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TRANSITION METAL PROMOTED ALKYLATIONS OF UNSATURATED ALCOHOLS: THE ETHYLATION OF ALKYNOLS VIA THE REACTION OF *cis*-ALKYNOXY(CHLORO)BIS(2,4-PENTANEDIONATO)TITANIUM(IV) COMPLEXES WITH DIETHYLALUMINUM CHLORIDE

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Summary

Complexes of the type [$TiCl(OR)(C_5H_7O_2)_2$] have been synthesized where R = 2-propyn-1-yl, 2-butyn-1-yl, 4-pentyn-1-yl, 5-hexyn-1-yl, 3-pentyn-1-yl, 4-pentyn-2-yl, and 4-phenyl-3-butyn-1-yl, and $C_5H_7O_2$ = 2,4-pentanedionate ligand. NMR studies establish the complexes as being neutral and monomeric and adopting the *cis* configuration. The complexes were used for the indirect hydroalkylation of the alkynols using diethylaluminum chloride and triethylaluminum. Moderate yields of ethylated products were obtained with diethylaluminum chloride under mild conditions for alkynols having the unsaturation in γ and δ positions. *Cis* addition of the organoaluminum reagent was observed.

Introduction

Within the last decade several studies have been reported on the synthesis and characterization of hexacoordinate [$TiX_2(C_5H_7O_2)_2$] complexes, where X represents a uninegative monodentate ligand and $C_5H_7O_2$ represents an oxygen-chelated 2,4-pentanedionate group. Dihalo- [1] and dialkoxy-bis(2,4-pentanedionato) [2] complexes have been studied particularly thoroughly. As part of our interest in the coordination chemistry of titanium(IV), we reported [3] recently on the preparation of several mixed chloro(alkoxy)bis(2,4-pentanedionato)titanium(IV) complexes. Alkoxy groups included methoxy, ethoxy, propoxy, 2-propoxy, and 2-propen-1-oxy. Characterization studies demonstrated that the complexes are neutral and monomeric, and adopt the *cis* configuration in solution. Subsequently, we observed that the chloro(alkoxy)bis(2,4-pentanedionato)titanium(IV) complexes, when combined with diethylaluminum chloride in methylene chloride or toluene, catalyzed the polymerization of ethylene

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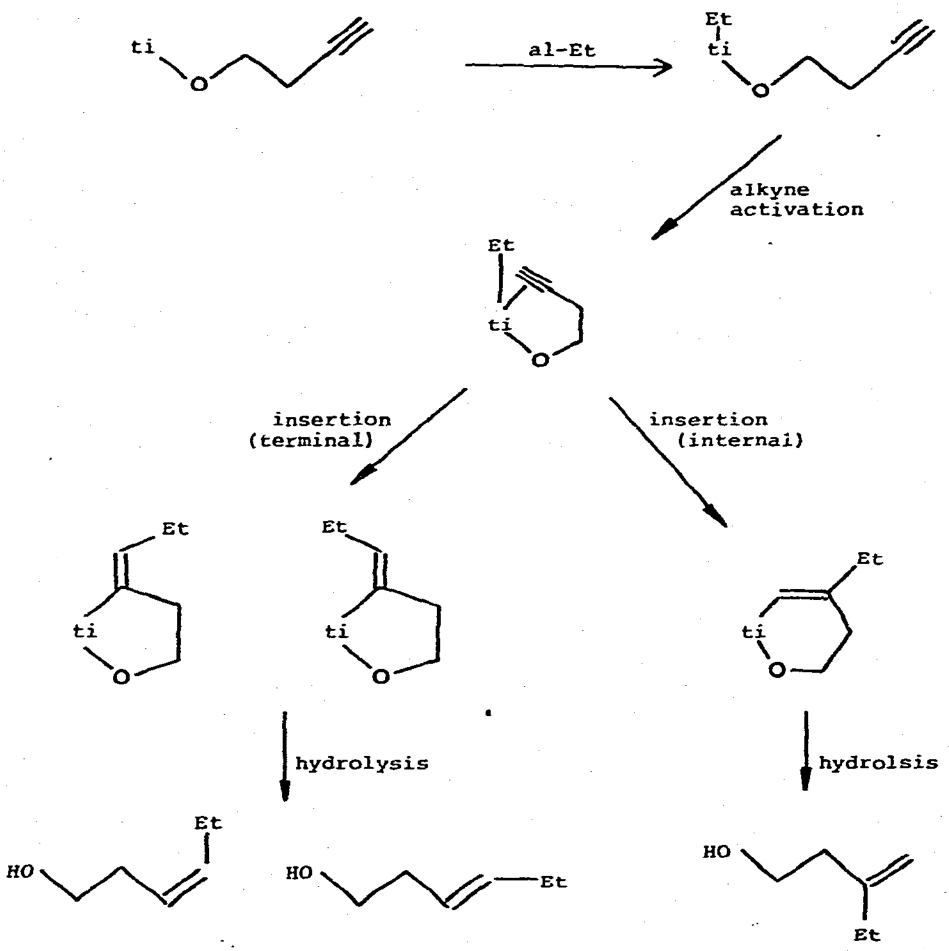

