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New Method of Synthesis of N-substituted β-Aminothiones and Their Compounds of Titanium

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Abstract

The synthesis of some new N-substituted β-aminothiones $R_\alpha CSCH{=}C(NHR)R_\gamma$($R_\alpha$ = C_6H_5, CH_3, R_γ = C_6H_5, $C_6H_4CH_3$, $C_6H_4OCH_3$, C_6H_4F, C_6H_4Cl and R = $(CH_3)_2CH$, $CH_3CH_2CH_2$), by a new, simpler route is described. Titanium derivatives of a few of these ligands were also synthesized by their reactions with bis(cyclopentadienyl)titanium dichloride and titanium isoproxide, and were characterized by elemental analyses, i.r. and p.m.r. spectral studies and molecular weight determinations.

Introduction

It has been reported that unsaturated N-substituted β-aminothione can be prepared in rather low yields by nucleophilic reaction of primary amines with 1,2-dithiolium salts or of hydrogen sulphide ion with O-alkylated ketoamine salts [1–6]. In view of the availability of monothio-β-diketones [7], a simpler route of their reactions with primary amines was explored for the synthesis of β-aminothiones and found to yield these ligands in good yields. A perusal of the literature reveals that although few transition metal derivatives of similar type of ligands have been synthesized [8–12], no work has been carried out on the ligands of the present series. We also report in this paper the derivatives of β-aminothiones with titanium compounds.

Results and Discussion

The β-aminothiones synthesized during the course of the present investigation are coloured solids or viscous liquids which are soluble in common organic solvents. Molecular weight determinations in refluxing benzene show them to be monomeric (Table I).

In the i.r. spectra of these β-aminothiones, a broad band appearing at 3200 cm^{-1} and a weak band in the region 2550–2850 cm^{-1} may be assigned to ν(N–H) and ν(S–H) vibrations, respectively [9–12]. Presence of vibrations due to S–H groups in addition to the vibration of N–H groups indicate the existence of β-aminothiones in two tautomeric forms (Fig. 1). Strong bands in the region 1610–1580 cm^{-1} may be due to the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ vibrations [9]. Another sharp band in the region 1525–1505 cm^{-1} may be described as being due to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ vibrations [10, 13]. $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ vibrations due to the aromatic group also appear in this region (1590–1520) cm^{-1} [11]. A medium to strong intensity band appearing in the region 1285–1240 cm^{-1} is probably due to $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ vibrations [14].

The p.m.r. spectra of all the new β-aminothiones show some common resonance signals due to (i) N–H groups which appear at δ (11.76–10.76) ppm as a triplet or as a broad band [10], and (ii), to >CH– groups at 5.78–4.88 ppm as a singlet. γ-phenyl groups give two distinct multiplets in the region δ 7.00–7.66 and δ 7.43–7.03 ppm. In the ligands where R_α is also a phenyl group resonance signals of both the phenyl groups overlap with each other and appear as two multiplets only. Methyl groups

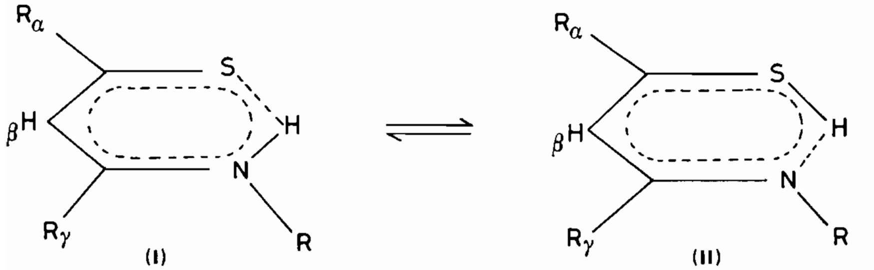

Fig. 1. R_α = C_6H_5, CH_3. R_γ = C_6H_5, $C_6H_4CH_3$, $C_6H_4OCH_3$, C_6H_4F, C_6H_4Cl. R = $(CH_3)_2CH$, $CH_3CH_2CH_2$.

