Journal of Organometallic Chemistry, 159 (1978) C13—C19

Preliminary Communication

Regiospecific and Stereoselective Carbometallation of Alkynylsilanes by Ziegler-Natta Alkylating Agents*

John J. Eisch, Robert J. Manfre and David A. Komar

Department of Chemistry
State University of New York at Binghamton
Binghamton, New York 13901

(Received June 9th, 1978)

Summary

A 1:1 combination of dichloro(bis-η^5-cyclopentadienyl)titanium and alkylaluminum halide in methylene chloride solution effects the regiospecific alkylation of alkynyl(trimethyl)silanes in 60-95% yields. With $R-C\equiv C-SiMe_3$ substrates, where R= saturated alkyl group, the carbometallation (introduction of a methyl or an ethyl group) occurs regiospecifically and stereoselectively in a trans- manner, giving a 75:25 to a 90:10 ratio of isomers. When the R in $R-C\equiv C-SiMe_3$ is phenyl or 1-cyclohexenyl, then a non-stereoselective carbometallation is observed (50:50 mixtures of isomers). These results, which are explicable in terms of the formation of the $(C_5H_5)_2\overset{+}{Ti}-R$ cation and its attack on the alkynylsilane, offer stereochemical evidence for a cationic initiating step in the polymerization of ethylene by homogeneous Ziegler-Natta catalysts.

---

* Part 36 of the series, "Organometallic Compounds of Group III", devoted to carbometallation and hydrometallation. Cf ref. 1 for the previous part.

Much effort has been expended toward elucidating the mechanism whereby combinations of dichloro(bis-η^5-cyclopentadienyl)titanium and aluminum alkyls effect the polymerization of ethylene under homogeneous conditions.** Extensive kinetic, ESR, electrodialytic and solvent studies have tended to implicate a quadrivalent titanium cation, $[(C_5H_5)Ti-CH_3]^+$, as the active initiating center in the polymerization of ethylene. Because this type of catalyst will not homopolymerize propylene and higher olefins and because its action on terminal alkynes is to cause cyclotrimerization to trisubstituted benzenes[11], no stereochemical information has been available on the initiating step of such homogeneous catalysts.

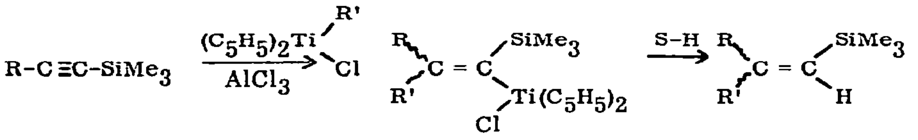
We now wish to report that, by use of alkynylsilanes as substrates with such Ziegler-Natta reagents, we have been able to effect the carbometallation of the unsaturated linkage in a controlled fashion, limiting the alkyne insertion largely to the initial step, and thus to examine the stereochemistry of the initiating carbometallation process. For example, alkynylsilanes*** of the type, $R-C\equiv C-SiMe_3$ (I, where $R=n-C_6H_{13}$, $c-C_6H_{11}$, C_6H_5 and 1-cyclohexenyl), reacted readily in methylene chloride solution with combinations of dichloro(bis-η^5-cyclopentadienyl)titanium (II) and R_nAlCl_{3-n} (III) where R=Me or Et and n=0-2). (Table 1) Hydrolytic work-up led to the isolation of the regiospecifically alkylated silane IV in yields ranging from 60-95%. The alternative treatment of the reaction mixture with D_2O gave the same undeuterated vinylic silanes IV, demonstrating that IV had acquired a proton from the reaction mixture (S-H) and that little or no vinylic-metal bond was present at

---

**Excellent reviews of Ziegler-Natta polymerization catalysis are available (2-4), as well as numerous studies of various aspects (*Cf.*, *inter* alia, ref. 5-10 and literature cited therein).

***Combinations of aluminum alkyls with titanium (IV) salts have been used to effect the alkylation of alkynols and alkenols, but the reaction yields mixtures of carbometallated regioisomers and has not been reported for ordinary alkynes (*Cf.* ref. 12 a-c). Combinations of aluminum alkyls with zirconium (IV) salts have been found to alkylate alkynes [12d] and, most recently, nickel salts have been shown to catalyze the addition of methyl, but not ethyl, Grignard reagents to alkynylsilanes [12e].

the time of work-up (eq. 1):

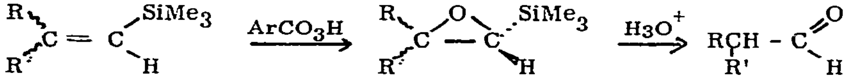


(1)

I

IV a= R' and H cis
b= R' and H trans

The regiochemistry of these carbometallated products was determined by a sequence of epoxidation with m-chloroperbenzoic acid and protodesilylation [13] to give the carbonyl compound (eq. 2):



(2)

IVa, b

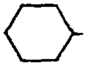
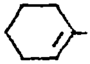
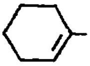
That an alkyl group bonded to titanium, rather than aluminum, was responsible for the alkylation of I was demonstrated by control experiments. Under the reaction conditions successful for II and III, namely 6-24 h at 25° C, trialkylaluminums or alkylaluminum chlorides and I gave 0-5% of IV. Only by heating alkynylsilanes with triethylaluminum in refluxing benzene for 18 h were ca 50% yields of IV obtained upon hydrolysis.

