Table I. Reaction of Organotransition Metals with LiCH(Cl)SiMe<sub>2</sub>R'<sup>a</sup>

	-			
L,MR	R' <sup>b</sup> of LiCH(Cl)SiMe <sub>2</sub> R'	RCH <sub>2</sub> SiMe <sub>2</sub> R' (%) <sup>c</sup>	Me <sub>3</sub> SiR' (%)	RR (%) <sup>d</sup>
$\overline{Cp_2Ti(Bu-n)_2}$	Ph (1)	13	67	е
$Cp_2Zr(Bu-n)_2$	Ph (1.5)	85 (65)	15	е
$Cp_2Zr(Cl)Oct-n$	Ph (1)	55	40	е
Cp <sub>2</sub> ZrPh <sub>2</sub>	Ph (1)	60	29	4
$Cp_2Zr(Tol-p)_2$	Me (1)	70 (54)	е	е
$Cp_2ZrCl(Octenyl-1-E)$	Me (1)	75	е	е
$Cp_2Zr(Octenyl-1-E)_2$	Me (1)	45 <sup>f</sup>	е	20
$Cp_2Hf(Bu-n)_2$	Ph (1)	55	22	е
Cp <sub>2</sub> HfPh <sub>2</sub>	Me (1.3)	65	е	2
VPh <sub>3</sub>	Me (1.5)	56	е	22
CrPh <sub>2</sub>	Me (1.5)	76 (53)	е	е
MnPh <sub>2</sub>	Me (2)	82	е	4
MnBu <sub>2</sub>	Ph (1.5)	97 (88)	е	е
FePh <sub>2</sub>	Me (1.5)	39	е	29
CoPh <sub>2</sub>	Me (1.5)	12	е	70
(Et <sub>1</sub> P),NiPh,	Me (1.5)	9	е	65
LiCuPh <sub>2</sub>	Me (1.0)	35	е	е

<sup>a</sup> The reactants were mixed in THF at -78 °C. After 1 h the temperature was raised to 25 °C over 1 h. <sup>b</sup>The number in parentheses indicates the molar quantity of the reagent relative to L<sub>n</sub>MR. <sup>c</sup>By GLC. The numbers in parentheses indicate isolated yields. "The % figure corresponds to the number of mmol of this byproduct per 100 mmol of L<sub>n</sub>MR. "The yield was not determined. <sup>f</sup>A 1:1 mixture of (E)-1-(Nonenyl)SiMe<sub>3</sub> and (E)-2-(Nonenyl)SiMe<sub>3</sub>.

the envne was chromatographically isolated as a pure sample in 61% yield.

Acknowledgment. We thank the National Science Foundation (CHE-8503075) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (18710-AC1), for support of this research. We thank F. E. Cederbaum and Y. Zhang of our laboratories for their technical assistance in obtaining 2D NOESY <sup>1</sup>H NMR spectra.

## Virtually Complete Diastereofacial Selectivity in the S<sub>N</sub>2' Allylation of Organocopper Reagents

Eiichi Nakamura,\* Kouichi Sekiya, Masayuki Arai, and Satoshi Aoki

Department of Chemistry, Tokyo Institute of Technology Meguro, Tokyo 152, Japan Received December 8, 1988

Diastereoselective carbon-carbon bond formation in acyclic systems continues to attract the interest of chemists. Numerous examples of 1,2-asymmetric induction involving nucleophilic additions to carbonyl compounds have been reported,<sup>1</sup> and considerable progress has been made for controlling the stereochemistry of chiral centers bearing a heteroatom. On the other hand, there have been only scattered reports on acyclic asymmetric induction involving additions to olefins,<sup>2</sup> a process which can be employed as a means for the stereoselective construction of tertiary and quaternary carbon centers. In this paper we describe a highly regio- and diastereoselective  $S_N 2'$  reaction of organocopper reagents with 4-alkoxy allylic chlorides (1 and 2) that creates tertiary and quaternary carbon centers often with virtually complete diastereofacial selectivity (eq 1). To our knowledge, this reaction represents the first example where an S<sub>N</sub>2' allylation reaction of carbon nucleophile3 has been examined for its potential in asymmetric induction.

