Journal of Organometallic Chemistry, 69 (1974) C27—C30

Preliminary communication

TRANSITION METAL PROMOTED ALKYLATIONS OF ALKENOLS

THOMAS V. HARRIS, R.A. COLEMAN*, ROBERT B. DICKSON and D.W. THOMPSON*
Department of Chemistry, College of William and Mary, Williamsburg, Virginia 23185 (U.S.A.)
(Received December 18th, 1973)

As a part of our continuing interest in the coordination chemistry of the Group IVA elements, we recently published work on the synthesis and characterization of monomeric and hexacoordinate alkoxy(chloro)bis(2,4-pentanedionato)titanium(IV) complexes, $(RO)ClTi(C_5H_7O_2)_2$ [1]. Alkoxy groups utilized include methoxy, ethoxy, 1-propoxy, 2-propoxy, and 2-propen-1-oxy.

Having prepared this new class of titanium complexes we decided to investigate their usefulness in a Ziegler-type catalytic system for the polymerization of ethylene. Indeed, we found that all of the alkoxy(chloro)bis(2,4-pentanedionato)titanium(IV) complexes, when mixed with diethylaluminum chloride in either methylene chloride or toluene, catalyzed the polymerization of ethylene at atmospheric pressure and ambient temperatures to yield linear high density polyethylene.

The observed catalytic activity of the new alkoxytitanium complexes, when combined with diethylaluminum chloride, suggested that a new synthetic procedure for rapidly alkylating alkenols under mild conditions via the (alkenoxy)chlorobis(2,4-pentanedionato)titanium(IV) complexes might be possible. Examination of the literature showed that there has been recent interest in the addition of main group organometallic reagents to the double bond of alkenols. Although in general the reluctance of main group alkylmetals to add under mild conditions across isolated olefinic moieties is well-known, several studies have recently appeared reporting the addition of organolithium and Grignard reagents across the double bonds of alkenoxy groups. Crandall and Clark [2], Felkin, Swierczewski, and Tambute [3], and Dimmel and Huang [4] have reported the addition of various organolithium reagents to the double bonds of several allylic alcohols. A few of the organolithium reagents added unaided to some allylic alcohols, however, the majority of the additions required the promoting effect of *N,N,N′,N′*-tetramethylethylenediamine. The addition of Grignard reagents to alkenols has been reported recently by Eisch and coworkers [5] and by Felkin and coworkers [6]. Only reactive Grignard reagents such as the allyl and benzyl reagents add to allylic and some other alcohols. Unusually long reaction times at

---

* Address correspondence to these authors.

reflux conditions are required to obtain only moderate yields in most instances of alkylated products.

The ethylation of 3-buten-1-ol described below is representative of the experimental approach used in our preliminary investigations. 3-Buten-1-ol was converted to chloro(3-buten-1-oxy)bis(2,4-pentanedionato)titanium(IV) as described by Thompson, Munsey, and Harris [1] by direct reaction of dichlorobis(2,4-pentanedionato)titanium(IV) (commercially available), 3-buten-1-ol, and pyridine in ca. 1/1/1 molar ratios. A methylene chloride solution of the 3-buten-1-oxy complex was placed in a previously dried reaction vessel and maintained under a nitrogen atmosphere. To this complex at 0°C was added dropwise a hexane solution of diethylaluminum chloride (3 molar equivalents vs. the 3-buten-1-oxy complex). The reaction mixture was stirred 3 h (including addition) at 0°. The reaction was terminated by hydrolyzing with a 10% sulfuric acid solution saturated with sodium chloride. The system was stirred in air for several hours until the color changed from purple to yellow-brown (presumably due to oxidation of titanium(III) species). The methylene chloride layer was separated off, and the aqueous layer extracted with several portions of diethyl ether. The organic portions were combined, dried over magnesium sulfate, reduced in volume, and analyzed by gas chromatography using dodecane as an internal standard. The yield of C_6 alcohols was 50%, and the per cent conversion of 3-buten-1-ol was 84%.

