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M. S. Singh [a] & Prem Narayan [a]
[a] Department of Chemistry , D.D.U. Gorakhpur University , Gorakhpur, 273 009, India

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COMPLEXES OF TITANIUM TETRACHLORIDE WITH BENZILMONOXIME AND BENZILDIOXIME

M. S. Singh* and Prem Narayan

Department of Chemistry, D.D.U. Gorakhpur University,
Gorakhpur 273 009, India

ABSTRACT

Some new titanium(IV) derivatives of benzilmonoxime and benzildioxime have been synthesized by the reactions of titanium tetrachloride and the sodium salt of oximes in different molar ratios. All of the newly synthesized complexes have been characterized by elemental analyses, molecular weight determinations, and spectral (IR, ^{1}H, and ^{13}C NMR) studies.

INTRODUCTION

Titanium tetrachloride (1) and titanium compounds (2,3) have been used to perform a wide variety of different reactions in organic synthesis. These include $TiCl_4$-mediated Friedel-Crafts reactions, $Ti(OR)_4$-promoted transesterifications, olefin metathesis (4), and the all important Sharpless epoxidation (5). It became clear that the transmetallation of classical 'carbanions' using titanating agents produces new reagents which display a high degree of chemo-, regio- and

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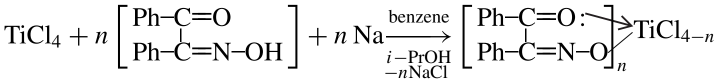
*Corresponding author. E-mail: dr_m_s_singh@yahoo.com stereoselectivity (6). A number of oximates (7–9) of transition metals have been reported having interesting stereochemistry. Benzilmonoxime and benzildioxime are important from the biochemical and analytical point of view. In view of this and our continuing studies on the synthesis of new titanium(IV) complexes (10–12), we herein describe the synthesis and characterization of some new titanium(IV) derivatives of oximes.

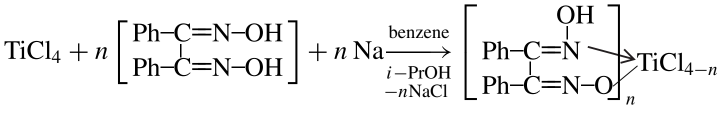
RESULTS AND DISCUSSION

The reaction of $TiCl_4$ with the sodium salt of benzilmonoxime and benzildioxime (prepared in situ by the reaction of sodium isopropoxide with benzilmonoxime or benzildioxime in 1:1 molar ratio in a refluxing benzene-isopropanol mixture) in different stoichiometric ratios in dry benzene leads to the formation of Ti(IV) complexes. These reactions were found to be quite facile and the sodium chloride formed during the course of the reaction was filtered off.



$$\mathrm{TiCl_4} + n\left[\begin{array}{l}\mathrm{Ph{-}C{=}O}\\ \mathrm{Ph{-}C{=}N{-}OH}\end{array}\right] + n\,\mathrm{Na} \xrightarrow[\substack{i-\mathrm{PrOH}\\ -n\mathrm{NaCl}}]{\text{benzene}} \left[\begin{array}{l}\mathrm{Ph{-}C{=}O:}\\ \mathrm{Ph{-}C{=}N{-}O}\end{array}\right]_n \mathrm{TiCl}_{4-n}$$

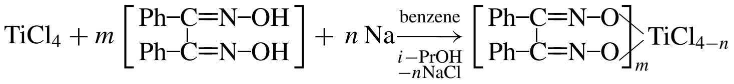
$n = 1$, Compd. (**1**); $n = 2$, Compd. (**2**;) $n = 3$, Compd. (**3**); ($n = 4$), Compd. (**4**).



$$\mathrm{TiCl_4} + n\left[\begin{array}{l}\mathrm{Ph{-}C{=}N{-}OH}\\ \mathrm{Ph{-}C{=}N{-}OH}\end{array}\right] + n\,\mathrm{Na} \xrightarrow[\substack{i-\mathrm{PrOH}\\ -n\mathrm{NaCl}}]{\text{benzene}} \left[\begin{array}{l}\qquad\quad\mathrm{OH}\\ \mathrm{Ph{-}C{=}N}\\ \mathrm{Ph{-}C{=}N{-}O}\end{array}\right]_n \mathrm{TiCl}_{4-n}$$

$n = 1$, Compd. (**5**); $n = 2$, Compd. (**6**); $n = 3$, Compd. (**7**); $n = 4$, Compd. (**8**).

