2$ Ti(DMGH)₂ was obtained. These complexes have been characterized by elemental analysis, IR and electronic spectra. Molecular weight determination in benzene indicated that the complexes were monomeric.

1. Introduction

Much work has been carried out on the oxime derivatives of aluminium [1], titanium [2], zirconium [3] and tin [4]. These complexes are reported to be of great industrial importance [5] and useful as fungicides, bactericides, flame-retarding additives, polymerization catalysts etc.

A survey of the literature revealed that no work has been done on the reactions of $(C_5H_5)_2TiCl_2$ with oximes. It was therefore considered of interest to carry out systematically reactions of $(C_5H_5)_2TiCl_2$ with various types of oximes. On the basis of elemental analyses, molecular weight determinations, IR and electronic spectra, it was concluded that the complexes are obtained by replacement of the hydroxy hydrogen of oximes by an organometal moiety of the titanium metal. Reactions were facilitated by the presence of a suitable hydrogen chloride acceptor such as triethylamine, pyridine etc. The reactions may be represented by the following equations:



where (a) R' = H, R = H; (b) R' = H, CH_3 , C_2H_5 , C_3H_7 , $R = CH_3$.



where $R = H, C_6H_5$

$$(C_{5}H_{5})_{2}TiCl_{2} + CH_{3}-C - CH_{3} + 2(C_{2}H_{5})_{3}N \longrightarrow$$

$$NOH NOH$$

$$(C_{5}H_{5})_{2}Ti + OH + CCH_{3} + 2(C_{2}H_{5})_{3}N + HCl \quad (III)$$

$$(III)$$

Complexes of type (I) were pale or deep brown amorphous solids which were appreciably soluble in benzene, tetrahydrofuron, chloroform, acetone etc. The dioximates (II) and (III) were pale or deep yellow insoluble complexes. Owing to the insoluble nature of these complexes, their molecular weights could not be determined.

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2. Experimental

2.1. Materials

THF (BDH) was dried by distilling it over lithium aluminium hydride. Benzene and titanium tetrachloride were purified by a method described in the literature [6]. $(C_5H_5)_2$ TiCl₂ was prepared by a known method [7]. A.R. grade DMGH₂ and glyoxime were used in the synthesis of complexes. α -benzildioxime was prepared from benzil by a method given in the literature [8]. *o*-hydroxy oximes were prepared according to a known method [9]. Triethylamine was purified by a known method [8].

2.2. Apparatus

Glass apparatus with interchangeable standard joints was used throughout this work; stringent precautions were taken to exclude moisture from the system.

2.3. Analytical methods

The titanium content of the complexes was determined as TiO_2 [6]. Nitrogen was estimated using the Kjeldahl method; chlorine was determined as silver chloride.

2.4. Reaction of $(C_5H_5)_2TiCl_2$ with 2-hydroxy-5-methyl acetophenone oxime (molar ratio 1:1)

A mixture of $(C_5H_5)_2$ TiCl₂ and 2-hydroxy-5-methyl acetophenone oxime in a 1:1 molar ratio and 2 moles of triethylamine was stirred in THF/ benzene for about 48 h at room temperature. The reaction mixture was filtered to remove triethylamine hydrochloride and the clear filtrate was evaporated to dryness under reduced pressure. The residue was washed several times with petroleum ether (60 - 80 °C) and dried. The complex was recrystallized from a THF/petroleum ether mixture (yield 78%). Analysis showed: Ti, 13.84; N, 4.56%. $(C_5H_5)_2$ Ti(C₉H₉NO₂) requires: Ti, 14.05; N, 4.47%. For the sake of brevity, the reactions of $(C_5H_5)_2$ TiCl₂ with other o-hydroxy oximes are summarized in Table 1.

2.5. Reaction of $(C_5H_5)_2$ TiCl₂ with dimethylglyoxime using excess triethylamine

Various amounts of $(C_5H_5)_2$ TiCl₂ and DMGH₂ and an excess of triethylamine were mixed in benzene. The mixture was stirred at room temperature for about 45 h to ensure a complete reaction. The insoluble complex and triethylamine hydrochloride were removed by filtration. Unreacted DMGH₂, if present in the residue, was removed by extraction with THF. The triethylamine hydrochloride was removed by dissolving the mass in dichloromethane leaving the insoluble compound. Analysis showed: Ti, 11.75; N, 13.20%. $(C_5H_5)_2$ Ti $(C_4N_2O_2H_7)_2$ requires: Ti, 11.73; N, 13.72%. Other reactions of $(C_5H_5)_2$ TiCl₂ with glyoxime and α -benzildioxime are given in Table 2.

