

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

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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.

- (12) (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.
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 (15) Cf.: Rousch, W. R.; Lesur, B. M. *Tetrahedron Lett.* **1983**, *24*, 2231.
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Selective Polymerization of Double Bonds in 1,5-Bis(trimethylsilyl)-3-methylenepentadiyne and 1,5-Bis(trimethylsilyl)-3-(2-propylidene)pentadiyne

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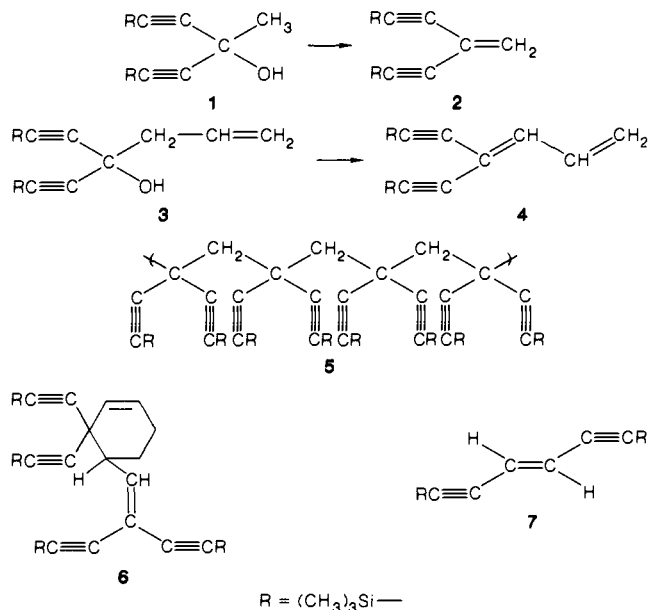
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In the context of the current interest in conductive hydrocarbon polymers and densely crosslinked organic solids,^{1,2} we are investigating the syntheses and polymerization propensities of highly unsaturated hydrocarbon monomers.³ In this report we 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 tertiary 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 tertiary alcohol **3** was obtained in high yield (95%)

- (1) *Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: 1986; 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* **1988**, *21*, 3528. Rutherford, R.; Stille, J. K. *Macromolecules* **1988**, *21*, 3530.
 (3) Alberts, A. H.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1988**, 748.
 (4) The unprotected compound has been characterized previously: Böhm-Gössl, T.; Huisman, W.; Rohrschneider, L.; Schneider, W. H.; Ziegenbein, W. *Chem. Ber.* **1963**, *96*, 2504.



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 (0 °C, 4–5 days, 60%, MW 4000) or an ochre-colored (80 °C, 30 min, 40%, MW 14 000) solid isolated after reprecipitation from chloroform 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 CHCl₃ 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 (CDCl₃, 60 and 300 MHz, 2 H, 1.5–1.6 ppm) and no appreciable detection of vinylic or aromatic resonances (broad multiplet SiMe₃ 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 silyl groups are characteristically hydrolyzed (extractive workup with CH₂Cl₂).

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}

(5) **7** 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.

(6) 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% w/w 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 30 000 by GPC) clearly revealed the presence of allenic functions (1920 cm⁻¹). Ziegler–Natta catalysts (TiCl₄–AlEt₃, Ti(OEt)₄–AlEt₃, 20 °C) in hexane did NOT promote the polymerization of **2**.

(7) 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).

(8) Japanese workers have demonstrated the protection of triple bond in polymerization reactions of silylated vinyl acetylene and butadiyne: Kanedo, I.; 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.

Heating the *E*-isomer of silylated 1,2-diethynylethene **7** for 20 h at 120 °C did NOT lead to polymerization. This monomer was recovered unchanged.^{5,10}

The transformation of **2** into **5** under mild conditions is a unique example of an uncatalyzed carbon-carbon bond-forming reaction. We are confident that examples of selective polymerization of double bonds in **2** and **4** will render considerable impulse to the development of new (conducting) hydrocarbon polymers and polymeric nets. A macromolecular blend¹ as intimate as two polyacetylene strands anchored to one polyethylene backbone (conceivable from the desilylated structure **5**) seems sterically possible in CPK models.

