and S_N2 reactions share a common intermediate complex, $[(CN)_2CH_2 \cdot Cl^-]$.[41] The observation of proton transfer indicates that the lifetime of the complex is sufficiently long to allow for structural rearrangement and rules out a mechanism in which the leaving group (Cl^-) is ejected immediately following the substitution event. The lifetimes of S_N2 reaction intermediates may provide insight about the details of ion–molecule complex dissociation dynamics and energy transfer within the ion–molecule complex. Recent theoretical results of Vande Linde and Hase[36] and the experimental results of Graul and Bowers,[33] Viggiano and co-workers,[42] and Buckner and co-workers[39] on S_N2 reactions have suggested that energy transfer between certain modes within the ion–molecule complex may be inefficient. A detailed interpretation of our results, and their relationship to inefficient energy transfer, will be the subject of a forthcoming publication.

Acknowledgment. We are grateful to the National Science Foundation for support of this research.

Registry No. $(CN)_2CH^-$, 41470-37-5; CN^-, 57-12-5; $ClCH_2CN$, 107-14-2.

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[41] The expected structures for the S_N2 and proton-transfer complexes may be different. The energy difference is expected to be small, however, and interconversion should be facile.

[42] Viggiano, A. A. Personal communication.

Ring-Opening Metathesis Polymerization of Substituted Bicyclo[2.2.2]octadienes: A New Precursor Route to Poly(1,4-phenylenevinylene)

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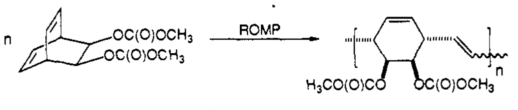
Received July 9, 1992

Poly(1,4-phenylenevinylene) (PPV),[1] a perfectly alternating copolymer of *p*-phenylene and *trans*-vinylene units, possesses attractive material properties. Thin films of PPV display high electrical conductivity when doped (σ = 5000 S/cm),[2] a large, third-order nonlinear optical response ($\chi^{(3)} = 1.5 \times 10^{-10}$ esu),[3] and photo- and electroluminescence in the visible region.[4] However, the extended planar topology of the PPV backbone, which renders it infusible and insoluble in nonreactive media, limits the capacity for post-synthesis fabrication of the material. A convenient method to circumvent this problem consists of a two-step synthesis via a processable intermediate polymer.[5] This precursor polymer can be fabricated into the desired form and subsequently converted to the target polymer by a clean, intramolecular chemical reaction. Wessling and Zimmerman have reported the synthesis of a processable, water-soluble poly(1,4-xylylenesulfonium salt) that undergoes a thermally-induced elimination to PPV under mild conditions.[6] The precursor polymer formation occurs via the generation and in situ polymerization of *p*-xylylenesulfonium chloride, a very reactive intermediate.[7] Therefore, certain aspects of the polymer structure, for example, the degree of polymerization, polydispersity, and sequence homology of copolymers, are difficult to control in this synthetic route. We report an alternative precursor synthesis of poly(1,4-phenylenevinylene) based on the *living* ring-opening metathesis polymerization (ROMP)[8] of bis(carboxylic ester) derivatives of bicyclo[2.2.2]octa-5,8-diene-*cis*-2,3-diol **1** and subsequent pyrolytic acid elimination from the polymer.[9]

In contrast to bicyclo[2.2.1]heptenes, few examples of the ring-opening metathesis polymerization of bicyclo[2.2.2]octenes or -octadienes have been reported[10] although the calculated strain energies of the two ring systems (16.0 and 20.4 kcal/mol, respectively)[11] are significantly larger than cycloalkenes that undergo successful polymerization. The lack of general synthetic routes to simple bicyclo[2.2.2]octenes and -octadienes, compared to the readily available norbornenes, has hindered their utilization as ROMP substrates. The synthesis of the bicyclo[2.2.2]octadiene monomers of type **1** is depicted in Scheme I. Diels–Alder reaction between the acetonide adduct of 3,5-cyclohexadiene-*cis*-1,2-diol and ethynyl *p*-tolyl sulfone generates the anti cycloadduct as the sole product.[12] Reductive desulfonylation[13] followed by acid-catalyzed hydrolysis of the acetonide yields the bicyclic diol, which may be converted into bis(carboxylate) derivatives **1a** and **1b**.[14]