Fig. 1. Hypothetical reaction schemes for the ethylation of 3-butyn-1-ol via the reaction of a (3-butyn-1-oxy)titanium complex with an ethylaluminum compound.

under conditions of low temperature and pressure *. This observed Ziegler-type catalytic activity of the chloro(alkoxy) complexes suggested that a new synthetic procedure for the facile alkylation of unsaturated alcohols via reaction of $[TiCl(OR)(C_5H_7O_2)_2]$, R representing an unsaturated hydrocarbyl group (alkenyl or alkynyl), with alkylaluminum reagents might be developed.

The observation that the $[TiCl(OR)(C_5H_7O_2)_2]$ complexes can be used in Ziegler systems to polymerize ethylene, and knowledge of the generally accepted Ziegler mechanism [5,6—8] led us to hypothesize that a chloro(alkynoxy or alkenoxy)bis(2,4-pentanedionato)titanium(IV) complexes, upon addition of an

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* Ethylene polymerized with a $Ti(CH_3O)Cl(C_5H_7O_2)_2/Al(C_2H_5)_2Cl$ catalyst system in toluene gave a polyethylene with a viscosity average molecular weight of 1.8×10^5 g/mol, a density of 0.94 g/cm^3 (quenched), and 2.2 CH_3 groups per 1000 C atoms. These data indicate a linear Ziegler-type polyethylene [4].

organoaluminum reagent, would be alkylated via ligand exchange to give an (alkynoxy or alkenoxy)alkyltitanium species. Intramolecular activation of the unsaturated linkage could then occur at titanium with subsequent insertion into the alkyl—titanium bond, i.e., a carbotitanation of the multiple bond. Hydrolysis would then yield the satuarated hydroalkylated alcohol in the case of alkenols or the hydroalkylated olefinic alcohol for alkynols. For example, since alkynols are the subject of this paper, were an ethylaluminum species utilized with the 3-butyn-1-oxy-titanium complex the possible products include *cis*- and *trans*-3-hexen-1-ol and 3-ethyl-3-buten-1-ol as illustrated in Fig. 1 *.

Indeed, we have reported [9] preliminary observations that 3-butyn-1-ol plus several other alkynols can be ethylated by allowing the appropriate $[TiCl(OR)(C_5H_7O_2)_2]$ complexes to react with diethylaluminum chloride. In this paper we wish to report full details of studies on the chemistry involved in the ethylation of alkynols as $[TiCl(OR)(C_5H_7O_2)_2]$ complexes.

Experimental

Materials

2-Propyn-1-ol (Eastman) was redistilled and stored over Linde 3-A Molecular Sieves prior to use. The remaining alkynols were obtained from Farchan Research Laboratories and were used without further purification except for storage over 3-A sieves. Diethylaluminum chloride and triethylaluminum were obtained as the neat liquids from Ethyl Corporation and utilized without further purification. Standard methylene chloride solutions (ca. 2 *M*) of the organoaluminum reagents were prepared for use in the alkylation reactions. All reaction solvents were redistilled under nitrogen over an appropriate drying agent (calcium hydride for hydrocarbons and phosphorous pentoxide for methylene chloride) and stored under an inert gas (argon or nitrogen). Dichlorobis(2,4-pentanedionato)-titanium(IV) was prepared according to the procedure of Fay and Lowry ** [10]. Pyridine was distilled from barium oxide and stored over 4-A sieves. Air sensitive liquids and solutions were transferred using syringe and glovebox techniques.