Similarly, the disodium salt of benzildioxime was reacted with $TiCl_4$ in benzene in 1:1 and 2:1 molar ratios to give titanacyclic complexes.



$$\mathrm{TiCl_4} + m\left[\begin{array}{l}\mathrm{Ph{-}C{=}N{-}OH}\\ \mathrm{Ph{-}C{=}N{-}OH}\end{array}\right] + n\,\mathrm{Na} \xrightarrow[\substack{i-\mathrm{PrOH}\\ -n\mathrm{NaCl}}]{\text{benzene}} \left[\begin{array}{l}\mathrm{Ph{-}C{=}N{-}O}\\ \mathrm{Ph{-}C{=}N{-}O}\end{array}\right]_m \mathrm{TiCl}_{4-n}$$

$m = 1, n = 2$, Compd. (**9**); $m = 2, n = 4$, Compd. (**10**).

All of these new complexes are fairly soluble in common organic solvents and coordinating solvents like DMSO and DMF. The molecular weight determination in $CHCl_3$ solution shows the monomeric nature of these complexes at room temperature. These complexes are susceptible to hydrolysis. The compounds with their physical properties and elemental analyses are listed in Table 1.

Table 1. Synthetic and Analytical Data of Titanium(IV) Complexes

Compd. No.	Reactants in g			Molar Ratio	Product/ Mol. Wt. Found/(Calcd.)	Yield (%)	M.p. (°C)	Analysis: % Found (Calcd.)				
	$TiCl_4$	Ligand	Sodium					C	H	N	Ti	Cl
(**1**)	1.19	1.42	0.15	1:1:1	$C_{14}H_{10}NO_2TiCl_3$ 378 (354.6)	75	178	44.08 (44.36)	2.72 (2.62)	3.52 (3.71)	12.42 (12.66)	28.04 (28.16)
(**2**)	0.52	1.23	0.13	1:2:2	$C_{28}H_{20}N_2O_4TiCl_2$ 567 (583)	73	188	59.04 (59.29)	3.42 (3.53)	4.74 (4.94)	8.22 (8.47)	12.36 (12.53)
(**3**)	0.37	1.31	0.13	1:3:3	$C_{42}H_{30}N_3O_6TiCl$ 765.0 (755.5)	69	200	66.41 (66.74)	3.76 (3.97)	5.24 (5.56)	6.02 (6.36)	4.89 (4.70)
(**4**)	0.32	1.52	0.16	1:4:4	$C_{56}H_{40}N_4O_8Ti$ 923 (944)	66	212	71.08 (71.21)	4.16 (4.24)	5.66 (5.93)	4.96 (5.09)	–
(**5**)	0.91	1.15	0.11	1:1:1	$C_{14}H_{11}N_2O_2TiCl_3$ 412.0 (393.5)	65	186	42.66 (42.75)	2.72 (2.80)	6.96 (7.12)	12.02 (12.18)	26.76 (27.08)
(**6**)	0.47	1.19	0.11	1:2:2	$C_{28}H_{22}N_4O_4TiCl_2$ 572 (597)	77	231(d)	56.11 (56.28)	3.74 (3.69)	9.08 (9.38)	8.24 (8.04)	11.66 (11.89)
(**7**)	0.26	0.99	0.10	1:3:3	$C_{42}H_{33}N_6O_6TiCl$ 779.0 (800.5)	80	200	62.58 (62.96)	4.26 (4.12)	10.32 (10.49)	5.92 (6.00)	4.26 (4.43)
(**8**)	0.18	0.90	0.09	1:4:4	$C_{56}H_{44}N_8O_8Ti$ 1026 (1004)	78	310(d)	66.69 (66.93)	4.12 (4.38)	11.09 (11.16)	4.41 (4.78)	–
(**9**)	0.51	0.64	0.12	1:1:2	$C_{14}H_{10}N_2O_2TiCl_2$ 338 (357)	82	172	47.26 (47.06)	2.67 (2.80)	7.42 (7.83)	13.11 (13.43)	19.66 (19.90)
(**10**)	0.37	0.92	0.18	1:2:4	$C_{28}H_{20}N_4O_4Ti$ 506 (524)	80	242(d)	64.02 (64.12)	3.76 (3.82)	10.41 (10.69)	9.02 (9.15)	–