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(9) The presence of silyl groups is essential for the selectivity of the polymerization. Similar experiments with 1,1-diethynylethene derivatives **2** in which R is *tert*-butyl, 1-adamantyl, or phenyl invariably led to destruction of the triple bonds (IR).

(10) Anionic polymerization by adventitious basic initiators is unlikely because of the preparative history of monomers **2** and **4**. BF₃·(OEt)₂ and *n*-butyllithium in THF do not promote polymerization of **2**. Although the trimethylsilyl function is base-sensitive, we will pursue the possibility of an ionic polymerization in the near future.

Enzymatic Resolution of Racemic Amines: Crucial Role of the Solvent

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Asymmetric esterifications or transesterifications catalyzed by hydrolytic enzymes in nonaqueous media are emerging as a method of choice for facile kinetic resolutions of racemic alcohols, acids, and their derivatives.¹ In order to broaden this promising methodology, in the present study we have extended its applicability to another class of organic compounds with great synthetic utility²—chiral amines.

Our experimental strategy was based on the ability of lipases and other hydrolases to catalyze the reaction between carboxylic esters and amines in anhydrous organic solvents.³ With the objective of finding a stereoselective enzyme, we tested the protease subtilisin Carlsberg and lipases from *Candida cylindracea*, *Pseudomonas* sp., *Mucor* sp., porcine pancreas, and *Chromobacterium viscosum* as catalysts⁴ of the reaction between trifluoroethyl butyrate and the enantiomers of α -methylbenzylamine in octane.⁵ To our disappointment, for no enzyme was any

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(3) Zaks, A.; Klivanov, A. M. *Proc. Natl. Acad. Sci. USA* **1985**, *82*, 3192.

(4) The six enzymes were obtained and used as described previously.^{5b}

(5) Riva, S.; Klivanov, A. M. *J. Am. Chem. Soc.* **1988**, *110*, 3291.

(6) Trifluoroethyl butyrate is a highly activated ester that has been successfully used² for enzymatic acylation of alcohols in organic solvents. Octane as the reaction medium has been found to afford the optimal catalytic activity both with lipases³ and with subtilisin (Zaks, A.; Klivanov, A. M. *J. Biol. Chem.* **1988**, *263*, 3194).

Table I. Enantioselectivity of Subtilisin in the Acylation of α -Methylbenzylamine as a Function of the Solvent⁷

solvent	initial reaction rate (v), mM/h		v_S/v_R
	<i>S</i> -amine	<i>R</i> -amine	
toluene	0.38	0.40	0.95
cyclohexane	1.1	0.87	1.3
acetonitrile	1.8	1.4	1.3
octane	1.3	0.9	1.4
carbon tetrachloride	0.71	0.46	1.5
ethyl acetate	1.4	0.88	1.6
butyl ether	0.24	0.13	1.8
pyridine	8.3	3.3	2.5
dimethylformamide	0.66	0.23	2.9
tetrahydrofuran	2.6	0.75	3.5
<i>tert</i> -amyl alcohol	4.5	1.1	4.1
3-methyl-3-pentanol	23	3.0	7.7

Table II. Preparative Resolution of Racemic Amines via the Acylation with Trifluoroethyl Butyrate Catalyzed by Subtilisin in Anhydrous 3-Methyl-3-pentanol^a

racemic amine	product ^b	$[\alpha]^{25}_D$	ee, %
α -methylbenzylamine	<i>S</i> -amide ^c	-103° (c 2, MeOH)	85 ^c
1-(1-naphthyl)ethylamine	<i>S</i> -amide ^c	-49.9° (c 2, MeOH)	98 ^d
1-(1-naphthyl)ethylamine	<i>R</i> -amine	+54.8° (c 2, EtOH)	99 ^e
1-methyl-3-phenylpropylamine	<i>S</i> -amide ^f	-25.2° (c 1, MeOH)	90 ^g
2-aminoheptane	<i>S</i> -amide ^c	-4.6° (c 1, MeOH)	63 ^h
α -methyltryptamine	<i>R</i> -amine ⁱ	-32.3° (c 1, MeOH)	95 ^e
α -methyltryptamine	<i>S</i> -amide ^j	-2.7° (c 1, MeOH)	99 ^j
1,3-dimethylbutylamine	<i>S</i> -amide ^k	+5.5° (c 2, MeOH)	59 ^h
1-cyclohexylethylamine	<i>S</i> -amide ^c	-21.9° (c 1, MeOH)	88 ^c
phenylalaninamide	<i>S</i> -amide ^c	+13.3° (c 2, MeOH)	80 ^c
1,2,3,4-tetrahydro-1-naphthylamine	<i>S</i> -amide ^l	-85.1° (c 1, MeOH)	88 ^m

