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Insertion of Aldehydes and Ketones into a Methyl–Titanium Bond. Synthesis and Reactivity of Alkenoxy Derivatives

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The selective insertion of carbonyl groups of aldehydes and ketones such as acetaldehyde or acetone, into the titanium–carbon bond of the methyl trialkoxy titanium $CH_3Ti(OR)_3$ *(with* $R = C_2H_5$, *i-*C_3H_7, *t-*C_4H_9*) produces mixed tetra-alkoxy titanium complexes. Alkenoxy derivatives are obtained in this way starting from olefinic aldehydes and ketones such as methyl vinyl ketone or acrolein. Alkenoxy derivatives are also obtained by more classical substitution reaction using vinylic alcohol. Their characterization by spectroscopical data and hydrolysis products as well as their reactivity towards* $AlMe_3$ *is also described.*

Introduction

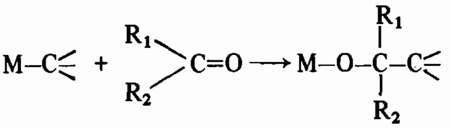
Reactions of unsaturated molecules on the metal–carbon bond of early transition metals are of interest because the primary step of Ziegler catalysis is considered to be insertion of the olefin into the titanium–carbon σ bond.

In this work, we reacted methyltrialkoxytitanium $CH_3Ti(OR)_3$ (with R = Et, i-Pr, t-Bu) with aldehydes and ketones and particularly with unsaturated ones (acrolein, methyl-vinyl ketone). In alkenoxy derivatives generated by this or other ways, the reactivity of the double bond was investigated. By reaction of $AlMe_3$, a σ bonded methyl group was introduced at the titanium center in an attempt to reproduce a model for the Ziegler polymerization process.

Results and Discussion

Insertion of Aldehydes and Ketones into the Titanium–Carbon σ Bond, a Route to Alkoxy and Alkenoxy Derivatives

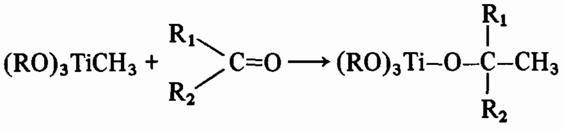
Insertion reactions involving a metal–carbon bond and the carbonyl group of a wide variety of reagents have been reviewed some years ago [1] and are summarized as:



$$\mathrm{M{-}C}\leqq + \begin{matrix}\mathrm{R_1}\\\mathrm{R_2}\end{matrix}\!\!>\mathrm{C{=}O} \longrightarrow \mathrm{M{-}O{-}}\overset{\mathrm{R_1}}{\underset{\mathrm{R_2}}{\mathrm{C}}}\mathrm{{-}C}\leqq$$

In fact, very little has been published concerning the action of aldehydes and ketones on alkyl derivatives of early transition metals: the formation of tert-butoxy was obtained from methyl-niobium by action of acetone [2] while from phenyl-zirconium, the carbinol Me_2PhCOH was characterized after hydrolysis [3].

In this work, reactions of acetone, acetaldehyde, methyl-vinyl ketone and acrolein on methyl trialkoxy titanium were studied. Using stoichiometric amounts, alkoxy ($R_1 = CH_3$) or alkenoxy (R_1 = vinyl) groups were generated in clean processes described by the general scheme:



$$\mathrm{(RO)_3TiCH_3} + \begin{matrix}\mathrm{R_1}\\\mathrm{R_2}\end{matrix}\!\!>\mathrm{C{=}O} \longrightarrow \mathrm{(RO)_3Ti{-}O{-}}\overset{\mathrm{R_1}}{\underset{\mathrm{R_2}}{\mathrm{C}}}\mathrm{{-}CH_3}$$

with R = Et, i-Pr, t-Bu
R_1 = Me, vinyl
R_2 = H, Me

IR spectra showed the disappearance of the carbonyl absorption near 1700 cm^{-1} (and the persistence of the olefin stretching frequency near 1620 cm^{-1} in the case of vinylic compounds). In ^1H n.m.r. spectra, disappearance of the methyl–titanium group ($\delta \simeq 0.57$ ppm) and appearance of the expected alkoxy or alkenoxy group were observed. Hydrolysis products were characterized chromatographically (see Table I).

Other Routes to Alkenoxy Derivatives

Among other possible routes, total transesterification of $Ti(Oi\text{-}Pr)_4$ by cinnamyl alcohol was used by Mehrotra to prepare tetracinnamoxides of titanium [4] while Clark obtained but-3-en-1oxy derivatives

TABLE I. Reaction Products.