Ring-opening polymerization of **1a** and **1b** was attempted with the olefin metathesis catalyst $[Mo({=}NAr)({=}C(H)CMe_2Ph)(OCMe_2(CF_3))_2]$ **2** (Ar = 2,6-diisopropylphenyl),[15] which initiates the polymerization of both monomers at ambient temperature (eq 1). However, only **1b** undergoes polymerization under these conditions in high yield.[16] A single downfield doublet (12.69 ppm), characteristic of a propagating alkylidene $C_\alpha H$, is observed in the ^1H NMR spectra of polymerizations in THF. This resonance increases in intensity at the expense of the initiating alkylidene as the reaction proceeds to completion. Preliminary investigations indicate that the rate of polymerization in CH_2Cl_2 is at least an order of magnitude faster than in THF and that the rate of initiation is marginally slower than the rate of propagation in both cases. Typical preparative-scale polymerizations are performed in CH_2Cl_2, terminated by capping with benzaldehyde, and isolated by precipitation.[17] Relatively narrow molecular



(1)

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[1] Kossmehl, G. A. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1, Chapter 10.

[2] (a) Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Synth. Met.* **1987**, *17*, 639. (b) Han, C. C.; Elsenbaumer, R. L. *Synth. Met.* **1989**, *30*, 123.

[3] (a) Bubeck, C.; Kaltbeitzel, A.; Lenz, R. W.; Neher, D.; Stenger-Smith, J. D.; Wegner, G. *NATO ASI Ser. E* **1989**, *162*, 143. (b) Kaino, T.; Kobayashi, H.; Kubodera, T.; Kurihara, T.; Saito, S.; Tsutsui, T.; Tokito, S. *Appl. Phys. Lett.* **1989**, *54*, 1619.

[4] (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539. (b) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47.

[5] (a) Feast, W. J.; Friend, R. H. *J. Mater. Sci.* **1990**, *25*, 3796. (b) Feast, W. J. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1, Chapter 1.

[6] (a) Wessling, R. A.; Zimmerman, R. G. U.S. Patents 3 401 152, 1968, and 3 705 677, 1972. (b) Wessling, R. A. *J. Polym. Chem.: Polym. Symp.* **1985**, *72*, 55. (c) Lenz, R. W.; Han, C. C.; Stenger-Smith, J.; Karasz, F. E. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 3241.

[7] Lahti, P. M.; Modarelli, D. A.; Denton, F. R.; Lenz, R. W.; Karasz, F. E. *J. Am. Chem. Soc.* **1988**, *110*, 7258.

[8] (a) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907. (b) Schrock, R. R. *Acc. Chem. Res.* **1990**, *24*, 158.

[9] A similar thermal aromatization of a cyclohexenyl ring in a polymer has been employed in the precursor synthesis of poly(*p*-phenylene): (a) Ballard, D. G. H.; Courtis, A.; Shirley, I. M.; Taylor, S. J. *J. Chem. Soc., Chem. Commun.* **1983**, 954. (b) Ballard, D. G. H.; Courtis, A.; Shirley, I. M.; Taylor, S. J. *Macromolecules* **1988**, *21*, 294. (c) McKean, D. R.; Stille, J. K. *Macromolecules* **1987**, *20*, 1787.

[10] The ring-opening metathesis polymerization of bicyclo[2.2.2]octene has been described with classical catalyst systems: (a) Hamilton, J. G.; Ivin, K. J.; Rooney, J. J. *Br. Polym. J.* **1985**, *17*, 41. (b) Ofstead, E. A. *Makromol. Chem.* **1972**, *154*, 21.

[11] Allinger, N. A.; Sprague, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734.

[12] The Diels–Alder reaction between the acetonide derivative of 3,5-cyclohexadiene-*cis*-1,2-diol and linear dienophiles affords the anti cycloadducts with high stereoselectivity: (a) Mahon, M. F.; Molloy, K.; Pittol, C. A.; Pryce, R. J.; Roberts, S. M.; Ryback, G.; Sik, V.; Williams, J. O.; Winders, J. A. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1255. (b) Cotterill, I. C.; Roberts, S. M. *J. Chem. Soc., Chem. Commun.* **1988**, 1628.

[13] Künzer, H.; Stahnke, M.; Sauer, G.; Wiechert, R. *Tetrahedron Lett.* **1991**, *32*, 1949.