R Spectral Data

The broad band present in the region 3450–2900 cm^{-1} in the infrared spectrum of the ligand is due to ν(N–OH) (13). This band is absent in Ti(IV) derivatives of benzilmpnoxime and in compounds (**9**) and (**10**) of benzildioxime, suggesting replacement of the proton from the N–OH group. A new band in the region 580–560 cm^{-1} appears, which can be attributed to the formation of titanium- oxygen (Ti–O) bonds (2,14). This is further supported by the fact that the ν(N–O) mode shifts from 860 cm^{-1} in the ligand to higher wave numbers (by 20–25 cm^{-1}) in the complexes suggesting strong coordination of the ligand to titanium through oxygen. The band due to the keto carbonyl, which is observed at 1685 cm^{-1} in benzilmonoxime is shifted to a lower energy (by 30–35 cm^{-1}) in the compounds (**1**)–(**4**) indicating the participation of the carbonyl group in coordination. A comparison of the IR spectrum of the ligands with those of the complexes shows that the band at 1615 cm^{-1} due to ν(C=N) in benzilmonoxime is observed almost at the same position in compounds (**1**) to (**4**) indicating that the C=N group is not taking part in coordination, whereas the band at 1620 cm^{-1} due to ν(C=N) in benzildioxime is observed at lower frequency (by 20–25 cm^{-1}) in the complexes (**5**)–(**8**) indicating the involvement of the C=N group in coordination (15) (Table 2), which is further confirmed by the appearance of a Ti–N band at ~540 cm^{-1}.

NMR Spectral Data

All titanium(IV) complexes exhibit a multiplet due to the phenyl group in the region d 6.75–8.25 ppm in their ^{1}H NMR spectra. The signal due to the –OH proton at d 10.20 ppm in benzilmonoxime is absent in its complexes (**1**)–(**4**) and compounds (**9**) and (**10**), again suggesting deprotonation and the formation of Ti–O bonds. In compounds (**5**)–(**8**) a signal at d 10.35–10.45 ppm integrates for the N–OH proton. ^{13}C NMR spectroscopy is a good diagnostic tool for determining the mode of bonding. On coordination the resonances of the carbon atoms bonded to oxygen and nitrogen atoms shift some 12–18 ppm downfield in the complexes (15). There is no significant shift in the resonances of the carbons of the phenyl group in all of the complexes as compared to the ligands (Table 2).

Although the actual structure may be elucidated only after an X-ray crystal diffraction study of at least one of the products, yet on the basis of the above studies coordination numbers of four (**9**),(**10**), five (**1**),(**5**), six (**2**),(**6**), seven (**3**),(**7**) and eight (**4**),(**8**) may be proposed around titanium(IV).

EXPERIMENTAL

All operations were performed under nitrogen atmosphere and with thoroughly dried solvents and glassware. Solvents (benzene, isopropanol) were dried

Table 2. Spectral Data of Titanium(IV) Complexes

	IR (cm^{-1})						NMR (d ppm)	
Compound	ν(C=N)	ν(C=O)	ν(O–H)	ν(Ti–O)	ν(Ti–Cl)	ν(N–O)	^{1}H	^{13}C
(**1**) $[C_{14}H_{10}NO_2]TiCl_3$	1615 s	1650 m	–	565 m	355 m	885 m	6.88–8.12 (m, 10H, arom.)	186.4 (C=O), 152.4 (C=N), 129.4–140.6 (Ph)
(**2**) $[C_{14}H_{10}NO_2]_2TiCl_2$	1618 s	1655 m	–	570 m	350 s	882 s	6.85–8.16 (m, 20H, arom.)	185.2 (C=O), 152.7 (C=N), 128.6–139.4 (Ph)
(**3**) $[C_{14}H_{10}NO_2]_3TiCl$	1616 s	1648 s	–	580 m	360 m	880 m	6.87–7.96 (m, 30H, arom.)	185.7 (C=O), 151.9 (C=N), 128.2–139.7 (Ph)
(**4**) $[C_{14}H_{10}NO_2]_4Ti$	1615 s	1652 m	–	575 m	–	884 s	6.85–8.14 (m, 40H, arom.)	186.3 (C=O), 151.9 (C=N), 129.2–139.7 (Ph)
(**5**) $[C_{14}H_{11}N_2O_2]TiCl_3$	1600 sh	–	3315 m	560 m	352 sh	883 m	6.76–8.22 (m, 10H, arom.) 10.44 (s, 1H, OH)	153.4 (C= N), 128.6–139.2 (Ph)
(**6**) $[C_{14}H_{11}N_2O_2]_2TiCl_2$	1595 sh	–	3305 m	572 m	350 m	885 sh	6.82–8.10 (m, 20H, arom.) 10.35 (s, 2H, 2XOH)	153.7 (C=N), 129.3–140.7 (Ph)
(**7**) $[C_{14}H_{11}N_2O_2]_3TiCl$	1590 s	–	3295 m	576 m	358 s	878 m	6.78–8.15 (m, 30H, arom.) 10.45 (s, 3H, 3XOH)	153.9 (C=N), 129.7–140.6 (Ph)
(**8**) $[C_{14}H_{11}N_2O_2]_4Ti$	1598 s	–	3310 s	563 m	–	880 s	6.80–8.25 (m, 40H, arom.) 10.40 (s, 4H, 4XOH).	153.1 (C=N), 128.5–139.8 (Ph)
(**9**) $[C_{14}H_{10}N_2O_2]TiCl_2$	1620 s	–	–	578 m	356 m	885 sh	6.84–8.10 (m, 10H, arom.)	154.1 (C=N), 129.3–140.7 (Ph)
(**10**) $[C_{14}H_{10}N_2O_2]_2Ti$	1622 s	–	–	566 m	–	884 m	6.75–8.15 (m, 20H, arom.)	153.9 (C=N), 129.3–140.7 (Ph)

