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TRANSITION METAL PROMOTED ALKYLATIONS OF UNSATURATED ALCOHOLS: THE METHYLATION AND ETHYLATION OF 3-BUTEN-1-OL USING TITANIUM TETRACHLORIDE-ORGANOALUMINUM SYSTEMS

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Summary

The ethylation and methylation of the olefinic linkage in 3-buten 1-ol by incorporating the alkenol into a titanium—organoaluminum system was studied under a variety of conditions. Systems were derived from titanium tetrachloride and the organoaluminum compounds $Al(C_2H_5)_3$, $Al(C_2H_5)_2Cl$, $Al(CH_3)_3$, and $Al(CH_3)_2Cl$. With diethylaluminum chloride the major products obtained were 1-hexanol, 3-methyl-1-pentanol, *trans*-3-hexen-1-ol, and 1-butanol. Triethylaluminum gave no alkylation products. Dimethylaluminum chloride and trimethylaluminum gave product distributions similar to the analogous diethylaluminum chloride system.

Introduction

Titanium tetrachloride—alkylaluminum systems alkylate simple olefins such as ethylene, propylene, and 4-methyl-1-pentene rapidly and repetitively under mild conditions. Thus, these and related systems have been of importance in the catalytic synthesis of linear and stereoregular polyhydrocarbons. In this paper studies are described which bear upon the use of titanium—organoaluminum systems, which resemble Ziegler—Natta type catalysts, as alkylating reagents in (non-macromolecular) organic synthesis and the development of a chemical system which models a single growth step in Ziegler—Natta catalyzed olefin polymerization.

Considering the facility with which titanium—aluminum based Ziegler—Natta catalysts undergo alkylmetal addition to carbon—carbon multiple bonds and the interest in synthetic techniques to extend carbon frameworks [1], there have

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TABLE 1

ETHYLATION REACTIONS

Reaction temperature (°C) [a]	Reaction time (h) [c]	Molar ratios (ROH/Al/Ti)	Products (yields (%)) [d]				Total C_6–OH (yield (%))	Total C_6–OH and C_4–OH (yield (%))
			3-Methyl-1-pentanol	1-Hexanol and *trans*-3-hexen-1-ol [e]	1-Butanol	3-Buten-1-ol		
Reactions of the type $TiCl_4 + [xAl(C_2H_5)_2Cl + HOCH_2CH_2CH{=}CH_2] \rightarrow$								
−78	4	1/2/1	4 (12)	30 (88) (65/35)	8 (17)	39 (83)	34	81
−45	4	1/2/1	16 (26)	44 (72) (56/42)	20 (91)	2 (9)	61	83
0	4	1/2/1	9 (23)	29 (74) (47/53)	9 (60)	6 (40)	39	64
0 [b]	4	1/2/1	10 (25)	29 (73) (42/58)	5 (45)	6 (55)	40	61
−45	0.25	1/2/1	6 (13)	38 (83) (42/58)	24 (80)	6 (20)	46	76
−45	4	1/2/1	16 (26)	44 (72) (58/42)	20 (91)	2 (9)	61	83
−45	9	1/2/1	16 (26)	45 (73) (62/38)	17 (89)	2 (11)	62	81
−45	4	1/1/1	1	negligible 1	4 (7)	55 (93)	~0	59
−45	4	1/2/1	16 (26)	44 (58/42)	20 (91)	2 (9)	61	83
−45	4	1/3.5/1	7 (23)	23 (38/62)	9 (25)	27 (75)	31	67
−45	4	1/2/0.25	1 (20)	4 (64/36)	5 (8)	55 (92)	5	65
Reactions of the type $TiCl_3(OCH_2CH_2CH{=}CH_2) + 2Al(C_2H_5)_2Cl \rightarrow$								
−45	4	1/2/1	1.5 (6)	26 (94) (35/65)	10 (46)	12 (54)	28	50
Reactions of the type $[TiCl_4 + 2Al(C_2H_5)_2Cl] + HOCH_2CH_2CH{=}CH_2 \rightarrow$								
−45	4	1/2/1	4 (11)	33 (89)	32 (56)	25 (44)	38	95
0				(40/60)				
0	4	1/2/1	~0		~0	[g]	~0	—
Reaction of the type $TiCl_4 + [2Al(C_2H_5)_3 + HOCH_2CH_2CH{=}CH_2] \rightarrow$								
−78	4	1/2/1	1	2	3	36	3	42
−45	4	1/2/1	1	4	5	53	5	63

Footnotes to this Table are on next page.