^a All reaction mixtures were stirred vigorously under the following conditions (in the order of entries from top to bottom): racemic amine concentrations (M)—0.2, 0.5, 0.42, 0.2, 0.2, 0.2, 0.2, 0.24, 0.2, 0.12, and 0.2; trifluoroethyl butyrate concentrations (M)—0.2, 0.5, 0.56, 0.4, 0.4, 0.4, 0.4, 0.48, 0.4, 0.12, and 0.2; subtilisin concentrations (mg/mL)—5, 2, 6, 10, 10, 10, 10, 12, 12, 4, and 8; solvent volumes (mL)—50, 20, 15, 30, 30, 25, 25, 25, 25, 25, and 30; temperatures (°C)—30, 30, 30, 30, 45, 45, 30, 45, 30, 45, and 30; reaction times (hours)—25, 22, 141, 64, 54, 142, 69, 96, 101, 23, and 52. ^b The products were obtained as follows (in the order of entries from top to bottom): degrees of conversion (%)—35, 33, 57, 38, 36, 54, 39, 30, 31, 42, and 36; isolated yields (%)—33, 26, 46, 32, 32, 30, 25, 27, 35, and 32; melting points (°C)—39–41, 126–127, oil, 44–45, oil, 126–127, 74–75, oil, 83–85, 174–175, and 77–78; purities by GC (%)—100, 99, 99 (contains some solvent), 100, 99, 100, 100, 99, 100, 99, and 100. All products were purified by silica gel column chromatography. The identity of all products was confirmed by high-resolution mass spectrometry and ¹H NMR and, whenever possible, by comparison with authentic samples. ^c Determined by comparison of $[\alpha]^{25}_D$ with that of the chemically butyrylated authentic *S*-amine. ^d Determined by HPLC on a chiral column (Regis's Pirkle 1A). ^e Determined by capillary GC following acylation with the Mosher acid chloride (Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543). ^f Concluded from comparison with its acetyl analogue (Yamamoto, Y.; Oda, J.; Inouye, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3744). ^g The ee of the unreacted amine was determined as outlined in footnote e, and then the amine was chemically butyrylated, and its $[\alpha]^{25}_D$ was compared with that of the amide product of the enzymatic reaction. ^h Determined by partial acid hydrolysis, followed by the procedure outlined in footnote e. ⁱ Determined from the literature data (Reppe, D. B.; Ferguson, W. J. *J. Heterocycl. Chem.* **1976**, *13*, 775). ^j See footnotes c and i. ^k Determined from the analysis of $[\alpha]^{25}_D$ of the unreacted amine which was compared to the literature data (Mazur, R. H. *J. Org. Chem.* **1970**, *35*, 2050). ^l Determined as in footnote k, except that the literature reference was: Ghislandi, V.; Vercesi, D. *Farmaco, Ed. Sci.* **1971**, *26*, 474. ^m Determined as described in footnote k, except that [Eu(tfc)₃] was used as the NMR shift reagent (Goering, H. L.; Eikenberry, J. N.; Koremer, G. S. *J. Am. Chem. Soc.* **1971**, *93*, 5913).

substantial enantioselectivity observed: the ratio of the initial rates for *S* and *R* isomers (v_S/v_R) was found to be⁷ 1.4, 0.88, 0.94, 1.0, 1.5, and 0.66, respectively.

(7) 100 mg/mL (except for 10 mg/mL subtilisin) enzyme suspensions in anhydrous octane containing 200 mM trifluoroethyl butyrate and 100 mM amine were shaken at 45 °C and 250 rpm; the reactions were followed by capillary gas chromatography on the basis of the appearance of the amide product. No appreciable aminolysis reaction was detected without enzymes.