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TABLE I. Analytical Data and Molecular Weight of β-Aminothiones.

β-Aminothione	M.P.°/B.P. °C[a] (% yield)	Nature	%N		%S		Molecular weight	
			Found	(calcd.)	Found	(calcd.)	Found	(calcd.)
$C_6H_5CSCH_2C(NP_r^i)C_6H_4CH_3$	102°	Orange yellow crystal	4.3	(4.7)	10.7	(10.9)	265	(295)
$CH_3CSCH_2C(NP_r^i)C_6H_5$	145–160°/1.5 mm (80)	Orange red liquid	6.2	(6.4)	14.5	(14.6)	233	(219)
$C_6H_5CSCH_2C(NP_r^i)C_6H_5$	175–180°/0.1 mm (80)	Dark red liquid	4.7	(4.8)	11.3	(11.4)	270	(281)
$CH_3CSCH_2C(NP_r^n)C_6H_4F$	148–150°/1.5 mm (65)	Orange red liquid	6.0	(5.9)	13.5	(13.7)	220	(237)
$CH_3CSCH_2C(NP_r^i)C_6H_4Cl$	145°/1 mm (60)	Orange red liquid	5.6	(5.5)	12.5	(12.7)	240	(253)
$CH_3CSCH_2C(NP_r^i)C_6H_4OCH_3$	70°(d) (70)	Orange crystal	5.4	(5.6)	13.0	(12.9)	257	(249)
$CH_3CSCH_2C(NP_r^i)C_6H_4CH_3$	160°/0.9 mm (60)	Orange yellow crystal	5.7	(6.0)	13.2	(13.7)	215	(233)

[a] d = decomposes.

give a single line in the region δ 2.04–1.96 ppm. In the spectra a doublet due to methyl groups of isoproxy group is present in the regions δ 1.22–1.16 and δ 1.25–1.23 and a heptet due to the methine proton appears in the region δ 3.75–3.67 ppm. The UV spectra of β-aminothiones in methanol exhibit two characteristics bands of high intensity in the region 250–245 nm and 355–335 nm, which can be associated with transitions of the β-aminothiones arising from SC=C–C=N and NC=C–C=S chromophores, respectively [14].

On the basis of the above studies we can confirm for the new ligands synthesized during the course of the present investigations that both β-aminothione form (I) and thiol form (II) are in equilibrium with a preponderance of the aminothione form, and the equilibrium shifts almost entirely to aminothione form (I) in chloroform solution.

The reactions of Cp_2TiCl_2 with β-aminothiones were carried out in different molar ratios in refluxing tetrahydrofuran solution using triethylamine (Et_3N) as hydrogen chloride acceptor. The $Et_3N\cdot HCl$ was filtered off and the progress of the reaction could be followed by estimating the $Et_3N\cdot HCl$ formed during the course of reaction:

$$(Cp)_2TiCl_2 + nCH_3CSCH_2C(NP_r^i)C_6H_5 + nET_3N \longrightarrow (Cp)_2Ti[CH_3CSCH{=}C(NP_r^i)C_6H_5]_n[Cl]_{2-n} + nEt_3N\cdot HCl$$

Where n = 1, 2, P_r^i = isopropyl.

The reactions of β-aminothiones with titanium isoproxide were also carried out in different molar ratios in refluxing benzene solutions. The isopropanol was fractioned off azeotropically with benzene and the progress of the reaction could be followed by estimating the isopropanol in the azeotrope by a simple oxidimetric procedure:

$$Ti(OP_r^i)_4 + nCH_3CSCH_2C(NP_r^i)C_6H_5 \longrightarrow [Ti[(CH_3CSCH{=}C(NP_r^i)C_6H_5]\,[OP_r^i]_{4-n} + nP_r^iOH$$

Where n = 1, 2.