[14] (a) The ^1H and ^{13}C NMR and analytical data are consistent with the structural formulations of the intermediates and products in Scheme I.[14b] (b) Please see supplementary material.

[15] Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3877.

[16] Monomer **1a** undergoes irreversible carbonyl olefination with the propagating alkylidene under these conditions, forming the oxo complex, $[Mo({=}NAr)({=}O)(OCMe_2(CF_3))_2]$, and terminating the polymerization after only a few turnovers.

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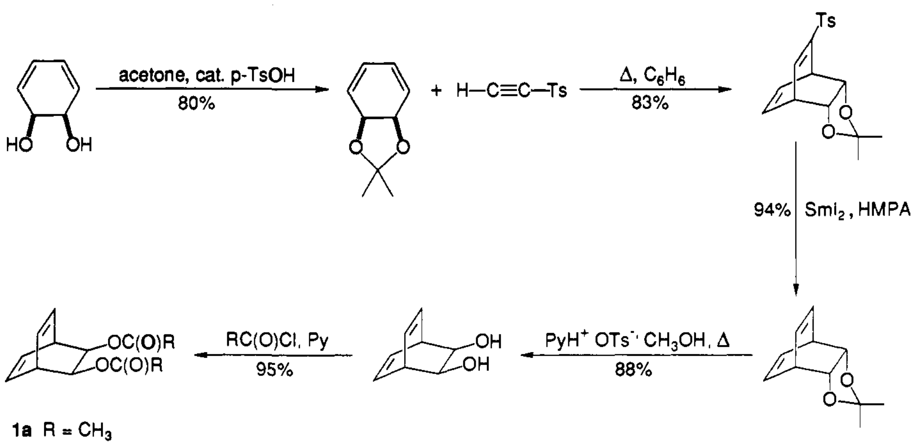
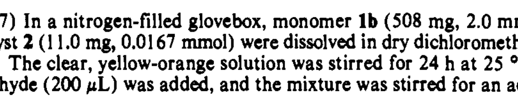
Scheme I



1a R = CH_3
1b R = OCH_3

weight distributions (PDI ≈ 1.2–1.3) of the polymers were obtained, consistent with a living polymerization with slow initiation.[18] Ratios of monomer:catalyst as high as 250:1 have been employed without diminution of yield or broadening of the molecular weight distribution. The ^1H and ^{13}C NMR spectroscopic analyses of the microstructure of poly-**1b** suggest a polymer structure that consists of alternating sequences of vinylene and 1,4-cyclohexenylene groups.[19] An approximately equal distribution of *cis*- and *trans*-vinylene units is inferred from the exact doubling of the nonolefinic resonances in the ^1H NMR spectrum of poly-**1b**. In addition, a four-line pattern for the vinylene carbon resonances is observed in the ^{13}C NMR spectrum, indicating the presence of four pairs of double bond isomers in approximately equal amounts.

The depicted syn orientation of the methoxycarbonyl groups and the ring-junction protons in poly-**1b** represents the preferred geometry for a concerted elimination of acid, which is supported by the facile thermolytic conversion of poly-**1b** to PPV (eq 2).



(2)

This orientation should arise from metathesis of the least hindered of the two unsubstituted double bonds of the substrate, that is, the exo-substituted olefin.[20] Thermogravimetric analysis of poly-**1b** indicates a 60% mass loss at an onset temperature of 265 °C, which corresponds to the loss of 2 equiv of methylcarbonic acid per repeat unit. Infrared analysis of the gases evolved during the pyrolysis suggests that the predominant volatile products are carbon dioxide and methanol from decomposition of methylcarbonic acid.[21] Isothermal pyrolysis of thin films of poly-**1b**, spin-coated onto NaCl disks, under flowing argon at 280 °C affords yellow films of PPV. The elimination process may be catalyzed by the addition of catalytic amounts of tri-*n*-octylamine, which lowers the pyrolysis temperature by approximately 80 °C.[22] Optically clear, coherent films of poly-**1b** containing 3 mol % $(n\text{-octyl})_3N$ may be cast from 1,2-dichloroethane, which upon heating at 200 °C yield free-standing films of PPV that retain their original shape. The IR and UV spectroscopic analyses of these films[23] are identical to PPV prepared via the Wessling route.[24] Although the precursor polymer consists of both *cis*- and *trans*-vinylene units, only the trans isomer could be detected in the IR spectra of the product (δ_{CH} = 960 cm^{-1}). This indicates that a thermal cis to trans isomerization occurs during the elimination. The optical absorbance spectrum of this PPV is essentially superimposable with the reported spectrum, suggesting similar structures for the two materials. The ^{13}C CPMAS NMR spectra of the PPV films display two resonances at 135 (1,4-phenylene C's) and 127 ppm (vinylene and 2,3-phenylene C's) in accord with literature values.[25] The absence of resonances in the carbonyl and aliphatic carbon regions of the spectrum indicates that the conversion proceeds to completion with negligible formation of saturated defects in the PPV backbone.