Even though the combination of II and III undoubtedly produces the alkyl(chloro)bis-η^5-cyclopentadienyltitanium (V), the separate preparation of V from II and the Grignard reagent [14] and the admixture of V and I led to no alkylation. This finding demonstrates that Cp_2TiRCl requires $AlCl_3$ for activation.

In addition to rate, the most arresting feature of these titanium-mediated carbometallations is the stereochemistry. With alkynylsilanes bearing saturated groups (I, R=n-C_6H_{13} and c-C_6H_{11}) the vinylic silane products IV consisted of Z, E-isomers ranging from a 25:75 up to a 10:90 ratio (IVa:IVb). In other words, the carbometallation had proceeded principally in a trans or anti fashion. The mode of addition was determined by a:) obtaining the isomeric ratio by GLPC

TABLE I

CARBOTITANATIONS OF ALKYNYLSILANES BY COMBINATIONS OF DICHLORO(BIS-η^5-CYCLOPENTADIENYL)TITANIUM AND ALKYLALUMINUM CHLORIDES IN METHYLENE CHLORIDE AT 20-25°C [a]

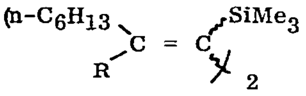
Alkynylsilane	Source of R Group	Yield	Z:E Ratio
n-C_6H_{13}-C≡C-$SiMe_3$	$EtAlCl_2$[b]	60[c, d]	10:90
n-C_6H_{13}-C≡C-$SiMe_3$	$MeAlCl_2$	67[d]	15:85
-C≡C-$SiMe_3$	Et_3Al	57	30:70
-C≡C-$SiMe_3$	Me_2AlCl	67	25:75
C_6H_5-C≡C-$SiMe_3$	$EtAlCl_2$[b]	95	50:50
C_6H_5-C≡C-$SiMe_3$	Me_2AlCl_2	95	50:50
-C≡C-$SiMe_3$	$EtAlCl_2$[b]	95	50:50
-C≡C-$SiMe_3$	Me_2AlCl	60	50:50

[a] In a typical procedure, 3.0 g (12 mmol) of II and 2.25 g (12 mmol) of trimethyl(1-octynyl)silane in 250 ml of purified CH_2Cl_2 were treated dropwise with 1.26 ml (12 mmol) of $EtAlCl_2$ over 2-3 min at 20-25° C and under a nitrogen atmosphere. The flask was covered with aluminum foil to exclude light and the mixture was stirred for 12-25 h at 20-25° C. Then 6.8 ml (48 mmol) of anhydrous Et_3N was added (this acted as a buffer; without it, hydrolysis led to extensive desilylation of IV) and this was followed by 0.7 ml of H_2O. The resulting orange-red solution was dried over anhydrous Na_2SO_4 and the solvent removed. The residue was extrated with hexane and the extracts passed through a short silica gel column. The eluates were freed of solvent and then distilled (bp 35-37° C (0.15 mm)) or analyzed by GLPC and NMR spectroscopy.

b. In these cases, the use of Et_2AlCl or Et_3Al as ethylating agent gave significant amounts of butyl- and hexyl-vinylsilanes, presumably via the generation of ethylene and its prior insertion into ethyl-titanium bonds.

c. Yields indicated were determined by GLPC analysis; isolated yields were ca 10% lower.

d. The most significant minor product, as shown by GLPC-MS analysis, was a stereoisomeric mixture of dimers,



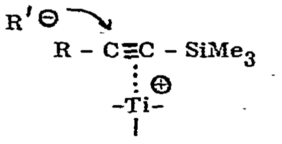
analysis of the vinylic products or, for those cases where the isomers were not separable (IV, R=n-C_6H_{13} and R'=Et), by epoxidizing IV with m-chloroperbenzoic acid and recording the separate epoxide protons in the presence of $Eu(fod)_3$ shift reagent; and b) noting the larger, long-range splitting of the CH_3-C=C-H or CH_3-CH_2-C=C-H protons in IV (R'-=CH_3 or CH_3CH_2 when these groups have a cis-configuration*. By this means the carbotitanation of trimethyl(1-octynyl)silane by either $(C_5H_5)_2TiCH_3(Cl)$ or $(C_5H_5)_2TiCH_2CH_3(Cl)$ was shown to proceed principally in a trans fashion to give a 85:15 or 90:10 ratio, respectively. This ratio of isomers was essentially invariant during the course of the reaction. For comparison, the forced carbometallation of trimethyl(1-octynyl)silane at 80°C with$(CH_3CH_2)_3Al$ gave a 50:50 mixture of Z and E-ethyl isomers (IV, R=n-C_6H_{13}, R'=Et).