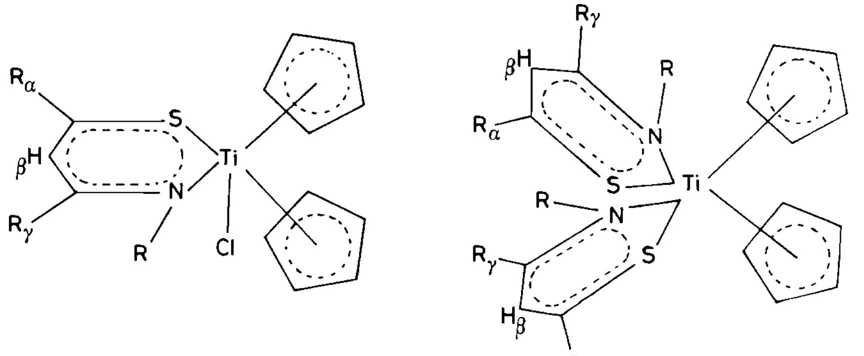

Fig. 2. $R_\alpha = C_6H_5, CH_3$. $R_\gamma = C_6H_5, C_6H_4CH_3, C_6H_4OCH_3, C_6H_4Cl$. $R = (CH_3)_2CH, CH_3CH_2CH_2$.

TABLE II. Analytical Data and Molecular Weight of Titanium Compounds of β-Aminothiones.[a]

Compound	Colour	M.P. (°C)	Molecular weight		% Ti		%N		%S	
			Found	(calcd)	Found	(calcd)	Found	(calcd)	Found	(calcd)
$Cp_2TiCl(CH_3CSCHNP_r^iC_6H_4\text{-}CH_3)$	Reddish brown	135	504	(446)	10.4	(10.7)	3.0	(3.1)	7.1	(7.2)
$Cp_2Ti(CH_3CSCHNP_r^iC_6H_4\text{-}CH_3)_2$	Reddish brown	160(d)	669	(644)	7.1	(7.5)	4.2	(4.4)	9.7	(10.0)
$Cp_2TiCl(C_6H_5CSCHCNP_r^iC_6H_4CH_3)$	Reddish brown	160(d)	570	(508)	9.4	(9.5)	2.5	(2.8)	6.1	(6.3)
$Cp_2Ti(C_6H_5CSCHCNP_r^iC_6H_4CH_3)_2$	Reddish brown	200(d)	802	(766)	6.1	(6.3)	3.4	(3.7)	8.1	(8.4)
$(OP_r^i)_3Ti(C_6H_5CSCHCNP_r^nC_6H_5)$	Yellowish green	120	565	(505)	9.3	(9.5)	2.7	(2.8)	5.9	(6.3)
$(OP_r^i)_2Ti(C_6H_5CSCHCNP_r^nC_6H_5)_2$	Yellowish green	145	742	(726)	6.4	(6.6)	3.7	(3.9)	8.6	(8.8)
$(OP_r^i)_3Ti(CH_3CSCHCNP_r^iC_6H_4CH_3)$	Yellowish green	132	520	(457)	10.2	(10.5)	2.8	(3.0)	6.8	(7.0)
$(OP_r^i)_2Ti(CH_3CSCHCN_r^{\Delta i}C_6H_4CH_3)_2$	Yellowish green	154	708	(630)	7.5	(7.6)	4.2	(4.4)	9.8	(10.2)

[a] d = decomposes, Cp = cyclopentadienyl.

The sticky coloured solids isolated from tetrahydrofurane or benzene solution could be crystallized by addition of hexane to their solution in benzene. These products have sharp melting points, except for $(Cp)_2TiCl[RCSCH{=}CR(NP_r^i)]$, but undergo decomposition on attempted distillation even under reduced pressure (Table II).

Molecular weights of these compounds in boiling benzene suggest them to be monomers. Their i.r. spectra show the disappearance of bands at 3200 cm^{-1} (band due to νN–H) and at 2850–2550 cm^{-1} (band due to ν(S–H). Both the bands at 1610–1580 and at 1525–1505 cm^{-1} due to $\nu C\overset{\cdots}{-}C$ and $\nu(C\overset{\cdots}{-}N)$ respectively are shifted slightly to the lower frequency side. However, the band at 1590–1520 cm^{-1} (assigned to aromatic $(C\overset{\cdots}{-}C)$) is observed at the same position in the metal derivatives as in the corresponding ligand.