In order for this allylation method to constitute a useful synthetic strategy, it is first necessary that the reaction be highly  $S_N 2'$ 

Academic Press: New York, 1983; Vol. 2, Chapter 5.
(2) Cf.: Yamamoto, Y.; Nishii, S.; Ibuka, T. J. Chem. Soc., Chem. Commun. 1987, 464. Yamamoto, Y.; Nishii, S.; Ibuka, T. J. Am. Chem. Soc. 1988, 110, 617. Kruger, D.; Sopchik, A. E.; Kingsbury, C. A. J. Org. Chem. 1984, 49, 778. Salomon, R. G.; Miller, D. B.; Raychaudhuri, S. R.; Avasthi, K.; Lal, K.; Levison, B. S. J. Am. Chem. Soc. **1984**, 106, 8296. Nicolaou, K. C.; Pavia, M. R.; Seitz, S. P. J. Am. Chem. Soc. **1981**, 103, 1224.

(3) Review: Magid, R. M. Tetrahedron 1980, 36, 1901.



selective.<sup>4</sup> Unfortunately, the reaction of a standard cuprate reagent, e.g.,  $Bu_2CuLi$ , with *trans*-chloride 1 ( $R^1 = i$ -Pr,  $R^2 =$ benzyl,  $R^3 = H$ ) in THF gave predominantly the S<sub>N</sub>2 product<sup>5</sup> (Table I, entry 1). On the basis of our previous experience on the reactions of zinc alkyls,<sup>4c</sup> we next examined the reaction of the "zinc cuprate",6 prepared by treatment of a Gilman reagent with 1 equiv of anhydrous ZnCl<sub>2</sub> prior to addition of the substrate. The reagent " $R_2CuZnCl$ " reacted quantitatively with 1 at -70 °C to afford the desired  $S_N2'$  allylation product 3 with 98% regioselectivity and, more importantly, a single anti diastereomer<sup>6c</sup> (entry 2) was realized. No trace ( $\ll 0.2\%$ ) of the other diastereomer could be detected by capillary GLC analysis versus an authentic mixture of diastereomers. Excellent selectivities were also observed for the reaction of 1 with " $Me_2CuZnCl$ " (entry 7), "Bu<sub>2</sub>CuTi(*i*-PrO)<sub>3</sub>" (entry 3),<sup>6b</sup> and BuCu·BF<sub>3</sub><sup>7</sup> (entry 4). The moderately regioselective reaction of a vinyl cuprate reagent<sup>4b</sup> was also diastereoselective to give a 1,4-diene containing a chiral center between the olefins (entry 8). Not unexpectedly, the reaction of a lithium alkyl showed little selectivity.

A high level of anti selectivity has been consistently observed for 1 ( $R^3 = H$ ) regardless of the nature of the  $R^1$  substituent on the C(4) stereogenic center (entries 11 and 12), the  $R^2$  protecting group on oxygen (entries 9 and 10), or the nature of the leaving group (entry 13). The reaction of the cis isomer  $2 (R^3 = H)$  was also anti selective<sup>6c</sup> (entries 14 and 15).

We also found that a catalytic reagent generated in situ from a zinc alkyl and a catalytic amount of CuBr·Me<sub>2</sub>S<sup>4c</sup> can lead to results comparable to those observed with more elaborate stoichiometric reagents (entry 5). The advantages of the catalytic system follow from the characteristics of the reagent: (1) higher thermal stability that allows a >99% diastereoselective reaction to be performed at room temperature, (2) diverse and generally simpler preparation of organozinc reagents,<sup>8</sup> and (3) distinctively higher functional group tolerance, as has recently demonstrated.<sup>8</sup> This last point is illustrated by the reaction of a zinc homoenolate<sup>9</sup> (entry 6) which gives the  $S_N 2'$  product 4 as a single diastereomer.

(5) The formation of 1:1 stereoisomeric  $S_N 2$  products from 2 indicates that the " $S_N 2$ " reaction of Bu<sub>2</sub>CuLi is not a simple substitution reaction.

(6) (a) Presently, the nature of the "zinc cuprate" is totally unknown. Interestingly, BF<sub>3</sub>·Et<sub>2</sub>O<sup>4a,7a</sup> and Me<sub>3</sub>SiCl,<sup>7b</sup> which strongly assist conjugate addition of cuprates, were completely ineffective in the  $S_N 2'$  reaction. For an excellent study on the nature of such reagents, see: Lipshutz, B. H.; Ellsworth, D. L.; Siahaan, T. J. Am. Chem. Soc. 1988, 110, 4834. (b) General procedure: To a suspension of CuBr-Me<sub>2</sub>S (1.10 mmol) in 2 mL of THF is added BuLi in hexane (2.20 mmol) at -70 °C, and the clear solution was stirred at -40 °C for 40 min. Freshly fused ZnCl<sub>2</sub> (or TiCl(<sup>i</sup>PrO)<sub>3</sub>) (1.15 mmol) in THF is added, and, after 15 min, allylic halide 1 (1.00 mmol) in 1 mL of THF is added. After 15 h at -70 °C or at -40 °C, the reaction mixture is worked up, and the product is purified by chromatography. (c) The Masamune nomenclature is applied for the original carbon skeleton in 1 taken as the main chain: Masamune, S.; Ali, S. A.; Snitman, D. L.; Garvey, D. S. Angew. Chem., Int. Ed. Engl. 1980, 19, 557