Reactants	$CH_3Ti(OR)_3$	Insertion products	Hydrolysis products
Acetone	R = i-Pr	$(i\text{-}PrO)_3Ti(Ot\text{-}Bu)$	i-PrOH + t-BuOH
	R = Et	$(EtO)_3Ti(Ot\text{-}Bu)$	EtOH + t-BuOH
Acetaldehyde	R = i-Pr	$Ti(Oi\text{-}Pr)_4$	i-PrOH
	R = Et	$(EtO)_3Ti(Oi\text{-}Pr)$	EtOH + i-PrOH
Acrolein	R = i-Pr	$(i\text{-}PrO)_3Ti[OCH(CH_3)CH{=}CH_2]$	i-PrOH + But-3-en-2-ol
Methyl vinyl ketone	R = i-Pr	$(i\text{-}PrO)_3Ti[OC(CH_3)_2CH{=}CH_2]$	i-PrOH + 3Me-But-1-en-3-ol

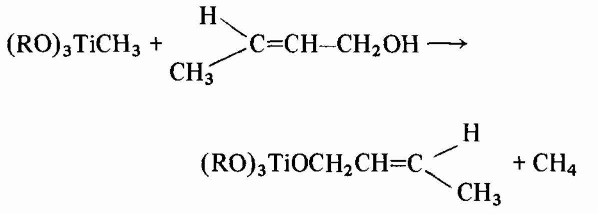
TABLE II. ^1H n.m.r. and I.R. Data.[a]

Compounds	CH=CH–CHO α β γ					
	δ_α	δ_β	δ_γ	δ_{CH_3}	$\nu_{C=O}$	$\nu_{C=C}$
$CH_2{=}CHCHO$	6.27(m)		9.54(m)		1690	1615
$(i\text{-}PrO)_3Ti[OCH(CH_3)CH{=}CH_2]$	5.06–5.32(m)	5.83(m)		1.26(d)		1630
$CH_2{=}CHCH(CH_3)OH$	5.07–5.25(m)	5.88(m)	4.10(m)	1.19(d)		1640
$CH_2{=}CHC(CH_3)O$[b]	5.54(m)	6.20(m)		1.96(s)	1690	1620
$(i\text{-}PrO)_3Ti[OC(CH_3)_2CH{=}CH_2]$[b]	5.02–5.32(m)	6.00(m)		1.36(s)		1640
$CH_2{=}CHC(CH_3)_2OH$[c]	4.98–5.17(m)	6.00(m)		1.32(s)		1640
$(t\text{-}BuO)_3Ti[OCH_2CH{=}CHCH_3]$	5.58(m)		4.65(m)	1.67(d)		1670
$CH_3CH{=}CHCH_2OH$	5.68(m)		4.08(m)	1.71(d)		1670
$Ti(OCH_2CH{=}CHC_6H_5)_4$[d]	6.25–6.83(m)		4.23–4.58(m)			1650
$Cl_3Ti(OCH_2CH_2CH{=}CH_2)$[e]	5.26(m)	5.87(m)	4.86(m)			1638

[a] δ in ppm downfield from internal Me_4Si, in CCl_4 as solvent except where stated otherwise. m = multiplet, s = singlet, d = doublet; ν in cm^{-1}. [b] In C_6H_6 as solvent. [c] In $CDCl_3$ as solvent [6]. [d] Ref. [4]. [e] Ref. [5].

by metathesis reacting alkenoxy lithium on the titanium–chlorine bond [5].

In this work, we obtained mixed alkenoxy-trialkoxy derivatives by a clean substitution reaction using for example crotyl alcohol and $CH_3Ti(OR)_3$ as starting materials according to the scheme:



$$(RO)_3TiCH_3 + \overset{H}{\underset{CH_3}{>}}C{=}CH{-}CH_2OH \longrightarrow (RO)_3TiOCH_2CH{=}C\overset{H}{\underset{CH_3}{<}} + CH_4$$

The reaction is followed by measuring the volume of methane evolved (CH_4:Ti = 1) and by the disappearance of the Ti-CH_3 peak in the ^1H n.m.r. spectrum.

Spectroscopic Data

^1H n.m.r. (δ) and I.R. data of the alkenoxy compounds are listed in Table II and compared to corresponding unsaturated aldehydes or ketones, alkenols and literature related complexes.

Deshielding of the olefinic protons (especially β protons) and decrease in the C=C stretching frequency have often been taken as criteria of the strength of the metal–olefin π bond [5].

Data collected in Table II are consistent with neglibible olefin titanium interaction in trialkoxy alkenoxy compounds as well as in tetraalkenoxy [4] and trichloroalkenoxy ones [5].

Reactivity towards $Al(CH_3)_3$

Thompson reported a few years ago that ethylation of alkenol may be obtained by reaction of diethyl-aluminium chloride on an alkenoxy titanium compound. The reaction is supposed to proceed via alkylation at the titanium center of the alkenoxy species followed by double bond activation and subsequent titanium-alkyl addition to the olefinic linkage [7]. In a previous paper, we reported on the reaction of various alkoxy titanium compounds with $AlMe_3$ in stoichiometric amounts resulting in monomethylation of titanium and formation of bimetallic complexes bridged by alkoxy groups [8].