Preparation of chloro(alkynoxy)bis(2,4-pentanedionato)titanium(IV) complexes

All complexes were prepared by the following general procedure and characterized by temperature dependent NMR measurements. All manipulations and reactions were carried out under a dry nitrogen atmosphere *** [11]. An alkynol (100 mmol) and pyridine (100 mmol) were dissolved in 15 ml of benzene and added dropwise to a benzene slurry (ca. 60 ml) of dichlorobis(2,4-pentanedionato)titanium (100 mmol) at 0°C. The mixture was stirred for 3 h at 0°C and 2 h at room temperature. During this time the solution gradually changes color from orange to yellow, and pyridinium chloride forms as a white solid. Pyridinium chloride was filtered from the solution and washed with benzene until white.

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* Since the exact structures of most Ziegler catalyst systems are still somewhat uncertain, we have chosen to designate only the essential features of the chemistry germane to the alkylation reactions reported herein.

** This compound is available commercially from Ventron Corporation, Alfa Products, Danvers, Massachusetts 01923.

*** Kontes Glass Company, Vineland, N.J., "Airless-Ware".

Benzene was removed from the filtrate under vacuum at room temperature. The 2-propyn-1-oxy and 3-butyn-1-oxy complexes yielded solids at this point; however, all of the longer chain alkynols gave only viscous oils. The reactions are essentially quantitative. NMR characterization data for the complexes is reported in Table 1.

For use in alkylation reactions stock solutions of the complexes in methylene chloride were prepared and transferred as needed using syringe techniques.

General procedure for the alkylation of alkynoxy(chloro)bis(2,4-pentanedionato)titanium(IV) complexes with diethylaluminum chloride

A 250-ml three-necked round-bottomed flask was equipped with a 50-ml dropping funnel, a condenser fitted with a gas inlet stopcock, and a magnetic stirring bar. The dropping funnel and the remaining neck of the flask were fitted with rubber septa to allow transfer of materials with syringes. The apparatus was flame-dried under a brisk flow of argon. All subsequent operations were carried out under an argon atmosphere.

Methylene chloride solutions (ca. 0.7 *M*) of the alkynoxy complexes were prepared. An aliquot of solution (15 to 20 mmol of complex) plus an additional 50 ml of methylene chloride were transferred to the reaction flask via syringes. An appropriate volume of ca. 2 *M* diethylaluminum chloride was transferred to the dropping funnel containing an additional 25 ml of methylene chloride. The complex was then cooled to the reaction temperature, after which the diethylaluminum chloride solution was added dropwise over a period of 20—30 min. The reaction was terminated by the addition of 5—8 ml of methanol followed by 10—15 ml of water. The resulting mixture was then washed into a 500-ml conical flask with a small volume of water followed by 75 ml of 6 *N* sodium hydroxide and stirred under an atmosphere of oxygen until colorless (30—60 min). Solid material was filtered through a bed of Celite and washed with water and diethyl ether. The filtrate was saturated with sodium chloride. The organic layer was separated and the aqueous layer extracted with 5 50-ml portions of diethyl ether. The combined organic layers were dried over anhydrous magnesi-

TABLE 1

NMR DATA FOR CHLORO(ALKYNOXY)BIS(2,4-PENTANEDIONATO)TITANIUM(IV) COMPLEXES[a]

$TiCl(OR)(C_5H_7O_2)_2$ Complexes	CH_3	—CH=	$—OCH_2—$[b]
R = 2-propyn-1-yl	—2.07	—5.75	—5.23
R = 3-butyn-1-yl	—2.02	—5.68	—4.67
R = 4-pentyn-1-yl	—2.07	—5.71	—4.67
R = 5-hexyn-1-yl	—2.04	—5.79	—4.72
R = 3-pentyn-1-yl	—2.05	—5.69	—4.66
R = 4-pentyn-2-yl	—2.03	—5.69	—4.94[c]
R = 4-phenyl-3-butyn-1-yl	—1.98	—5.71	—4.81
R = hex-1-yl	—2.05	—5.68	—4.66
cis-$TiCl_2(C_5H_7O_2)_2$[d]	—2.17	—6.00	—
cis-$Ti(OC_2H_5)_2(C_5H_7O_2)_2$[d]	—1.99	—5.54	—
cis-$TiCl(OC_2H_5)(C_5H_7O_2)_2$[e]	—2.07	—5.70	—

[a] Chemical shifts at 35°C in $CDCl_3$ with TMS as an internal standard. Concentrations are ca. 0.2 *M*. [b] Chemical shift value is for the center of the multiplet. [c] Chemical shift for O—CH multiplet center. [d] Ref. 13. [e] Ref. 3.

um sulfate and reduced to a volume appropriate for GLC analysis.