(7) (a) R<sub>2</sub>CuLi-BF<sub>3</sub>: Smith, A. B.; Jerris, P. J. J. Am. Chem. Soc. 1981, Matsuzawa, S.; Horiguchi, Y.; Kuwajima, I. Tetrahedron Lett. 1986, 27, 4029. Horiguchi, Y.; Matsuzawa, S.; Nakamura, E.; Kuwajima, I. Tetra-hedron Lett. 1986, 27, 4025. Johnson, C. R.; Marren, T. J. Tetrahedron Lett. 1987, 28, 27. Nakamura, E.; Matsuzawa, S.; Horiguchi, Y.; Kuwajima, I. Tetrahedron 1989, 45, 349.

(9) Nakamura, E.; Aoki, S.; Sekiya, K.; Oshino, H.; Kuwajima, I. J. Am. Chem. Soc. 1987, 109, 8056.

<sup>(1)</sup> Review: Eliel, E. L. In Asymmetric Synthesis; Morrison, J. D., Ed.;

<sup>(4)</sup> Only a few, highly  $S_N 2'$  selective allylations have been reported: (a) RCu-BF<sub>3</sub>: Yamamoto, Y.; Yamamoto, S.; Yatagai, H.; Maruyama, K. J. Am. Chem. Soc. 1980, 102, 2318. (b) RCu(CN)MgBr: Tseng, C. C.; Paisley, S. D.; Goering, H. L. J. Org. Chem. 1986, 51, 2884. (c) Sekiya, K.; Nakamura, E. Tetrahedron Lett. 1988, 29, 5155.

<sup>(8)</sup> Cf.: Tamaru, Y.; Ochiai, H.; Nakamura, T.; Yoshida, Z.-i. Angew. Chem., Int. Ed. Engl. 1987, 26, 1157. Knochel, P.; Yeh, M. C. P.; Berk, S. C.; Talbert, J. J. Org. Chem. 1988, 53, 2390. Nakamura, E.; Sekiya, K.; Kuwajima, I. Tetrahedron Lett. 1987, 28, 337.

Table I. Rokio and Steleoselective Reaction of Anylic Handes I (R - H) and Z (R -	= H)a
---	-------

	h	nalide		temn <sup>e</sup>	%		S <sub>N</sub> 2′	product			
entry	<b>R</b> <sup>1</sup>	R <sup>2</sup>	"RCu"	°C	yield	S <sub>N</sub> 2':S <sub>N</sub> 2 <sup>d</sup>	(major di	astereomer)	anti:syn <sup>d</sup>	S <sub>N</sub> 2	product
							trans-Chloride (1: )	( = Cl)			
1	'Pr	Bn	Bu <sub>2</sub> CuLi	-70, rt	61	12:88	$7 (R^2 = Bn)$	OR <sup>2</sup>	100:0	8 (R <sup>2</sup> = Bn)	OR <sup>2</sup> Bu
2 3 4 5			$\begin{array}{l} Bu_2CuZnCl\\ Bu_2CuTi(O'Pr)_3\\ BuCu \cdot BF_3\\ Bu_2Zn/catalytic\\ Cu^b \end{array}$	70 70 70 rt	100 91 87 80	98:2 98:2 98.6:1.4 98:2			100:0 100:0 99.6:<0.4 99.3:0.7		
6			Zn(CH <sub>2</sub> ) <sub>2</sub> CO- O'Pr/catalytic Cu <sup>e</sup>	25	73	93:7	4	OBn COO'Pr	100:0°		
7			Me <sub>2</sub> CuZnCl	-70, rt	98	95:5	<b>9</b> (R <sup>2</sup> = Bn)		100:0	10 (R <sup>2</sup> = Bn)	OR <sup>2</sup> Me
8			( <i>trans</i> -1-hex- enyl) <sub>2</sub> - CuZnCl	–70, rt	67	72:28	11		>95:5	12	
9 10	′Pr ′Pr	MOM TBDMS	Bu2CuZnCl Bu2CuZnCl	-70 -70	67 93	99:1 97:3	7 (R = MOM) 7 (R = TBDMS)		100:0 94:6	8 (R <sup>2</sup> = MOM) 8 (R <sup>2</sup> = TBDMS)	
11	'Bu	мом	Bu <sub>2</sub> CuZnCl	-70	79	99:1	13		100:0		
12	"Pen	мом	Bu <sub>2</sub> CuZnCl	-70	73	99:1	14		75:25	15	OMOM Pen Bu
13	'Pr	Bn	Bu <sub>2</sub> CuZnCl	70	93	57:47	trans-Bromide (1: $\lambda$ 7 (R <sup>2</sup> = Bn)	K = Br)	100:0	$8 (R^2 = Bn)$	
14 15	'Pr	Bn	BuCu·BF <sub>3</sub> Bu <sub>2</sub> CuZnCl	-70 -70	100 100	100:0 100:0	cis-Chloride (2: X 7 ( $R^2 = Bn$ ) 7 ( $R^2 = Bn$ )	= Cl)	82:18 78:22		