The ethylation of chloro(3-buten-1-oxy)bis(2,4-pentanedionato)titanium(IV) with diethylaluminum chloride was the most extensively studied reaction in our preliminary investigations. For this system two major products were produced and identified to be the expected 1-hexanol and the somewhat unexpected *trans*-3-hexen-1-ol by comparison of VPC, IR, and NMR data of VPC prepared samples with similar data from authentic samples. The combined average yields of C_6 alcohols ran between 40 to 55%; conversions (%) to C_6 alcohols relative to 3-buten-1-ol ran about 30% greater than the overall yield. For reactions run between 0° and room temperature approximately equal amounts of 1-hexanol and *trans*-3-hexen-1-ol were formed. However, at —78 and —23° the *trans*-3-hexen-1-ol increased with respect to 1-hexanol although the overall yields decreased to 15 and 43%, respectively. Variation of the Al/Ti mole ratio from 1/1 to 6/1 had a slight effect (5—10%) on the overall yield of ethylated product with the optimum ratio being between 2/1 and 3/1. This optimum mole ratio range is close to that often reported for Ziegler olefin polymerization systems. No significant effect on yields was noted among ethylation reactions run for 0.3, 3, 6, and 18 h at 0°, thus indicating a facile and rapid alkylation.

It seems reasonable to suggest that the ethylations observed proceed via ethylation of a titanium—alkenoxy species followed by double bond activation and subsequent titanium-ethyl addition to the olefinic linkage (see Fig. 1). That the addition involves a titanium-ethyl species rather than an aluminum-ethyl group is supported by studies on Ziegler catalyst systems which show that the titanium is the site of propagation [7] and by the fact that diethylaluminum chloride was found not to ethylate 3-buten-1-ol in the absence of a titanium center.

The formation of an olefinic ethylated alcohol such as *trans*-3-hexen-1-ol was somewhat unexpected. However, its presence may be attributed to a hydride

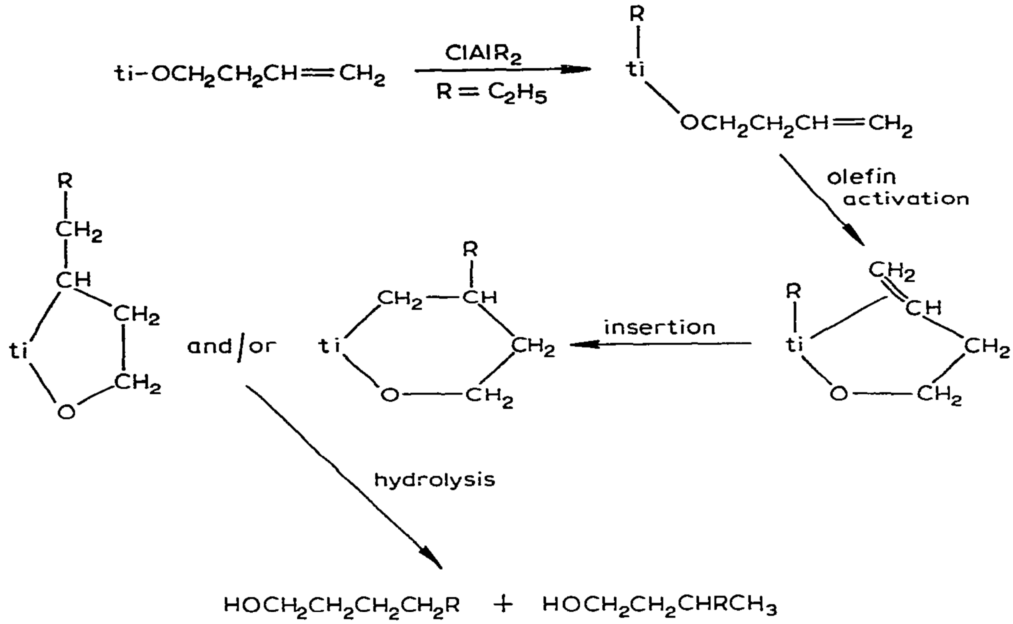
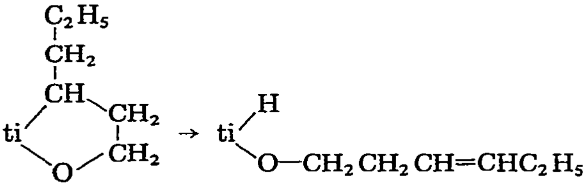