Footnotes to Table 1:

[a] The 3-buten-1-ol was added to the organoaluminum reagent at 0°C; the resulting reagent was added to the titanium component and the reaction allowed to proceed and subsequently terminated at the specified temperature. [b] The $[Al_2(OCH_2CH_2CH{=}CH_2)(C_2H_5)_3Cl_2]$ species was added at −78°C and then allowed to warm to 0°C at which temperature the reaction proceeded. [c] Time of reaction after addition of reagents was complete. Addition normally took 20—30 min. [d] Yields are based on initial amount of 3-buten-1-ol. The numbers in parentheses are relative percent yields within the C_6 alcohols and within the C_4 alcohols found. [e] As mentioned in the text it appeared that small amounts of *cis*-3-hexen-1-ol were formed. The amounts present ranged from 0 to 1% except for the 0.25 h reaction in which 2% was found. The combined C_6 alcohol yield contains the amount of *cis*-3-hexen-1-ol found. [f] In the preparation of $TiCl_3(OCH_2CH_2CH{=}CH_2)$ by reaction of $TiCl_4$ and 3-buten-1-ol some 3-chloro-1-butanol was formed. Thus these yields represent lower limits. [g] A large 3-buten-1-ol peak was observed but not quantified.

TABLE 2

METHYLATION REACTIONS

Reaction temperature (°C) [a]	Reaction time (h) [c]	Molar ratios (ROH/Al/Ti)	Products					Total C_5—OH (yield (%))	Total C_5—OH and C_4—OH (yield (%))
			3-Methyl-1-butanol	1-Pentanol	3-Penten-1-ols [c]	1-Butanol	3-Buten-1-ol		
Reactions of the type $TiCl_4 + [xAl(CH_3)_2Cl + HOCH_2CH_2CH{=}CH_2] \rightarrow$									
−78	4	1/2/1	~0	2	6	6	42	8	56
−45	4	1/2/1	3	4	32	28	27	39	94
0	4	1/2/1	4	3	20	6	22	27	55
Reactions of the type $TiCl_4 + [xAl(CH_3)_3 + HOCH_2CH_2CH{=}CH_2] \rightarrow$									
−78	4	1/2/1	~0	8	8	6	53	16	75
−45	4	1/2/1	~0	13	26	20	29	39	88
01	4	1/2/1	~0	3	19	~1	30	22	53

[a] See [a] for Table 1. [b] See [c] for Table 1. [c] *trans*-3-Penten-1-ol was the major product in all cases. A very small amount of what appeared to be the *cis* compound was observed; however, it was not isolable. The yield figure includes both products.

been relatively few studies reporting attempts to adapt the chemistry of titanium—aluminum catalyst systems to give single non-repetitive alkylations of isolated unsaturated carbon—carbon bonds of use in organic synthesis. Recently, we have reported work in this area leading to the alkylation of alkynols and alkenols [2]. There has also been recent interest in studying model systems to gain insight into the general mechanism of Ziegler—Natta catalysis [3,4]. Related to the chemistry described in this paper is the work of Clark and coworkers [3] who investigated several methyltitanium—aluminum systems as activating and alkylating agents toward the double bond in the 3-buten-1-oxy group in order to obtain information elucidating the growth step in polyolefin formation. Specifically, the 3-buten-1-oxy group was incorporated into titanium compounds such as $[TiCl_3(OCH_2CH_2CH{=}CH_2]$, $[Ti(\eta^5\text{-}C_5H_5)_2Cl(OCH_2CH_2CH{=}CH_2)]$, $[Ti(\eta^5\text{-}C_5H_5)_2(CH_3)(OCH_2CH_2CH{=}CH_2)]$, and $[Ti(\eta^5\text{-}C_5H_5)(CH_3)_2(OCH_2CH_2CH{=}CH_2)]$. It was concluded that there was not sufficient evidence to confirm the existence of a titanium—olefinic interaction nor were titanium—alkyl linkages found to add across the unsaturation.

In this paper we wish to report studies under a variety of conditions on the ethylation and methylation of the olefinic linkage in 3-butel-1-ol by incorporating the alkenol into systems derived from titanium tetrachloride and one of the organoaluminum compounds $Al(C_2H_5)_3$, $Al(C_2H_5)_2Cl$, $Al(CH_3)_3$, and $Al(CH_3)_2Cl$.