Reactions of	(C ₅ H ₅) ₂ TiCl ₂ with <i>o</i> -hydroxy oximes				
Sample no.	Reactants ^a (molar ratio)	Time of stirring (h)	Product, colour and decomposition temperature (°C)	% Ti found (calc.)	% N found (calc.)
1	$(C_{5}H_{5})_{2}T_{1}Cl_{2} + AOXH_{2} + (C_{2}H_{5})_{3}N$ (1:1:2)	48	(C ₅ H ₅) ₂ Ti(AOX) Brown, 155	13.84 (14.05)	4.56 (4.47)
5	$(C_5H_5)_2$ TiCl ₂ + POXH ₂ + $(C_2H_5)_3N$ (1:1:2)	50	(C ₅ H ₅) ₂ Ti(POX) Dark brown, 190	13.15 (13.50)	4.03 (3.95)
ŝ	$(C_{5}H_{5})_{2}$ TiCl ₂ + BOXH ₂ + $(C_{2}H_{5})_{3}N$ (1:1:2)	45	(C ₅ H ₅) ₂ Ti(BOX) Brown, 180	12.81 (12.98)	3.68 (3.79)
4	$(C_5H_6)_2$ TiCl ₂ + SOXH ₂ + $(C_2H_5)_3N$ (1:1:2)	45	(C ₅ H ₅) ₂ Ti(SOX) Light brown, 155	15.79 (15.30)	4.56 (4.47)
5	$(C_{5}H_{5})_{2}TiCl_{2} + B'OXH_{2} + (C_{2}H_{5})_{3}N$ (1:1:2)	40	(C ₅ H ₅) ₂ Ti(B'OX) Light brown, 140	11.50 (11.30)	3.59 (3.47)
^a AOXH ₂ , 2-	hydroxy-5-methyl acetophenone oxime; POX	H ₂ , 2-hydroxy-5	methyl propiophenone oxime; BO	XH ₂ , 2-hydroxy-	5-methyl

butyrophenone oxime; SOXH₂, salicyald oxime; B'OXH₂, α -benzoinoxime.