In contrast, the carbotitanation of alkynylsilanes bearing unsaturated groups α,β to the acetylenic likage (I, R-C_6H_5 or 1-cyclohexenyl) proceeded regio-specifically but in a completely non-stereospecific fashion. The ratios of Z, E-isomers formed at low conversion of I and that found at the end of the reaction were 50:50.

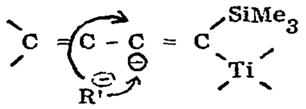
---

*By private communication with Professor Barry Snider, Department of Chemistry, Princeton University, we have learned of his complementary work on the cis-methylation of alkynylsilanes by nickel-catalyzed additions of Grignard reagents. By various structural proofs, he has shown that his major product from trimethyl(1-octynyl)silane, the cis-methylation product,has the GLPC and NMR properties displayed by our minor product [12e]. He has also drawn our attention to pertinent literature on the configurational assignments of vinylsilanes [15].

The foregoing carbometallation procedure constitutes a useful route to alkyl-substituted vinylsilanes, which are of growing significance in organic synthesis [16]. Moreover, the stereochemistry observed with these Ziegler-Natta alkylating agents offers support for the cationic mechanism deduced for the homogeneous polymerization of ethylene by the same reagents. Since it is known that $(C_5H_5)_2TiCl_2$ and various R_nAl_{3-n} lead to $(C_5H_5)_2TiR(Cl)$, [17], the reagent complex, $(C_5H_5)\overset{+}{Ti}R$ $AlCl_4^-$ should result from $(C_5H_5)_2TiCl_2$ and $RAlCl_2$. Such a complex is suggested as then accommodating the ethylene in the remaining unoccupied coordination site [8]. Applying this view to the carbotitanation of I, one would place the alkynylsilane in such an available site. The difference in stereoselectivity observed in the carbometallation of I may stem from the tightness of the cationic complex. A tight pi complex (VII) would favor a trans-alkylation; a loose or sigma-complex (VIII), (because of allylic charge delocalization possible with phenyl and 1-cyclohexenyl groups) would permit random cis or trans alkylation:



VII



VIII

Acknowledgements

The authors are indebted to the National Science Foundation for the support of this research by Grant CHE76-10119.

References

1. J. J. Eisch and G. A. Damasevitz, J. Org. Chem., 41 (1976) 2214.
2. J. Boor, Jr., Ind. Eng. Chem. Prod. Res. Dev., 9 (1970) 437.
3. S. Sivaram, Ind. Eng. Chem. Prod. Res. Dev., 16 (1977) 121.
4. L. L. Bohm, Polymer, 19 (1978) 545.
5. A. Ye. Shilov, A. K. Shilova and B. N. Bobkov, Polymer Sci., USSR 4 (1962) 526.

6. E. A. Fushman, V.I. Tsvetkova and N.M. Chirkov, Dokl. Akad. Nauk SSR 164 (1965) 1085.

7. E. A. Fushman, V.I. Tsvetkova and N.M. Chirkov, Izv. Akad. Nauk USSR (1965) 2075.

8. G. Henrici-Olivé and S. Olive, Angew, Chem., Internat. Ed., 6 (1967) 790.

9. W. P. Long and D. Breslow, Liebigs Ann. Chem., (1975) 463.

10. J. A. Waters and G. A. Mortimer, J. Organometal. Chem., 77 (1974) 231.

11. E. F. Lutz, J. Am. Chem. Soc., 83 (1961) 2551.

12. a) R. A. Colman, T. V. Harris, R. B. Dickson and D. W. Thompson, J. Organometal. Chem., 69 (1974) C27; b) R. A. Colman, H. E. Tweedy, D. W. Thompson, J. Organometal. Chem., 129 (1977) 69; c) R. A. Colman D. W. Thompson, L. C. Smedley and H. E. Tweedy, J. Org. Chem., 42 (1977) 4147; d) D.E. Van Horn and E. Negishi, J. Am. Chem. Soc., 100 (1978) 2252; e) B. B. Snider, M. Karras and R.S.E. Conn, J. Am. Chem. Soc., 100 (1978) 4624.

13. G. Stork and E. Colvin, J. Am. Chem. Soc., 93 (1971) 2080.

14. W. P. Long and D. S. Breslow, J. Am. Chem. Soc., 82 (1960) 1953.

15. a) M. S. Newman and C. D. Beard, J. Am. Chem. Soc., 92 (1970) 4309; b) M. S. Newman and T. B. Patrick, J. Am. Chem. Soc., 92 (1970) 4312.

16. P. F. Hudrlik in D. Seyferth, Ed., "New Applications of Organometallic Reagents in Organic Synthesis", Elsevier, Amsterdam, The Netherlands, 1976, pp. 127-160.

17. P. C. Wailes and R. S. P. Coutts, "Organometallic Chemistry of Titanium, Zironium and Hafnium", Academic Press, New York, N.Y., 1974, pp. 94 ff.