Results and discussion

The main approach to effect alkylation was to allow 3-buten-1-ol to react with an organoaluminum compound liberating alkane and forming an alkenoxyorganoaluminum species which subsequently was allowed to react with titanium tetrachloride. Alkylmetal addition to the olefinic group followed by hydrolysis was expected originally to yield 1-hexanol or 1-pentanol for terminal alkylation and 3-methyl-1-pentanol or 3-methyl-1-butanol for internal alkylation with ethyl and methylaluminum reagents, respectively.

Ethylation reactions. Results for the ethylation of 3-buten-1-ol using $Al(C_2H_5)_2Cl$ and $Al(C_2H_5)_3$—$TiCl_4$ systems are summarized in Table 1. Products unambiguously identified include *trans*-3-hexen-1-ol and 1-butanol in addition to the expected 1-hexanol and 3-methyl-1-pentanol *. *trans*-3-Hexan-1-ol can be explained by β-hydride transfer from the terminally alkylated intermediate. No evidence was obtained for the elimination product, 3-ethyl-3-buten-1-ol, which would arise from the internally ethylated intermediate. The production of 1-butanol must occur though metal hydride addition to the 3-buten-1-oxy group. The formation of metal—hydride linkages may well arise from β-hydride eliminations from titanium—ethyl groups since ethyl groups are commonly in excess; elimination to form *trans*-3-hexen-1-ol may also contribute metal—hydride species. Some Ziegler—Natta catalyst systems have been shown to be hydrogenation

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* Small amounts (0—2%) of *cis*-3-hexen-1-ol appeared to be present in these systems from GLC retention time comparisons with an authentic sample added to the product mixture. The limited quantity of this component and its proximity to other C_6 alcohols precluded isolation.

catalysts and thought to involve titanium-hydride addition [5]. In these studies the optimum conditions for the combined production of C_6 alcohols was found to be a 1/2/1 alkenol/$Al(C_2H_5)_2Cl$/$TiCl_4$ at —45°C for 4 h with the 3-buten-1-ol first being added to $Al(C_2H_5)_2Cl$. These conditions led to a yield of 61%. Reaction for 9 h gave approximately the same yield. Reactions at the 1/2/1 stoichiometry at —78 and 0°C and for 0.25 h at —45°C gave significantly lower yields. Reaction of 3-buten-1-ol with $TiCl_4$ to form [$TiCl_3OR$] followed by reaction with $Al(C_2H_5)_2Cl$ gives a similar product distribution with somewhat lower yields as does the reaction of $TiCl_4$ with $Al(C_2H_5)_2Cl$ at —45°C followed by addition of 3-buten-1-ol. These latter observations suggest that ligand exchange is facile and similar structures are generated leading to ethylation.

In Ziegler—Natta catalyzed olefin polymerization it is often advantageous to use the organoaluminum reagent in excess relative to the titanium component. It has been suggested [6] that this may reflect a dual role for the alkylaluminum species of alkylation of titanium and altering the electronic environment of the active center through formation of a bridged complex. Consistent with the above we found that ethylations run at a stoichiometry of 1/1/1 gave vritually no ethylated products. A large excess of $Al(C_2H_5)_2Cl$ (1/3.5/1) also gave a substantial reduction in C_6 alcohols. Attempts to use smaller amounts of $TiCl_4$ in hopes that it would function catalytically (i.e., a 1/2/0.25 reaction) gave only a 5% yield of C_6 alcohols. The yield of 1-butanol is largest (relative to 3-buten-1-ol and absolutely) in the alkylation reactions run at —45°C with a 1/2/1 stoichiometry. Metal-hydride formatinn and addition is rapid as evidenced by the relatively large amount of 1-butanol formed in only 0.25 h. On lowering the temperature to —78°C the amount of 1-butanol relative to 3-buten-1-ol decreases significantly which is probably a reflection of the decreased ability at low temperatures for β-hydride transfer to occur to produce the necessary metal—hydride linkages to add to the 3-buten-1-ol. This idea is supported by the larger 1-hexanol to *trans*-3-hexen-1-ol ratio observed at —78°C. At 0°C the yield of 1-butanol is decreased and the amount of 3-buten-1-ol recovered is quite low. Both high and low amounts of $Al(C_2H_5)_2Cl$ (1/3.5/1 and 1/1/1 reactions, respectively) give decreased amounts of 1-butanol. In all cases the lower yields of 1-butanol were also accompanied by lower yields of C_6OH alcohols. Thus, those factors which reduce the alkylating ability of the system also appear to decrease the formation and addition of metal—hydride linkages.