In summary, this method provides a new route to high-quality PPV from a precursor polymer that is amendable to conventional, nonaqueous fabrication techniques. In addition, the *living* metathesis polymerization of **1b** permits direct control over the structure of PPV, which includes the ability to narrowly define the degree of polymerization, the molecular weight distribution, the end group, and the sequence structure of copolymers.[8] The effect of these structural variations on the physical properties of PPV films is a subject of current investigation.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (AFOSR-88-0094). We thank Dr.

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(17) In a nitrogen-filled glovebox, monomer **1b** (508 mg, 2.0 mmol) and catalyst **2** (11.0 mg, 0.0167 mmol) were dissolved in dry dichloromethane (3.5 mL). The clear, yellow-orange solution was stirred for 24 h at 25 °C. Benzaldehyde (200 μL) was added, and the mixture was stirred for an additional 2 h. The reaction mixture was diluted to 20 mL by addition of dichloromethane; this solution was added dropwise to rapidly stirred methanol. The polymer was isolated by filtration and dried in vacuo for 12 h. The polymer was purified by reprecipitation from methylene chloride/methanol: yield, 492 mg (97%) of a colorless powder; IR (KBr) ν 3029, 2957, 1750, 1443, 1284, 1258, 944, 787, 732 cm^{-1}; DSC, T_g = 225–226 °C. Anal. Calcd for $(C_{12}H_{14}O_6)_n$: C, 56.69; H, 5.55. Found: C, 56.39; H, 5.41.

(18) (a) Viscotek GPC analysis of representative polymerizations in THF and CH_2Cl_2 under identical conditions (monomer:catalyst = 100:1) afforded polymers with PDI (M_n) of 1.23 (46 000) and 1.34 (63 000), respectively. (b) Viscotek GPC analyses were performed by the Separation Science Group at ICI Chemicals and Polymers, Runcorn, UK.

(19) ^1H NMR (300 MHz, $CDCl_3$): δ 5.53 (4 H, olefinic H's), 5.06 and 4.85 (2 H, alkoxy ring H's), 3.73 (6 H, methoxy), 3.26 and 3.18 (2 H, ring-junction H's). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 155.2 (carbonyl C), 132.3, 131.6, 131.4, and 130.8 (vinylene double bond pairs), 127.0 (cyclohexenyl C), 74.9 and 74.5 (ring alkoxy C's), 55.0 (methoxy C), 42.7 and 42.2 (ring-junction C).

(20) A kinetic preference for the metathesis of exo- versus endo-substituted olefins has been reported for the competitive polymerization of cis-2,3-disubstituted norbornenes, for example, bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid anhydride: (a) Ivin, K. J.; Kress, J.; Osborn, J. A. *J. Mol. Catal.* **1988**, *46*, 351. (b) Castner, K. F.; Calderon, N. *J. Mol. Catal.* **1982**, *15*, 47.

(21) (a) Dimethyl carbonate is also observed in the evolved gases as the elimination nears completion. This product arises from formation of trace amounts (3–4%) of a cyclic carbonate (ν = 1810 cm^{-1}) in the polymer backbone (cf. ref 8b). These cyclic carbonate residues may be completely removed by annealing the initial thermolysis product at 300 °C. (b) TGA-IR analyses were performed at Oneida Research Services, Inc.

(22) Catalysis of carbonate elimination by amines has been employed in the precursor synthesis of poly(*p*-phenylene) from poly(cyclohexa-3,5-diene-*cis*-1,2-diol bis(methyl carbonate)): (a) Cheshire, P. U.S. Patent 4 454 307, 1984. (b) Reference 8b.