In this work, the reactivity of alkenoxy titanium species on $AlMe_3$ was investigated. Following the preceding results and proposed mechanism, it was reasonable to expect that methylation would occur at titanium and result in activation of the double bond of the alkenoxy group to finally afford methyl addition to the olefinic linkage.

In fact, monomethylation of titanium was obtained once more and characterized by ^1H n.m.r. data (δ = 0.52 ppm for Ti-CH_3) and a bimetallic [Ti, Al] complex was identified by cryoscopic measurements and analytical data as $[CH_3Ti(OR)_2(OR'), Al(OR)(CH_3)_2]$ where R = tBu and R' = crotyl for example. So the crotyl group may be kept on titanium together with a methyl group without being methylated. This is in agreement with the possibility to prepare a stable butenoxy-methyl bis cyclopentadienyl titanium $Cp_2TiMe(OCH_2CH_2CH{=}CH_2)$ reported by Clark [5].

So the mechanism proposed to explain the reaction of alkylation of alkenols by action of ethylaluminium on alkenoxytitanium does not hold when methyl aluminium is used as alkylating agent. It may be suggested that reducing, non β elimination stabilized radicals must necessarily be used, so that a hydride active species may be generated.

Experimental

General Remarks

All reactions were carried out under dry argon using dry degassed solvents. $CH_3Ti(OR)_3$ were prepared by published procedures [9], ketones and aldehydes were dried and freshly distilled before use. IR spectra were recorded on a Perkin Elmer 225 spectrophotometer between KBr plates and ^1H n.m.r. spectra run on a Perkin Elmer R 12 at 60 MHz. Gas chromatographic analyses were performed with a Varian 705 chromatograph using 1/8 in × 10 ft column containing Porapak Q (N_2 as carrier gas). Reponse factors were compared with authentic alkenols and alcohols.

Synthesis of $(i\text{-}PrO)_3Ti(OtBu)$

Acetone (0.48 g; 6 mmol) was added dropwise to 1.5 g (6 mmol) of neat $CH_3Ti(Oi\text{-}Pr)_3$ at −15 °C. The mixture was stirred two hours at room temperature. The complex was characterized by IR and ^1H n.m.r. spectroscopy. All the other mixed alkoxy complexes were prepared and characterized in a similar way.

Synthesis of $(i\text{-}PrO)_3Ti[OC(CH_3)_2CH{=}CH_2]$

Methyl vinyl ketone (4.6 mmol; 0.32 g) was added dropwise to 4.6 mmol (1.10 g) of neat $CH_3Ti(Oi\text{-}Pr)_3$ at −15 °C. The mixture was stirred for 18 hours at room temperature. The complex was obtained as a yellow liquid in quantitative yield and characterized by spectroscopy (Table II) and analytical data.

Synthesis of $(i\text{-}PrO)_3Ti[OCH(CH_3)CH{=}CH_2]$

Acrolein (4.7 mmol; 0.26 g) was added to neat $CH_3Ti(Oi\text{-}Pr)_3$ (4.7 mmol; 1.12 g) according to the same procedure.

Hydrolysis Procedure

An excess of water (3 ml) was added to a solution of complex in 5 ml ether to obtain a white precipitate. The mixture was stirred for 0.5 hour, filtered and the ethereal phase was then extracted and chromatographied.

Synthesis of $(t\text{-}BuO)_3Ti(OCH_2CH{=}CHCH_3)$

$CH_3Ti(Ot\text{-}Bu)_3$ (3.00 g; 10 mmol) was stirred at 0 °C without any solvent and neat crotyl alcohol (0.76 g; 10 mmol) was added dropwise. The amount of methane evolved was volumetrically measured (260 ml; expected: 253 ml) and characterized by IR. The complex was obtained as a yellow liquid and characterized by spectroscopy (Table II).

Action of $Al(CH_3)_3$

A solution of $(t\text{-}BuO)_3Ti(OCH_2CH{=}CHCH_3)$ (2.49 g; 7.3 mmol) in 15 ml toluene was stirred at −30 °C and neat $Al(CH_3)_3$ was added slowly. Stirring was continued for 3 hours at room temperature and the mixture became orange then red. The complex is characterized by ^1H n.m.r. spectrum: δ (in ppm): 5.58 (2H, multiplet, HC=CH) 4.38–3.96 (2H, multiplet, CH_2) 1.25 (9 H, singlet, t-Bu) 0.52 (3H, singlet CH_3-Ti) −0.79 (6 H, singlet, CH_3Al). Molecular weight was determined in degassed C_6H_6 on the red liquid obtained by removing toluene. M (found: 404; calcd for monomer: 410).

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