Products of the ethylation were isolated by preparative GLC and characterized by NMR and IR measurements. IR measurements were particularly useful in establishing the substitution about the double bond [12]. Ethylation products isolated and reaction data are presented in Table 2.

Gas chromatographic analysis

Reaction mixtures were analyzed qualitatively with a Hewlett—Packard 5750 Research Chromatograph using 1/8 in 8 ft 5% Carbowax 20M and XE-60 columns. The carbowax column gives satisfactory separation of all product alcohols for qualitative work. However, since single ethylation products were observed, the XE-60 column was used for quantitative work because it gives excellent separation between starting alkynol and product. Analytical data for work involving the ethylation of 3-butyn-1-ol and 4-phenyl-3-butyn-1-ol were obtained by the internal standard technique using 1-heptanol and 1-decanol, respectively. Response factors were determined for each species. For products where authentic samples were not available, response factors were approximated using a saturated alcohol having the same number of carbon atoms. This procedure should give a yield less than actual since we have found for C_4 and C_6 alcohols that the response factors for the saturated alcohols were less than those for the unsaturated congeners. Products were isolated for spectral analysis by preparative GLC using a 1/4 in 6 ft SE-30 column.

TABLE 2

REACTIONS OF *cis*-CHLORO(ALKYNOXY)BIS(2,4-PENTANEDIONATO)TITANIUM(IV) COMPLEXES WITH DIETHYLALUMINUM CHLORIDE

Alkynol as $[TiCl(OR)(C_5H_7O_2)_2]$	Temperature (°C)	Product yield (%)	Starting alkynol recovered (%)	Molar ratio Al : Ti	Reaction time (h)
3-Butyn-1-ol	0	*trans*-3-Hexen-1-ol 28	2	2 : 1	4
	−46	*trans*-3-Hexen-1-ol 30	<2	2 : 1	4
	−78	*trans*-3-Hexen-1-ol 41	31	2 : 1	4
	−78	*trans*-3-Hexen-1-ol 19.5	59.5	2 : 1	0.25
	−78	*trans*-3-Hexen-1-ol 41	31	2 : 1	4
	−78	*trans*-3-Hexen-1-ol 56	24	2 : 1	8
	−78	*trans*-3-Hexen-1-ol 49	30	2 : 1	10
	−78	*trans*-3-Hexen-1-ol 50	18.5	2 : 1	12
	−78	*trans*-3-Hexen-1-ol 3	75	1 : 1	4
	−78	*trans*-3-Hexen-1-ol 41	31	2 : 1	4
	−78	*trans*-3-Hexen-1-ol 48	42	3.5 : 1	4
	−78	*trans*-3-Hexen-1-ol 41	32	3.5 : 1	9
2-Propyn-1-ol	−78	[a]	13	2 : 1	8
3-Butyn-1-ol	−78	*trans*-3-Hexen-1-ol 56	24	2 : 1	8
4-Phenyl-3-butyn-1-ol	−78	4-Phenyl-3-hexen-1-ol 50	50	2 : 1	8
3-Pentyn-1-ol	−78	4-Methyl-3-hexen-1-ol 44	21	2 : 1	8
4-Pentyn-1-ol	−78	*trans*-4-Hepten-1-ol 21	76	2 : 1	8
4-Pentyn-2-ol	−78	*trans*-4-Hepten-2-ol 36	20		
5-Hexyn-1-ol	−78	Negligible	96	2 : 1	8

[a] Very small peak in the C_5 region noted in the chromatogram; it was not analyzed.

Spectral analysis

Proton NMR spectra were run on a Perkin—Elmer R-20B spectrometer. Perkin—Elmer infrared spectrometers (Models 457 and 337) were used to obtain IR data.