<sup>a</sup> The cuprate reactions were carried out in THF as described in footnote 6b, unless otherwise noted. In entries 1, 5, and 6 the reaction mixture was warmed up soon after the addition of the substrate, and in entries 7 and 8 the temperature was kept at -70 °C for 4-12 h, -40 °C for 3-8 h, and finally warmed to 20 °C. Stereochemistry was assigned unambiguously for entries 5, 9, and 10 and the others by analogy. Bn = benzyl, MOM = methoxymethyl, TBDMS = *tert*-BuMe<sub>2</sub>Si, "Pen = *n*-pentyl. <sup>b</sup> The reaction was performed with 1.2 equiv of Bu<sub>2</sub>Zn (from 2 BuLi and ZnCl<sub>2</sub>) in the presence of 5% CuBr·Me<sub>2</sub>S and 2 equiv of HMPA in THF for 15 h. <sup>c</sup> Zinc homoenolate (ref 9) was reacted as in entry 4 (in DMF/THF) for 15 h. The diastereoselectivity was determined by 200 MHz <sup>1</sup>H NMR. <sup>d</sup> The 100:0 ratio is based on a value determined by capillary GLC, under conditions where at least 0.2% (3% in entry 1) of the other isomer can be detected. <sup>e</sup>rt stands for room temperature.

The reaction indicates that an internal functional group in the reagent may not affect the diastereoselectivity. Thus the catalytic methodology provides ready access to multifunctional compounds possessing elements of chirality.

One of the distinct advantages of this allylation reaction is its applicability to the stereoselective construction of a quaternary center in an acyclic system—generally a difficult synthetic operation.<sup>10</sup> Despite steric congestion at the alkylated center, the reaction of 5 with either "Bu<sub>2</sub>CuZnCl" (at -70 °C) or "Me<sub>2</sub>CuZnCl" (at -40 °C to room temperature) proceeded with good  $S_N2'$  selectivity and again with virtually complete diastereoselectivity (eq 2). Comparison of the product of methyl cuprate



addition with authentic samples confirmed that the course of the reaction was the same as that in the examples in Table I and that less than 0.1% of the other diastereoisomer was produced in the reaction. The homoallylic ethers such as **6** can be oxidatively converted to aldols and 1,3-diols bearing quaternary centers.<sup>11</sup> The abundance of synthetic entries to chiral allylic and propargylic alcohols<sup>12</sup> (which serve as starting materials for the present reaction) suggests that this reaction should prove to be very useful for the construction of chiral quaternary centers.

Conventional Felkin–Anh<sup>13</sup> considerations combined with the concept of  $d-\pi^*$  complexation in  $S_N 2'$  reactions<sup>14</sup> suggests that the observed diastereoselectivity can be explained on the basis of



the model depicted above.<sup>15</sup> Deviation from the Felkin-Anh model lies in the steric congestion of the "inside"<sup>16</sup> position: this

<sup>(10)</sup> Martin, S. F. Tetrahedron 1980, 36, 419. Cf.: Zweifel, G.; Shoup, T. M. J. Am. Chem. Soc. 1988, 110, 5578. Ibuka, T.; Miwa, T.; Nishi, S.; Yamamoto, Y. J. Chem. Soc., Chem. Commun. 1987, 1596.

