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Preliminary communication

TRANSITION METAL PROMOTED ALKYLATIONS OF ALKYNOLS

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During the past several years a substantial number of papers has appeared describing the synthesis and characterization of complexes of type [MXY(dik)$_2$] where M = Ti, Zr, Hf, Si, Ge, Sn, X and Y = uninegative monodentate ligands, and dik = β-diketonate anions [1-3]. We have prepared and characterized alkoxy(chloro)di-2,4-pentanedionatotitanium(IV) complexes, [TiCl(OR)($C_5H_7O_2$)$_2$] [4], and have found that these new complexes, when combined with diethylaluminum chloride, catalyze the polymerization of ethylene under very mild conditions, yielding linear high density polyethylene [5].

It is well accepted that the Ziegler polymerization process proceeds by the repetitive insertion of an olefinic monomer into a titanium—alkyl linkage. With this in mind, we were able to develop a procedure for alkylating unsaturated alcohols under mild conditions. Thus, by treatment of 3-buten-1-ol in the form of the complex [TiCl($OCH_2CH_2CH{=}CH_2$)($C_5H_7O_2$)$_2$] with Al(C_2H_5)$_2$Cl we obtained 1-hexanol and *trans*-3-hexen-1-ol in moderate yields [6]. In this paper we report our preliminary studies of the alkylation of five alkynols, propynol, 3-butyn-1-ol, 3-pentyn-1-ol, 4-pentyn-1-ol, and 5-hexyn-1-ol.

The ethylation of 3-butyn-1-ol is described below to illustrate the procedure used. The complex [TiCl($OCH_2CH_2C{\equiv}CH$)($C_5H_7O_2$)$_2$] was prepared by reaction of [TiCl$_2$($C_5H_7O_2$)$_2$] with 3-butyn-1-ol and pyridine as described by Thompson, Munsey and Harris [4]. The 3-butyn-1-oxy complex in methylene chloride was added dropwise at —78°C under an argon atmosphere to a methylene chloride solution of Al(C_2H_5)$_2$Cl, and the reaction mixture was stirred for 4 h at —78°C. Methanol, water, and dilute sodium hydroxide solution then were added successively. The resulting dark mixture was stirred under an atmosphere of oxygen to oxidize any lower valent titanium species. A white solid was produced which remained suspended in a pale yellow solution. After filtration, the methylene chloride layer was

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separated and the aqueous layer was extracted with diethyl ether. The combined organic portions were dried over magnesium sulfate, concentrated, and analyzed by GLC using 1-octanol as an internal standard. A single product, *trans*-3-hexen-1-ol, was isolated. Table 1 contains a summary of results of the alkylations studied. Ethylation products were isolated only in cases of γ and δ triple bonds. Further, ethylation occurs only at the carbon atom furthest from the hydroxyl group.

TABLE 1

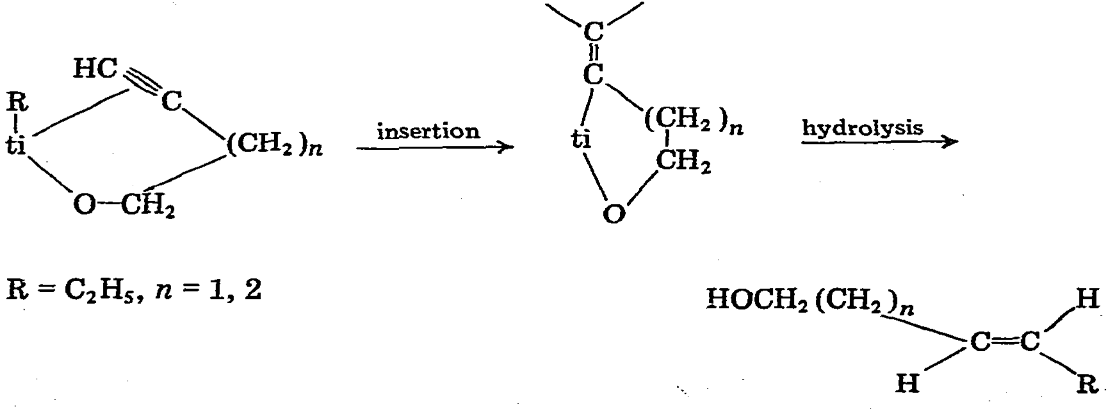
ALKYNOL ALKYLATIONS

Alkynol as $[TiCl(OR)(C_5H_7O_2)_2]$	Temp (°C)	Product (% yield)	Starting material recovered (%)	Molar ratio Al:Ti	Reaction time (h)
3-Butyn-1-ol	—78	*trans*-3-Hexen-1-ol (53)	21	3.5:1[a]	4
	—46	*trans*-3-Hexen-1-ol (35)	7	3.5:1	4
	0	*trans*-3-Hexen-1-ol (24)	< 5	2:1	4
Propynol	—78	Negligible	35	2:1	4
3-Pentyn-1-ol	—78	4-Methyl-3-hexen-1-ol (53)	12	2:1	4
4-Pentyn-1-ol	—78	*trans*-4-Hepten-1-ol (20)	55	2:1	4
5-Hexyn-1-ol	—78	Negligible	75	2:1	4

[a] Reaction at —78°C with a 2:1 molar ratio for 4 h gave a 34% yield; a similar 10 h reaction gave 49%. However, with 3-pentyn-1-ol a 3.5:1 molar ratio at −78°C gave a lower yield than a 2:1 reaction at the same temperature.

The ethylations may reasonably proceed by initial ethylation of an alkynoxytitanium species followed by activation of the acetylenic linkage and subsequent ethyltitanium addition. Studies [7] of Ziegler catalyst systems suggest that the addition involves an ethyltitanium species rather than an ethylaluminum group. Furthermore, $Al(C_2H_5)_2Cl$ was not found to alkylate 3-butyn-1-ol under our standard reaction conditions. A reaction scheme in part is illustrated in Scheme 1.

Scheme 1. Postulated alkynol alkylation



$R = C_2H_5$, $n = 1, 2$

The formation of *trans*-3-hexen-1-ol and *trans*-4-hepten-1-ol is consistent with *cis*-addition of the Ti—R linkage. In comparison with the ethylation of 3-buten-1-ol, where formation of a substantial amount of *trans*-3-hexen-1-ol occurs via β-hydride elimination, no hydride elimination was observed in the alkynol systems, This observation provides additional support for the reaction shown in Scheme 1. If *cis*-addition occurs to give the illustrated metallocyclic intermediate, then the exocyclic β-hydrogen is *trans* with respect to titanium. From studies of vinyliridium compounds by Schwartz et al. [8], it was shown that elimination can occur readily only when the metal and β-hydrogen are *cis* with respect to each other. Furthermore, McDermott, White and Whitesides [9] have presented evidence that elimination of β-hydrogens in metallocycles is a less favored process than for non-cyclic alkylmetal groups. Lastly, hydrolysis of the reaction mixture with D_2O in the 3-butyn-1-ol system gave 98% of (*Z*)-4-deuterio-3-hexen-1-ol. Iodination of an identical reaction mixture gave (*E*)-4-iodo-3-hexen-1-ol.

In summary, the mild conditions and regiospecificity involved in utilizing titanium alkynoxide species to effect the alkylation of γ and δ alkynols appear to offer synthetic promise. In current work we are varying the nature of the titanium alkoxide species and the organoaluminum alkylating agent in the hope of improving yields and controlling the regiospecificity. In addition, the deuteration and iodination mentioned for the 3-butyn-1-ol system indicate the possibility of additional functional conversions of the reaction intermediate. We are exploring this possibility.

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