Results and discussion

Alcoholato(chloro)bis(2,4-pentanedionato)titanium(IV) complexes

The title complexes are prepared virtually quantitatively by the following reaction:

$$[TiCl_2(C_5H_7O_2)_2] + ROH + C_5H_5N \xrightarrow{C_6H_6} [TiCl(OR)(C_5H_7O_2)_2] + (C_5H_6N)Cl$$

In benzene the alkoxy complexes remain in solution while pyridinium chloride is insoluble and easily removed. The lower alcohols give isolable solid complexes, while the higher alcohols generally yield viscous oils. All complexes used in this work were characterized by NMR. If the title complexes follow the structural pattern of other known $[TiXX'(C_5H_2O_2)_2]$ complexes and adopt the *cis* configuration, they should exhibit four methyl and two methine proton NMR peaks in the 2,4-pentanedionate region if exchange is slow. Furthermore, the chemical shift of the methine protons should reflect the mixed ligand coordination and differ significantly [3] from the shifts observed for the dichloro complex (—6.00 ppm $CDCl_3$) [13] and the dialkoxy complexes (ca. —5.5 ppm) [1a].

Figure 2 shows low temperature NMR spectra of the 2,4-pentanedionate and $—OCH_2—$ regions for the 2-propyn-1-oxy-, 3-butyn-1-oxy-, and (4-phenyl-3-butyn-1-oxy)chlorobis(2,4-pentanedionato)titanium(IV) complexes used in the alkylation studies. The first two complexes exhibit two methine proton peaks of similar intensity and methyl proton peaks with an intensity ratio of approximately 2 : 1 : 1. Thus in these cases the starting alkynol did undergo reaction with $TiCl_2(C_5H_7O_2)_2$ to give the mixed chloroalcoholato complex having the *cis* configuration. The overlapping of two of the four methyl proton peaks has been observed for several of the complexes reported earlier [3]. For the 4-phenyl-3-butyn-1-oxy complex all four methyl groups are resolved with an approximate intensity ratio of 1 : 1 : 1 : 1 although the methine proton peak, while broadened, remains unsplit probably due to a small separation between the symmetry non-equivalent sites. The observation of four methyl group resonances has only been observed for the chloromethoxy [3] and fluoroethoxy [13] complexes. All remaining complexes reported herein had spectra in the 2,4-pentanedionate regions virtually identical to the first two discussed above.

Table 1 presents partial chemical shift data at 35°C for the title complexes. In general, for varying alkynoxy groups the 2,4-pentanedionate resonance lie in the same region which is between the corresponding group shifts for *cis*-$TiCl_2(C_5H_7O_2)_2$ and *cis*-$Ti(OR)_2(C_5H_7O_2)_2$ complexes.

For the complexes *cis*-$TiCl_2(C_5H_7O_2)_2$, *cis*-$TiCl(OC_2H_5)(C_5H_7O_2)_2$, and *cis*-$Ti(OC_2H_5)_2(C_5H_7O_2)_2$, a plot (Fig. 3) of the 2,4-pentanedionate methyl and methine resonances versus the average σ_I for the monodentate ligands suggests that the resonance positions are governed to a large degree by inductive effects. For complexes of the type $SnXX'(C_5H_7O_2)_2$, X,X' = alkyl, aryl, and halogen, good correlation of the methine chemical shift with an averaged σ_I for the X and X' ligands was observed [14].