Fig. 1. Postulated reaction scheme for the hydroalkylation of 3-buten-1-ol as the chloro(3-buten-1-oxy)bis-(2,4-pentanedionato)titanium(IV) complex.

transfer with concommitant olefin formation after the ethylation initially takes place, i.e.



Hydride transfer reactions of this type have been found in titanium—alkyl [7, 8] and other metal—organic systems [9]. It is not known whether the formation of the *trans* alkenol is simply due to the greater thermodynamic stability of the *trans* versus *cis* isomer or due to steric constraints of the unhydrolyzed alkylated intermediate.

The ethylation of the 3-buten-1-oxy group is regiospecific with respect to formation of the secondary alkyl—titanium linkage. With the organolithium additions to allylic alcohols addition was usually such that a primary alkyl—lithium bond was formed [2, 3, 4]. However, with bulky alkyllithium groups such as t-butyl addition to give a secondary alkyllithium has been observed [2]. On the other hand, the reported reactions of Grignard reagents with alkenols give both primary and secondary alkyl—metal linkages [5, 6]. The apparent alkylation of the 3-buten-1-oxytitanium complex to give the secondary titanium—carbon linkage can be rationalized by the fact that five-membered rings in coordination chemistry are generally more stable than six-membered rings.

In summary, the short reaction times and mild conditions required for the ethylation of 3-buten-1-ol using the titanium-β-diketonate complex and diethylaluminum chloride appear to offer considerable synthetic promise. Indeed, preliminary investigations on a number of alkenols indicate the alkylation to be of some generality although yields at present in these systems are low. Additional work using other alkylaluminums, or alkyllithiums, in combination with alkenoxytitanium-β-diketonate complexes confirms our hypothesis that other organometallic reagents may be utilized. Consequently, we are continuing to explore this area with the hope of improving the yields of those reactions already under investigation, and extending the alkylation to other unsaturated systems as well.

Acknowledgement

We wish to express appreciation to the Research Corporation for funds allowing purchase of the gas chromatograph used in this investigation.

References

1 D.W. Thompson, W.R.C. Munsey and T.V. Harris, Inorg. Chem., 12 (1973) 2190.
2 J.K. Crandall and A.C. Clark, J. Org. Chem., 37 (1972) 4236.
3 H. Felkin, G. Swierczewski and A. Tambute, Tetrahedron Lett., (1969) 707.
4 D.R. Dimmel and S. Huang, J. Org. Chem., 38 (1973) 2756.
5 (a) J.J. Eisch and G.R. Husk, J. Amer. Chem. Soc., 87 (1965) 4194; (b) J.J. Eisch and J.H. Merkley, J. Organometal. Chem., 20 (1969) P27.
6 (a) M. Cherest, H. Felkin, C. Frajerman, C. Lion, G. Roussi and G. Swierczewski, Tetrahedron Lett., (1966) 875. (b) H. Felkin and C. Kaeseberg, ibid., (1970) 4587.
7 G. Henrici-Olivé and S. Olivé, Polymer Letters, 8 (1970) 271.
8 H. Bestian and K. Clauss, Angew. Chem. Int. Ed., 2 (1963) 704.
9 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd ed., Interscience Publishers, New York, N.Y., 1972, pp. 785—787.