(23) (a) UV (NaCl, thin film): λ_{max} 396, 244 (sh), 206 nm. (b) IR (KBr, thin film): ν 3022, 1516, 1422, 1335, 1107, 1014, 960, 836, 555 cm^{-1}.

(24) (a) Bradley, D. D. C.; Friend, R. H.; Lindenberger, H.; Roth, S. *Polymer* **1986**, *27*, 1709. (b) Gagnon, D. R.; Capistran, J. D.; Karasz, F. E.; Lenz, R. W. *Polymer* **1987**, *28*, 567. (c) Stenger-Smith, J. D.; Lenz, R. W.; Wegner, G. *Polymer* **1989**, *30*, 1048.

(25) Simpson, J. H.; Egger, N.; Masse, M. A.; Rice, D. M.; Karasz, F. E. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 1859.

Andy Muir of ICI Specialties and ICI Chemicals and Polymers, Runcorn, UK, for providing 3,5-cyclohexadiene-*cis*-1,2-diol and Viscotek GPC analysis. We thank Dr. Greg Fu for helpful discussions. D.L.G. thanks NSERC Canada for a predoctoral fellowship.

Registry No. 1b, 144193-12-4; **1b** (homopolymer), 144193-14-6; PPV, 26009-24-5.

Supplementary Material Available: Listing of ^1H and ^{13}C NMR spectroscopic and analytical data for synthetic intermediates in Scheme I (2 pages). Ordering information is given on any current masthead page.

Conversion of Alkenes to Enol Silyl Ethers of Acylsilanes by Iridium-Catalyzed Reaction with a Hydrosilane and Carbon Monoxide

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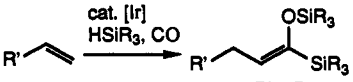
Received July 20, 1992

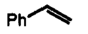
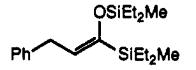
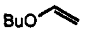
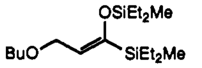
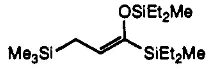
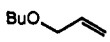
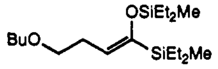
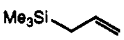
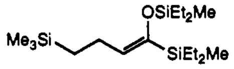
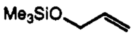
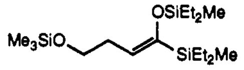
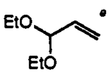
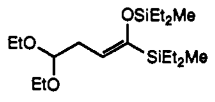
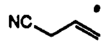
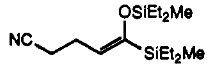
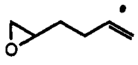
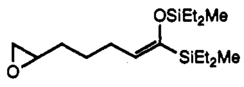
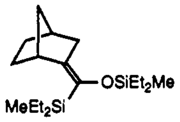
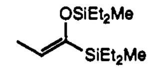
We wish to report that iridium complexes ($[IrCl(CO)_3]_n$ and $Ir_4(CO)_{12}$) catalyze the reaction of alkenes with a hydrosilane ($HSiR_3$) and carbon monoxide (eq 1) to yield enol silyl ethers of acylsilanes. This unprecedented reaction results in regioselective introduction of carbon monoxide into the terminal carbon atom of alkenes, forming a siloxy(silyl)methylene unit ($=C(SiR_3)OSiR_3$). The possibility that an acylsilane or its derivative can be a product of a catalytic reaction using $HSiR_3$ and CO has been pointed out.[1] Since then, a number of new catalytic reactions with $HSiR_3$ and CO have been reported.[2] Nevertheless, the present Ir-catalyzed reaction represents the first example of formation of acylsilane[3,4] derivatives from the $HSiR_3$/CO combination.[5]



1: R' = Bu
2: R' = Cy
3: R' = *t*-Bu

(1)

Table I. Iridium-Catalyzed Reaction of Alkenes with $HSiEt_2Me$ and CO[a]

alkene	product	yield, %[b]	*E*/*Z* ratio[c]
		(50)[d]	72/28
		67	57/43
		73	73/27
		75	68/32
		53	79/21
		67	67/33
 [e]		58	73/27
 [e]		45	73/27
 [e]		56	65/35
		85	36/64[f]
 [g]		67	66/34

[a] Reaction conditions: alkene (10 mmol), $HSiEt_2Me$ (1 mmol), $[IrCl(CO)_3]_n$ (0.02 mmol), CO (50 atm), C_6H_6 (2 mL), 140 °C, 48 h. Characterization of the products obtained is given in the supplementary material. [b] Isolated yields based on $HSiEt_2Me$. GLC yield is in parentheses. [c] Determined by ^1H NMR. [d] Dimerization and polymerization of styrene also took place. [e] An alkene (5 mmol) was used. [f] The assignment of the stereochemistry is tentative. [g] Ethylene (10 atm, initial pressure at 25 °C) was used.