by standard methods (16) prior to use. Melting points are uncorrected. The progress of the reactions was monitored by TLC on silica gel plates. IR spectra were measured on a Perkin-Elmer model 377 in KBr discs. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 250 instrument operating at 250 MHz and 62.9 MHz, respectively in DMSO-d_6 solution. All chemical shifts were recorded in ppm relative to TMS as an internal standard. Molecular weights were measured on a Knauer Vapour Pressure Osmometer in $CHCl_3$ solution at room temperature. Titanium was determined gravimetrically as titanium dioxide (16). Elemental analyses for C, H, and N were performed by the Central Drug Research Institute, Lucknow.

Titanium tetrachloride AR grade was obtained from Rideal-de Haen AG, Seelze-Hannover, Germany and used as such without further purification. Benzilmonoxime and benzildioxime were prepared by reported methods (17). Benzilmonoxime, m.p. 137–38°C (Lit. (17). 138–39°C). IR (KBr, cm^{-1}): 3450–2900 ν((N–OH); 1615 ν(C=N); 1685 ν(C=O). ^{1}H NMR (DMSO-d_6, d ppm): 6.80–8.20 (m, 10H, arom.); 10.20 (s, 1H, OH, D_2 O exchangeable). Analysis found: C, 74.48; H,4.94; N, 6.46%. C_{14} H_{11} NO_2 (225) requires: C, 74.66; H, 4.88; N, 6.22%. Benzildioxime, m.p. 237–39°C (Lit. (17) 239–40°C). IR (KBr, cm^{-1}): 3435–3085 ν((N–OH); 1620 ν(C=N). ^{1}H NMR (DMSO-d_6, d ppm): 7.05–8.16 (m, 10H, arom.); 10.45 (s, 2H, OH, D_2 O exchangeable). Analysis found: C, 70.09; H, 5.12; N, 11.50%. $C_{14}H_{12}N_2O_2$ (240) requires: C, 70.00; H, 5.00; N, 11.67%.

Reaction Between $TiCl_4$ and Sodium Salt of Benzilmonoxime in 1:1 Molar Ratio

A quantity of 0.15 g (6.3 m mole) of sodium metal and 25 mL of dry isopropanol were placed in a 100 mL three-necked round bottom flask fitted with an efficient magnetic stirrer, an addition funnel, a nitrogen balloon, and a condenser. The solution was stirred at reflux for about half an hour till a clear solution of sodium isopropoxide was obtained. After cooling, 1.42 g (6.3 m mole) of benzilmonoxime was added and the reaction mixture was refluxed again for 2 h. Subsequently the reaction mixture was allowed to attain room temperature. 1.19 g (6.3 m mole) of titanium tetrachloride was added dropwise with a dropping funnel to the reaction vessel. When the addition was completed, the contents were further stirred at reflux for 2 h to ensure the completion of the reaction. The solution was then filtered to remove the sodium chloride formed during the course of the reaction. The desired product was isolated by removal of the solvent under reduced pressure via rotary evaporator. The product was further purified by crystallization using a benzene-pet.ether (40–60°) mixture (20 mL each) to yield 1.78 g (75%) of product.

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All other titanium(IV) derivatives of the oximes were synthesized analogously. The pertinent data for this and other compounds are listed in Table 1.

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