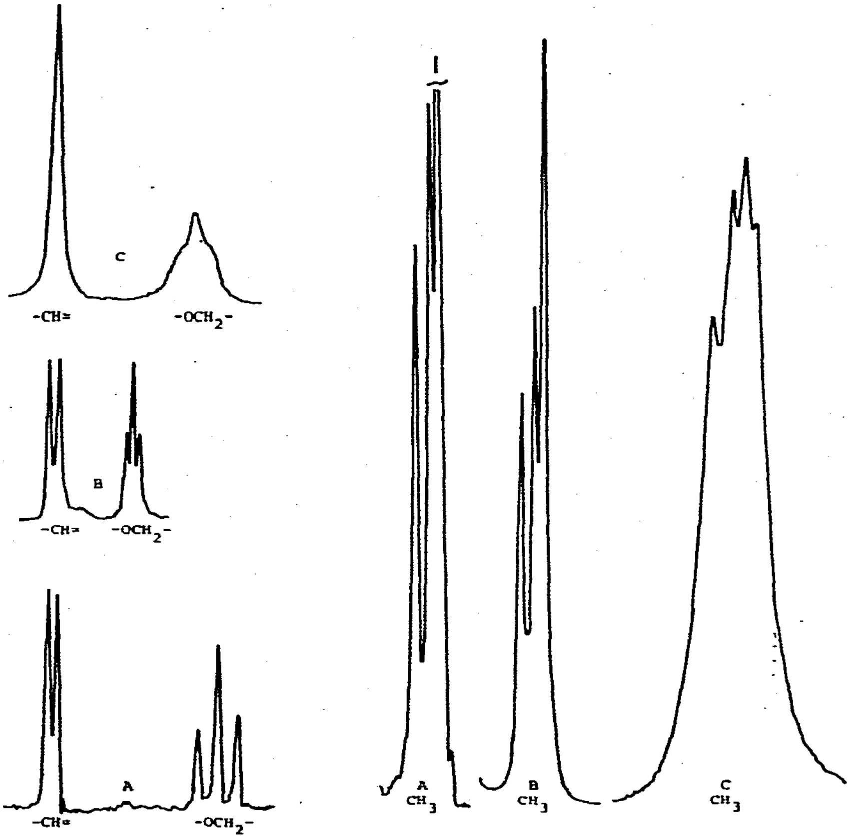

Fig. 2. Temperature dependent NMR spectra in the 2,4-pentanedionate region for the 3-butyn-1-oxy- (A), 2-propyn-1-oxy- (B), and (4-phenyl-3-butyn-1-oxy)chlorobis(2,4-pentanedionato)-titanium(IV) (C) complexes. (T ~ −35°C).

In summary, NMR data indicate clearly that the [TiCl(OR)($C_5H_7O_2$)$_2$] complexes are formed and that they adopt the *cis* configuration.

Alkynol alkylation reactions

Results of the reactions of chloro(alkynoxy)bis(2,4-pentanedionato)titanium-(IV) complexes with diethylaluminum chloride are presented in Table 2. In order to optimize the alkylation procedure a variety of experimental conditions were investigated for the 3-butyn-1-ol system. The remaining alkynols were then examined at the optimal conditions for the 3-butyn-1-ol system.

The chloro(3-butyn-1-oxy)bis(2,4-pentanedionato)titanium(IV)/diethylaluminum chloride system was investigated in methylene chloride with respect to temperature, time, titanium—aluminum alcohol stoichiometry, and order of reagent addition. For all reactions only *trans*-3-hexen-1-ol was observed as the product. The most productive set of conditions studied were found to be reaction for 8 h at a 2 : 1 diethylaluminum chloride to complex ratio at −78°C. Un-

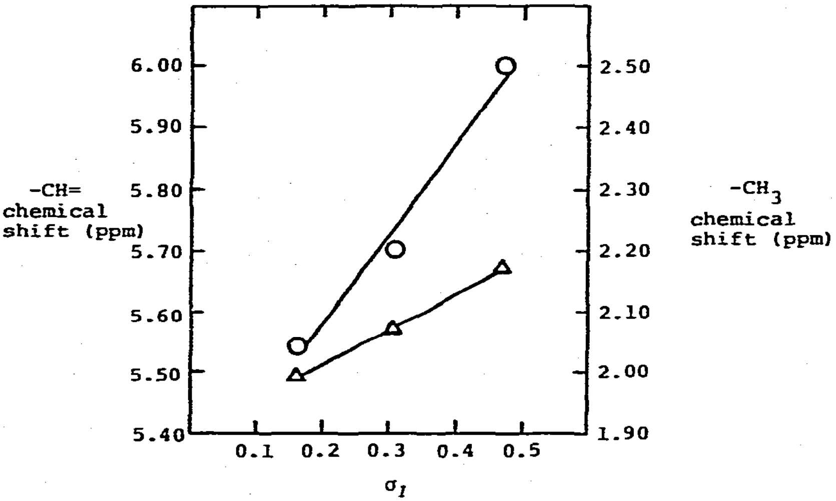

Fig. 3. Plot of the methyl and methine chemical shifts versus the average σ_I for monodentate ligands in the complexes $TiCl_2(C_5H_7O_2)_2$, $TiCl(OC_2H_5)(C_5H_7O_2)_2$, and $Ti(OC_2H_5)_2(C_5H_7O_2)_2$.