Typically, the reaction was carried out with alkene (10 equiv) and $HSiEt_2Me$ (1 equiv) in benzene (2 mL) at 140 °C under 50

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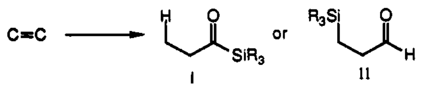
(1) (a) Seki, Y.; Hidaka, A.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 174. (b) Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837.

(2) For recent papers on transition metal catalyzed reaction with $HSiR_3$ and CO see: (a) Seki, Y.; Kawamoto, K.; Chatani, N.; Hidaka, A.; Sonoda, N.; Ohe, K.; Kawasaki, Y.; Murai, S. *J. Organomet. Chem.* **1991**, *403*, 73. (b) Ikeda, S.-i.: Chatani, N.; Kajikawa, Y.; Ohe, K.; Murai, S. *J. Org. Chem.* **1992**, *57*, 2. (c) Matsuda, I.; Ogiso, A.; Sato, S.; Izumi, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2332. (d) Matsuda, I.; Ogiso, A.; Sato, S. *J. Am. Chem. Soc.* **1990**, *112*, 6120. (e) Matsuda, I.; Sakakibara, J.; Nagashima, H. *Tetrahedron Lett.* **1991**, *32*, 7431. (f) Ojima, I. Ingallina, P.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 38. (g) Ojima, I.; Donovan, R. J.; Shag, W. R. *J. Am. Chem. Soc.* **1992**, *114*, 6580. (h) Matsuda, I.; Sakakibara, J.; Inoue, H.; Nagashima, H. *Tetrahedron Lett.* **1992**, *33*, 5799.

(3) Formal analogy to hydroformylation would suggest that i and ii could be products. Recently, catalytic reactions of acetylenes with $HSiR_3$ and CO to give products relating to ii have been reported.[2c–h]



i ii

(4) The product has functionalities of vinylsilane, enol silyl ether, and masked acylsilane. All of these functional groups are quite useful in organic synthesis. For reviews, see: Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. Magnes, P. D.; Sarkar, T.; Djurie, S. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W.; Eds.; Pergamon: Oxford, 1982; Vol. 7, Chapter 48. Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983.

(5) For recent reviews on acylsilanes, see: Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647. Bulman Page, P. C.; Klarir, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147. For recent papers on the synthetic application of acylsilanes, see: (a) Ricci, A.; Degl'Innocenti, A., Capperucci, A.; Reginato, G. *J. Org. Chem.* **1989**, *54*, 19. (b) Schinzer, D. *Synthesis* **1989**, 179. (c) Nowick, J. S.; Danheiser, R. L. *J. Org. Chem.* **1989**, *54*, 2798. (d) Yanagisawa, A.; Habaue, S.; Yamamoto, H. *J. Org. Chem.* **1989**, *54*, 5198. (e) Suzuki, M.; Morita, Y.; Noyori, R. *J. Org. Chem.* **1990**, *55*, 441. (f) Larson, G. L.; Soderquist, J. A.; Rivera, Claudio, M. R. *Synth. Commun.* **1990**, *20*, 1095. (g) Reich, H. J.; Holtan, R. C.; Bolm, C. *J. Am. Chem. Soc.* **1990**, *112*, 5609. (h) Cirillo, P. F.; Panek, J. S. *J. Org. Chem.* **1990**, *55*, 6071. (i) Yoshida, J.-i.; Matsunaga, S.-i.; Ishichi, Y.; Maekawa, T.; Isoe, S. *J. Org. Chem.* **1991**, *56*, 1307. (j) Cirillo, P. F.; Panek, J. S. *Tetrahedron Lett.* **1991**, *32*, 457.

0002-7863/92/1514-9710$03.00/0