<sup>(11)</sup> Cf. Häner, R.; Laube, T.; Seebach, D. J. Am. Chem. Soc. 1985, 107, 5396. Nakamura, E.; Yamago, S.; Machii, D.; Kuwajima, I. Tetrahedron Lett. 1988, 29, 2207.

may be rationalized as a consequence of the interaction between a copper d-orbital and an olefin's  $\pi^*$ -orbital that guides the bulky copper reagent to approach the olefin from above the center (as in hydroboration).<sup>16</sup> Any proposed model for organocopper couplings must, however, currently remain highly speculative owing to the mechanistic ambiguity associated with this chemistry.

Acknowledgment. We thank Professors Keiji Yamamoto and Bruce H. Lipshutz for helpful discussions and the Ciba-Geigy Foundation for financial support.

Supplementary Material Available: Typical experimental procedures, physical properties, and stereochemical assignment of the products (8 pages). Ordering information is given on any current masthead page.

 (13) (a) Chèrest, M.; Felkin, H.; Prudent, N. Tetrahedron Lett. 1968, 2199.
 (b) Anh, N. T.; Eisenstein, O. Nouv. J. Chim. 1977, 1, 61. Anh, N. T. Top. Curr. Chem. 1980, 88, 145.

(14) Corey, E. J.; Boaz, N. W. Tetrahedron Lett. 1984, 25, 3063.

(15) Cf.: Rousch, W. R.; Lesur, B. M. Tetrahedron Lett. 1983, 24, 2231. (16) Paddon-Row, M. N.; Rondan, N. G.; Houk, K. N. J. Am. Chem. Soc. 1982, 104, 7162.

## Selective Polymerization of Double Bonds in 1,5-Bis(trimethylsilyl)-3-methylenepentadiyne and 1,5-Bis(trimethylsilyl)-3-(2-propylidene)pentadiyne

Albert H. Alberts

Department of Chemistry, University of Groningen Nijenborgh 16, Groningen, The Netherlands 9747 AG Received September 1, 1988

In the context of the current interest in conductive hydrocarbon polymers and densely crosslinked organic solids,<sup>1,2</sup> we are investigating the syntheses and polymerization propensities of highly unsaturated hydrocarbon monomers.<sup>3</sup> In this report we describe the selective polymerization of double bonds in silylated 1,1-diethynylethene and butadiene and the characterization of a dimeric structure isolated from the polymeric product mixture of the latter.

Addition of 2 equiv of lithio(trimethylsilyl)acetylide in hexane to ethyl acetate in hexane at ambient temperature afforded the tertiairy alcohol 1 in good yield (70%) as a white solid, mp 41-42 °C, after recrystallization from octane at -20 °C. Dehydration of 1 in refluxing toluene was complete within 1-2 h (GC analysis), with use of a Dean-Stark trap and a catalytic amount of methanesulfonic acid. Removal of toluene under diminished pressure and subsequent purification of the product by column chromatography over silica gel eluting with pentane gave the silylated 3-methylene-1,4-pentadiyne 2, in 80% yield as a colorless oil.4 Last traces of toluene were removed in vacuum (0.1 mm), keeping 2 at 0 °C. Storage under inert atmosphere at -35 °C caused the compound to appear as a white crystalline solid (246.8 nm). The 1,1-diethynylbutadiene derivative 4 was synthesized in a similar manner. The tertiairy alcohol 3 was obtained in high yield (95%)



from addition of a 10-fold excess of allylmagnesium bromide to 1,5-bis((trimethylsilyl)ethynyl) ketone in dry ether at ambient temperature; 3 was purified by molecular distillation at 0.3 mm (bath temperature 85 °C) and obtained as a colorless oil. Dehydration analogous to the procedure for 2 gave 4 in 60% yield as a colorless liquid after chromatography over silica gel with pentane.

Monomer 2 can be polymerized without a catalyst in the absence of solvent in inert atmosphere to a pale yellow (O °C, 4-5 days, 60%, MW 4000) or an ochre-colored (80 °C, 30 min, 40%, MW 14000) solid isolated after reprecipitation from chlorocarbon solvents in methanol or acetone. We propose structure 5 for these polymers on the basis of the following evidence: (a) correct elemental analyses and determination of molecular weight (osmometry in  $CHCl_3$  and gel permeation), (b) the presence of the triple bond absorption in the IR (KBr pellet) spectrum at 2100  $cm^{-1}$ , (c) absence of absorptions in the 500–350-nm region (only a residual broad band around 252 nm), and (d) the appearance of a well-defined alkane C-H multiplet in H NMR (CDCl<sub>3</sub>, 60 and 300 MHz, 2 H, 1.5-1.6 ppm) and no appreciable detection of vinylic or aromatic resonances (broad multiplet SiMe<sub>3</sub> group, 18 H). After stirring the material in MeOH/KOH at 20 °C for 10 min more than 90% (H NMR, mass balance) of the silvl groups are characteristically hydrolyzed (extractive workup with CH<sub>2</sub>Cl<sub>2</sub>).