The presence of bands in the regions 990–1010 cm^{-1} in the i.r. spectra of isopropoxy derivatives of titanium have been assigned to ν(Ti–O–C) bands of terminal isopropoxy groups [15, 16]. The Ti–O absorptions observed in the region 450–500 cm^{-1} are also in accordance with the previous report [17]. The bands in regions 550–590, 315–335 and 340–370 cm^{-1} have been assigned to νTi–N, νTi–S and νTi–Cl respectively [18, 19]. On the basis of the above studies it is assumed that monoderivatives of β-aminothiones with bis(cyclopentadienyl)titanium dichloride and titanium isopropoxide are pentacoordinate. However, bis products could be either *cis*- or *trans*-octahedron (Fig. 2).

Experimental

All reactions were carried out in glass apparatus with interchangeable joints. Extreme precautions were taken to exclude moisture throughout the experiments. Bis(cyclopentadienyl)titanium dichloride was used after recrystallization from toluene. Titanium isopropoxide was prepared by the reported method [20]. Monothio β-diketones were prepared by known methods [7]. Benzene was vigorously dried over sodium before use.

Infrared spectra of these newly synthesized compounds were recorded on a Perkin-Elmer 621 spectrophotometer in the range 4000–200 cm^{-1}. PMR spectra were recorded on a Perkin-Elmer spectrometer R-32, 90 MHz in $CDCl_3$ using TMS as internal standard. Molecular weights were obtained using a semi-micro Ebulliometer (Gallenkamp) fitted with a thermistor sensor.

Isopropanol in the azeotrope was estimated by an oxidation method [21]. Titanium was estimated as oxide, sulphur as sulphate, chlorine as chloride. Nitrogen was estimated by Kjeldahl's method.

Synthesis of β-Aminothiones

An exothermic reaction occurred when a primary amine (1 mol) (in little excess) at −10 °C was added slowly dropwise with constant stirring to the corresponding mono-thio-β-diketone (1 mol) dissolved in benzene, at about 0 °C. The reaction mixture was stirred for three hours below 0 °C, after which the volatile solvents were removed under vacuum. Coloured compounds were obtained in all cases and were purified either by distillation at reduced pressure or by crystallization from benzene–petroleum ether (40–60 °C) mixture. It has been observed that similar reactions at room temperature result in β-ketamines instead of β-aminothiones. Therefore, extra precautions were taken to maintain the temperature below 0 °C throughout the course of the reactions.

Reaction of $(C_5H_5)_2TiCl_2$ with β-Aminothiones

The reactions of β-aminothiones with $(C_5H_5)TiCl_2$ were carried out in 1:1 and 1:2 molar ratios using anhydrous tetrahydrofuran as solvent and triethylamine as hydrogen chloride acceptor. The reaction mixtures were refluxed for 6–12 hours, after which the $Et_3N{\cdot}HCl$ precipitated during the reaction was filtered off. The solvent was removed from the filtrate under reduced pressure. Pasty solids were obtained in each case which gave crystalline powders after recrystallization from n-hexane.

Reaction of $Ti(OP_r^i)_4$ with β-aminothione

To $Ti(OP_r^i)_4$ (1 mmol) was added a calculated amount of β-aminothiones (1 mol) and 70 ml of benzene. The reaction mixture was refluxed on a fractionating column and the isopropanol liberated during the reaction was fractioned out azeotropically. The isopropanol in the azeotrope was estimated to monitor the extent of the reaction. When the refluxing temperature became constant at 80 °C heating was stopped. Excess of solvent was removed under reduced pressure. Pure products were isolated after recrystallization from n-hexane. The reactions of 1:2, 1:3 and 1:4 molar ratios were carried out similarly but we were unable to prepare the compounds of type $(OP_r^i)TiL_3$ and TiL_4 (L = β-aminothione).

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