Upon substituting $Al(C_2H_5)_3$ for $Al(C_2H_5)_2Cl$ the yields of C_6 alcohols and 1-butanol were drastically reduced. This was somewhat unexpected in the light of the fact that $Al(C_2H_5)_3$—$TiCl_4$ systems are good catalysts for propylene polymerization. On the other hand, these results are consistent with other observations in this work which suggest that the active valence state of titanium is +4. It is well established that $Al(C_2H_5)_3$ is a better reducing agent toward titanium(IV) than $Al(C_2H_5)_2Cl$ [7]. Thus rapid reduction of titanium by $Al(C_2H_5)_3$ may be responsible for the low yields. When $TiCl_3$ was used with $Al(C_2H_5)_2Cl$ no alkylated products were produced. Also, upon treating $TiCl_4$ with $Al(C_2H_5)_2Cl$ at 0°C and aging for 0.25 h followed by addition of 3-buten-1-ol, no ethylated products were obtained. These latter two observations implicate titanium(IV) as the necessary oxidation state for alkylation.

The ratio of 3-methyl-1-pentanol to the terminally alkylated C_6 alcohols varies little with reaction conditions with terminal addition predominant in all cases. In contrast chloro(3-buten-1-oxy)bis(2,4-pentanedionato)titanium(IV) reacts with $Al(C_2H_5)_2Cl$ to give virtually complete terminal addition products whereas replacing $TiCl_4$ with $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ leads to exclusive formation of 3-methyl-1-pentanol [2]. The ratio of 1-hexanol to *trans*-3-hexen-1-ol is not greatly affected by varying the reaction conditions either, although for a series of 1/2/1 reactions the relative amount of elimination product increases with increasing temperature as might be expected, i.e., lower temperatures reduce the rate of β-hydride transfer from the alkylated intermediate. It is interesting to note how facile β-elimination is even at —78°C.

Viewed broadly, the alkylations reactions using $Al(CH_3)_2Cl$ parallel those with $Al(C_2H_5)_2Cl$ (see Tables 1 and 2). Both terminal and internal methylation products are observed with terminal methylation predominating. *trans*-Penten-1-ol is the major elimination product. 1-Butanol is produced again in significant yield particularly at —45°C.

Reaction patterns with $Al(CH_3)_3$ were significantly different from those with $Al(C_2H_5)_3$. With $Al(CH_3)_3$ substantial terminal alkylation occurred with *trans*-3-penten-1-ol the predominant product. Yields were again maximal at —45°C.

The lower yields with the methylaluminum reagents may be due to greater difficulty of insertion into titatnium—methyl as opposed to titanium—ethyl linkage. This was found to be the case by Waters and Mortimer [8] using dicyclopentadienyltitanium(IV) catalyst systems. The enhanced reactivity of $Al(CH_3)_3$ relative to $Al(C_2H_5)_3$ may be due to the fact that titanium must be in the +4 oxidation for the alkylation to proceed and methylaluminum reagents are less active in reducing titanium than ethyl analogs [9]. Indeed, Bestian and Clauss [10] in ethylene oligomerization studies with the $Ti(CH_3)Cl_3$—$Al(CH_3)Cl_2$ catalyst system found the +4 state to be the active one.

While an intramolecular mechanism with alkylation of the unsaturated moiety occurring at a titatnium center and the alkenoxide bridging metal centers such as suggested in previous publications [2] is a plausible pathway, additional work will have to be done before definite conclusions can be drawn.

In conclusion, while it has been possible to alkylate the 3-buten-1-ol, it is not useful synthetically in its present form due to mixtures of terminal and internally alkylated products plus substantial amounts of elimination products. However, the possibility exists that suitable modification of the ligand environment about titanium would lead to higher yields with greater selectivity. With respect to polymerization catalysts, the types of systems studied here give information on the formation of primary versus secondary metal—alkyl linkages which may be of interest to the stereoregular polymerization of propylene [11]. The great facility of β-hydride elimination under such mild conditions suggests that in olefin polymerization systems the growing polymer chain or some other chemical feature must modify the systems to prevent β-hydride transfer from becoming an overwhelming termination step.