TABLE 1

$ \begin{array}{cccc} 1 & (C_{5}H_{5})_{2} \operatorname{TiCl}_{2} + \mathrm{GH}_{2} + (C_{2}H_{5})_{3} \mathrm{N} \\ (1:1:1) & (1:1:1) \\ 2 & (C_{5}H_{5})_{2} \operatorname{TiCl}_{2} + \mathrm{GH}_{2} + (C_{2}H_{5})_{3} \mathrm{N} \\ (1:1:2) & (1:1:2) \\ 4 & (C_{5}H_{5})_{2} \operatorname{TiCl}_{2} + \mathrm{DPGH}_{2} + (C_{2}H_{5})_{3} \mathrm{N} \\ (1:1:1) & (C_{5}H_{5})_{2} \operatorname{TiCl}_{2} + \mathrm{DPGH}_{2} + (C_{2}H_{5})_{3} \mathrm{N} \\ (1:1:1) \\ 6 & (C_{5}H_{5})_{2} \operatorname{TiCl}_{2} + \mathrm{DPGH}_{2} + (C_{2}H_{5})_{3} \mathrm{N} \\ \end{array} $	$H_{2} + (C_{2}H_{5})_{3}N = 40$ $H_{2} + (C_{2}H_{5})_{3}N = 40$ $H_{2} + (C_{2}H_{5})_{3}N = 35$ $PGH_{2} + (C_{2}H_{5})_{3}N = 40$	$(C_5H_5)_2 Ti(G)$ Light yellow, 195 $(C_5H_5)_2 Ti(G)$ Light yellow, 195 $(C_5H_5)_2 Ti(G)$ Light yellow, 195 $(C_5H_5)_2 Ti(DPG)$	17.93 (18.14 (18.14 (18.14 (18.14 17.89 (18.41)		10.53 10.61) 10.56 10.61) 10.59 10.61)
2 $(C_{5}H_{5})_{2}$ TiCl ₂ + GH ₂ + $(C_{2}H_{5})_{3}$ N (1:1:2) 3 $(C_{5}H_{5})_{2}$ TiCl ₂ + GH ₂ + $(C_{2}H_{5})_{3}$ N (1:2:2) 4 $(C_{5}H_{5})_{2}$ TiCl ₂ + DPGH ₂ + $(C_{2}H_{5})_{3}$ N (1:1:1) 5 $(C_{5}H_{5})_{2}$ TiCl ₂ + DPGH ₂ + $(C_{2}H_{5})_{3}$ N (1:1:2) 6 $(C_{5}H_{5})_{2}$ TiCl ₂ + DPGH ₂ + $(C_{2}H_{5})_{3}$ N	$H_{2} + (C_{2}H_{5})_{3}N = 40$ $H_{2} + (C_{2}H_{5})_{3}N = 35$ $PGH_{2} + (C_{2}H_{5})_{3}N = 40$	(C ₅ H ₅) ₂ Ti(G) Light yellow, 195 (C ₅ H ₅) ₂ Ti(G) Light yellow, 195 (C ₅ H ₅) ₂ Ti(DPG)	17.95 (18.14 17.89 17.89 (18.41)	·) (1	10.56 10.61) 10.59 10.61)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$H_{2} + (C_{2}H_{5})_{3}N = 35$ $PGH_{2} + (C_{2}H_{5})_{3}N = 40$	(C ₅ H ₅) ₂ Ti(G) Light yellow, 195 (C ₅ H ₅) ₂ Ti(DPG)	17.89 (18.41		10.59 10.61)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	$PGH_2 + (C_2H_5)_3N$ 40	(C ₅ H ₅) ₂ Ti(DPG)) (]	•
5 $(C_{5}H_{5})_{2}TiCl_{2} + DPGH_{2} + (C_{2}H_{5})_{3}N$ (1:1:2) 6 $(C_{5}H_{5})_{3}TiCl_{2} + DPGH_{2} + (C_{2}H_{5})_{3}N$		Yellow, 198	11.54 (11.50	1 C	6.67 (6.72)
6 $(C_5H_5)_3 TiCl_2 + DPGH_2 + (C_2H_5)_3 N$	PGH2 + (C2H5)3N 40	(C ₅ H ₅) ₂ Ti(DPG) Yellow, 198	11.47 (11.50	~ ()	6.63 (6.72)
(1:2:2)	$PGH_2 + (C_2H_5)_3 N$ 35	(C ₅ H ₅) ₂ Ti(DPG) Yellow, 198	11.61 (11.50	-1 @	6.64 (6.72)
7 $(C_{5}H_{5})_{2}$ TiCl ₂ + DMGH ₂ + $(C_{2}H_{5})_{3}$ l (1:1:1)	$MGH_2 + (C_2H_5)_3N$ 45	(C ₅ H ₅) ₂ Ti(DMGH) ₂ Dark yellow, 190	11.83 (11.73) 3) 3)	13.20 13.72)
8 $(C_{5}H_{5})_{2}$ TiCl ₂ + DMGH ₂ + $(C_{2}H_{5})_{3}$ (1:1:2)	$MGH_2 + (C_2H_5)_3N$ 40	(C ₅ H ₅) ₂ Ti(DMGH) ₂ Dark yellow, 190	11.75 (11.73	3) (13.18 13.72)
9 $(C_5H_5)_2 TiCl_2 + DMGH_2 + (C_2H_5)_3^{-1}$ (1:2:2)	$MGH_2 + (C_2H_5)_3N$ 40	(C ₅ H ₅) ₂ Ti(DMGH) ₂ Dark yellow, 190	11.74 (11.75	4 3) (13.40 13.72)

TABLE 2 Reactions of $(C_5H_5)_2TiCl_2$ with dioximes

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 $^{a}GH_{2},$ glyoxime; DPGH_2, $\alpha\text{-}benzildioxime;$ DMGH_2, dimethylglyoxime.

2.6. Physical measurements

The molecular weights of the soluble complexes were determined using a Gallenkamp ebulliometer (W.G. Pye & Co. Ltd., Cambridge, England). The IR spectra of the complexes and ligands were recorded on a Perkin–Elmer IR 621 spectrometer in KBr over the range 4000 - 200 cm⁻¹. The electronic spectra of the complexes were recorded on a Perkin–Elmer 4000A spectrometer over the range 400 - 750 nm.

3. Results and discussion

The stoichiometry of the reactions and the molecular formulae of the complexes (I), (II) and (III) suggest that all the oximes except DMGH₂ behave as dibasic ligands. Both the hydrogen atoms of the hydroxy and oxime groups are replaced, giving rise to five- or six-membered rings. The monobasic behaviour of DMGH₂ is probably due to its low acidity compared with that of glyoxime and α -benzildioxime. Methyl groups, being electron donating, decrease the acidic nature of the oxime group which is enhanced by phenyl groups in the case of α -benzildioxime. It is also suggested that α -benzildioxime isomerizes to γ -benzildioxime [10] which is dibasic in nature.

3.1. IR spectra

The important IR frequencies are given in Table 3. The presence of cyclopentadienyl groups in the complexes is indicated by the usual peaks in the IR spectra. The two bands at 1150 cm^{-1} and 1025 cm^{-1} are assigned as a ring breathing mode and a parallel (in-plane) wag frequency, respectively. The band at 815 cm^{-1} is due to a C-H out-of-plane deformation and the band at 1440 cm^{-1} is assigned to an asymmetric $\nu(\text{C-C})$ [11].