der these conditions a yield of 56% of a single hydroalkylated product, *trans*-3-hexen-1-ol was obtained with 24% of the starting material recovered. Considering the solubility of 3-butyn-1-ol in an aqueous medium, the mechanical steps required to isolate the products, and the cleanness of the chromatograms, the percent conversion to product is substantial. Carrying out the reactions at higher temperatures not only gave lower yields of alkylated products but led to a greatly reduced recovery of starting material which fact may be related to the thermal instability of many organotitanium species at higher temperatures. A 2 : 1 stoichiometry appeared optimal. Varying the order of addition of reagent did not lead to any significant differences in yield. The reactions surveyed in this work were run adding the titanium complex to diethylaluminum chloride. An attempt was made to allow the alkynol to react first with a solution of diethylaluminum chloride to give $[Al_2(C_2H_5)_3Cl_2(OR)]$ which was then added to *cis*-dichlorobis-(2,4-pentanedionato)titanium(IV). Synthetically this procedure would be more convenient than having to prepare the alkynoxytitanium complex. Through ligand exchanges we thought that this system might be similar to the previous ones. However, no alkylated products were observed. Finally, reaction of triethylaluminum with the 3-butyn-1-oxy complex at —78°C for 4 h with Al/Ti ratios of 2 : 1 and 3.5 : 1 gave yields of only 9 and 16%, respectively.

The remaining alkynols were treated at the 2 : 1 Al/Ti stoichiometry at —78°C for 8 h. The 2-propyn-1-oxy and 5-hexyn-1-oxy complexes did not react to give isolable amounts of products. However, the remaining complexes did react to give moderate percent conversions and yields of the hydroalkylated products. In all cases alkylation occurred at the terminal carbon; and for the terminal alkynoxy groups only *trans* isomers were produced. For the 3-pentyn-1-oxy and 4-phenyl-3-butyn-1-oxy groups the configuration about the double bond in the products was not determined but presumably it reflects *cis* addition of the M—R group.

Details of the alkylation mechanism have not yet been fully investigated. While an intramolecular pathway such as that illustrated in Fig. 1 is attractive, additional studies will have to be done before definite conclusions can be drawn.

There has been some recent interest in the addition of organometallic reagents to the unsaturation of alkynols. Normant, Alexakis, and Villieras [15] studied the addition under mild conditions of butylcopper to lithium and sodium salts of 2-propyn-1-ol, 1-methyl-2-propyn-1-ol, and 1,1-dimethyl-2-propyn-1-ol with maximum yields of alkylated products being 74, 56, and 46%, respectively. In all cases only *cis* addition products were observed although mixtures of both internally and terminally alkylated products were found. Eisch and Merkley [16] studied preliminarily the addition allylmagnesium bromide to 1-(1-propynyl)-cyclohexanol and 1-(2-butynyl)cyclohexanol. After eight days at reflux 2-allyl-2-methylvinylidenecyclohexane (80%) and 1-(3-methyl-2,5-hexadienyl)cyclohexanol (60%) were formed, respectively. The latter product was assigned the structure of the *cis* addition product from NMR coupling constant data. Richey and von Rein [17] reported preliminarily the addition of vinylmagnesium bromide and allylmagnesium bromide to 2-butyn-1-ol, 3-pentyn-1-ol, and 4-phenyl-3-butyn-1-ol. Moderate yields of alkylated dienols were obtained. Alkylation was predominately at the internal carbon. *Trans* addition of the alkenylmagnesium group was tentatively concluded. Phenyl- and methyl-magnesium bromide did not react with 2-butyn-1-ol. To the authors' knowledge full details of these Grignard systems have not been reported.

In conclusion, the stereo- and regio-selectivity and mild conditions found for the reaction of chloro(alkynoxy)bis(2,4-pentanedionato)titanium(IV) complexes with diethylaluminum chloride offers some synthetic promise for the alkylation of selected γ and δ alkynols. Clearly, it has been demonstrated that Ziegler-type principles and systems can be applied to single alkylations and should be investigated for further utility in forming carbon—carbon bonds. While the conversions and yields reported in this work are moderate, it may well be possible to adjust the ligand environment of titanium to improve yields and to control the stereo- and regio-selectivity. A wide variety of titanium/alkoxide systems is available for study [18].

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