In case of the thermal polymerization of 4 (80 °C, neat, complete within 15 min, tanned amorphous solid) after chromatography over silica gel with pentane, a low yield of a mixture of oligomers is obtained, from which a small amount of a white compound (mp 69-70 °C, 262 nm) can be secured after crystallization from EtOH. The latter was determined to have structure  $6.^7$  Again double bonds have interacted leaving the geminal diethynyl substitution pattern intact.6,8

<sup>(12) (</sup>a) Cf.: Carlier, P. R.; Mungall, W. S.; Schröder, G.; Sharpless, K. B. J. Am. Chem. Soc. 1988, 110, 2978. Kitano, Y.; Matsumoto, T.; Sato, F. J. Chem. Soc., Chem. Commun. 1986, 1323 and references therein. (b) Cf.: Asymmetric Synthesis; Morrison, J. D., Ed.; Academic Press: New York, 1983: Vol. 2.

<sup>(1)</sup> Conducting Polymers; Skotheim, T. A., Ed.; Marcel Dekker: 1986; (i) Containing Tolymers, Skohenni, T. A., Ed., Marcer Derkell, 1980, New York, Vol. I and II. Especially the references to blends of polyacetylene: Galvin, M. E.; Wnek, G. E. Polym. Comm. 1982, 23, 795. Rubner, M. F.; Tripathy, S. K.; Georg, J.; Cholewa, R. Macromolecules 1983, 16, 870. (2) Neenan, T. X.; Whitesides, G. M. J. Org. Chem. 1988, 53, 1800.
 Callstrom, M. R.; Neenan, T. X.; Whitesides, G. M. Macromolecules 1983, 2530.

<sup>21, 3528.</sup> Rutherford, R.; Stille, J. K. Macromolecules 1988, 21, 3530 (3) Alberts, A. H.; Wynberg, H. J. Chem. Soc., Chem. Commun. 1988, 748

<sup>(4)</sup> The unprotected compound has been characterized previously: Böhm-Gössl, T.; Huismann, W.; Rohrschneider, L.; Schneider, W. H.; Ziegenbein, W. Chem. Ber. 1963, 96, 2504.

<sup>(5) 7</sup> was prepared via a Wittig reaction of trimethylsilyl propargylic aldehyde and the required phosphonium salt similar to the procedure of Hann et al. Hann, M. M.; Sammes, P. G.; Kennewell, P. D.; Taylor, J. B. J. Chem. Soc., Perkin Trans. 1 1982, 307.

<sup>(6)</sup> At this stage we can not exclude initiation of the polymerization of 2 and 4 by traces of oxygen. When a radical initiator (AIBN) was added to a 50% ww solution of 2 in toluene or octane at 80-90 °C, the polymerization was complete within 1-2 h. In this case, as in runs assisted by UV irradiation, however, the IR spectrum of the solid product (MW 30000 by GPC) clearly revealed the presence of allenic functions (1920 cm<sup>-1</sup>). Ziegler-Natta catalysts (TiCl<sub>4</sub>-AlEt<sub>3</sub>, Ti(OEt)<sub>4</sub>-AlEt<sub>3</sub>, 20 °C) in hexane did NOT promote the polymerization of 2.

<sup>(7)</sup> Structure 6 was established via elemental analysis, a mass spectrum, IR data and H NMR (60 and 300 MHz), confirmed by a preliminary X-ray crystallographic analysis (in cooperation with F. van Bolhuis)

<sup>(8)</sup> Japanese workers have demonstrated the protection of triple bond in polymerization reactions of silylated vinyl acetylene and butadiyne: Kanedo, ; Hagihara, N., Polym. Lett. 1971, 9, 275. Tsuchida, E.; Kobayashi, N.; Nakada, M.; Ohno, H.; Matsuda, H.; Nakanishi, H.; Kato, M.; New polym. Mat. 1988, 1, 1.