Experimental

Materials. 3-Buten-1-ol and *cis*- and *trans*-3-hexen-1-ol were purchased from Chemical Samples Company; 3-butyn-1-ol was obtained from Farchan. All alcohols were used with further purification except for drying and storage over 3A Molecular Sieves. All organoaluminum reagents were purchased from the Ethyl Corporation as the neat liquid from which 1.5—2.0 *M* methylene chloride solutions were prepared. Titanium tetrachloride (Purified) was obtained from Fisher Scientific Company. Methylene chloride (Certified ACS) and diethyl ether (Laboratory) were purchased from Fisher. Methylene chloride was distilled from P_2O_5 under nitrogen and stored over 3A Molecular Sieves. All reagents were transferred under nitrogen or argon using standard syringe techniques.

General procedure for reaction of unsaturated alcohols with AlR_xCl_{3-x} reagents followed by reaction with titanium tetrachloride. Reactions were done in glassware dried at 110° C, assembled hot, and flushed with N_2 while cooling. Typically 20—70 mmol of a 1.5—2.0 *M* AlR_xCl_{3-x} solution in CH_2Cl_2 was transferred to a 250 ml three-necked round bottom flask equipped with a gas inlet, magnetic stirring bar, and a 50 ml dropping funnel. Additional solvent for 20—45 mmol AlR_3Cl_{3-x} reactions was added to give 1 *M* solutions. The unsaturated alcohol (20 mmol) was added by weight using a syringe to the dropping funnel containing 25 ml of CH_2Cl_2. The AlR_xCl_{3-x} solution was cooled to 0° C, and the 3-buten-1-ol solution added dropwise to form a mixed alkylchloro-3-buten-1-oxyaluminum system (solution I).

A second 250 ml flask equipped as described above was charged with 30 ml of CH_2Cl_2 and an appropriate amount of $TiCl_4$ and cooled to the desired temperature. Solution I was transferred via syringe to the dropping funnel and added dropwise over 20—30 min. The reactions were terminated by addition of 10 ml of methanol followed by 50 ml of a 5% H_2SO_4 solution saturated with NaCl. The resulting mixture was stirred over an oxygen atmosphere for 1 h. The methylene chloride layer was separated, and the aqueous layer extracted with 5—50 ml portions of diethyl ether. The combined organic layers were dried over $MgSO_4$ and filtered. The product solutions were reduced in volume with a rotary evaporator, furnished with an internal standard, and analyzed by GLC.

Reaction of titanium tetrachloride with diethylaluminum chloride followed by addition of 3-buten-1-ol. Using apparatus set up as described in the previous section 40 mmol of $Al(C_2H_5)_2Cl$ solution at a concentration of 1.0 *M* was added dropwise to 20 mmol of $TiCl_4$ dissolved in 30 ml of CH_2Cl_2 and cooled to −45 or 0° C. The resulting dark solution was allowed to age 15 min after addition was complete. A solution of 20 mmol of 3-buten-1-ol in 25 ml of CH_2Cl_2 was then added dropwise. The reactions were terminated, worked up, and analyzed as described previously.

Reaction of trichloro(3-buten-1-oxy)titanium with diethylaluminum chloride. Preparation of $TiCl_3(OCH_2CH_2CH{=}CH_2)$ was accomplished by adding an equivalent amount (40 mmol) of 3-buten-1-ol in 25 ml CH_2Cl_2 to a refluxing CH_2Cl_2 (30 ml) solution of $TiCl_4$ (40 mmol). During addition and subsequent reaction the system was continually purged with a slow stream of N_2 flowing up the condenser to remove HCl. This procedure results in some loss of 3-buten-1-ol through HCl addition to form 3-chloro-1-butanol. However, it is much more convenient than using a LiOR reagent [3].

The $Al(C_2H_5)_2Cl$ solution (1 *M*) was transferred to a 250 ml flas equipped as described above in the general procedure. The $TiCl_3(OR)$ solution was added dropwise at the desired temperature. The reactions were terminated and handled as described previously.

Gas chromatographic analyses. All products were analyzed with a Hewlett—Packard 5750 equipped with a mechanical integrator using 6 or 8 ft 1/8 in 10% Carbowax 20M columns. The quantitative results are corrected for response factors determined with authentic samples. n-Heptanol was used as an internal standard. Samples were isolated for spectral investigations by preparative GLC using a 10 ft 1/4 in 20% Carbowax 20M column.

Spectra. NMR and IR spectra were run on Perkin—Elmer R-20B and 457 spectrometers, respectively.

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