The IR spectra of the oximes exhibit a band at 3300 cm^{-1} which is assigned to ν (O-H); this vanishes in the complexes except in the case of the complex with DMGH₂ where it is retained. It is a broad band and is due to inter-molecular and intra-molecular hydrogen bonding. The non-conjugated ν (C=N) band normally appears in the range 1690 - 1650 cm⁻¹ [12]. Conjugation shifts it to a lower frequency and it appears around 1630 cm^{-1} in Schiff's bases [13]. In the spectra of all ketooximes and salicylaldoximes there are two strong sharp peaks at 1625 cm⁻¹ and 1612 cm⁻¹ which are missing from the spectra of the complexes. These bands are assigned to O-H deformations. The broad/medium band at 1585 cm^{-1} in ligands shifts to a lower frequency (around 1530 cm^{-1}) in the complexes and can thus be assigned to $\nu(C=N)$. Similar observations have been made by Birader et al. [14]. The lowering of ν (C=N) indicates that the bond order of the C=N bond decreases and the nitrogen atom coordinates to titanium metal. The large shift of C=N from the normal value of 1650 cm^{-1} to 1570 cm^{-1} in the ligands appears to be due to factors such as resonance, conjugation or coupling with C=C and hydrogen bonding [14]. A broad medium intensity band at 1280 cm⁻¹ in ligands is regarded as being due to ν (C-O) + δ (C-H) +

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TABLE	

IR frequencies $(cm^{-1})^a$

Sample	Complexes	μ-0) <i>u</i>	μ(C-H)	v(C-C)	δC-H) ^b		₽(C−N)	(O-N)4		₽(C−0)
no.					i-p	d-o				δ(C-H) δ(N-O)
	(C ₅ H ₅) ₂ TiCl ₂		3100 s	1435 s	1020 m	820 mb				
2	(C ₅ H ₅) ₂ Ti(AOX)	ł	3100 w	1440 m	1025 s	825 mb	1596 m	1205 s	960 m	1295 s
3	(C ₅ H ₅) ₂ Ti(POX)	I	2982 w	1445 s	1020 m	800 mb	1575 m	1210 m	955 s	1290 s
4	(C ₅ H ₅) ₂ Ti(BOX)	1	3000 wb	1445 mb	1023 mb	812 mb	1575 m	1200 m	I	1280 s
5	(C ₅ H ₅) ₂ Ti(SOX)	1	2980 w	1440 s	1015 mb	810 s	1590 s	1205 m	920 s	1275 mb
9	(C ₅ H ₅) ₂ Ti(B'OX)	I	2950 w	1440 s	1020 s	800 s	1592 s	1205 w	970 w	1250 wb
7	(C ₅ H ₅) ₂ Ti(OG)	1	2940 m	1444 b	1015 s	805 m	1550 mb	1185 b	985 s	1262 mb
8	(C ₅ H ₅) ₂ Ti(DPG)	I	2990 mb	1440 s	1016 mb	816 s	1545 w	1220 w	980 s	1265 wb
6	$(C_5H_5)_2$ Ti(DMGH) ₂	3200 s	2950 wb	1440 m	1025 mb	815 wb	1575 m	1250 w	980 s	1145 m

^as = sharp; m = medium; b = broad; mb = medium broad; wb = weak broad. ^bi-p = in-plane; o-p = out-of-plane. δ (N–O) vibrations [14]. The bands in the regions 1235 - 1190 cm⁻¹ and 968 - 935 cm⁻¹ in the complexes are assigned to ν (N–O). In the cases of glyoxime and α -benzildioxime, the two N–O bands are unequal; this probably indicates two different types of N–O linkage. In the complex with dimethylglyoxime the two N–O bonds are unequal [15]: one of the O–H groups is ionised and the other is not. In the case of bis(cyclopentadienyl) titanium bis(dimethylglyoximate), the various bands are in positions identical with those of the nickel and palladium dimethylglyoximate complexes [15], indicating close structural similarities. In the case of dimethylglyoxime complexes, the splitting of the O–H bands suggests that the hydrogen bond involved is not of a symmetrical type [15]. The bands in the regions 560 - 530 cm⁻¹ and 440 cm⁻¹ are attributed to ν (Ti–N) [17] and ν (Ti–O), respectively.

3.2. Electronic spectra

The electronic spectra of all these complexes have been recorded in chloroform and in Nujol. All the spectra show a single band in the region $24725 \cdot 24375 \text{ cm}^{-1}$ which can be assigned to the charge transfer band [16] and is in accord with their $(n-1)d^0ns^0$ electronic configuration.

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