1.872-1.831 (m, 2 H), 1.508 (br, 1 H); ^{2}H NMR (61.4 MHz, $CHCl_3$) δ 4.085 (s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.79, 140.84, 128.34, 128.27, 125.71, 114.83, 71.84 (t, $^1J_{CD}$ = 21.8 Hz), 38.27, 31.49.

5-Deuterio-1-phenylpentan-3-one (32). Isomerization of **31** (110.4 mg, 0.676 mmol) with **22** (44.5 mg, 61.3 μmol) and **33** (32.4 mg, 123 μmol) in dioxane (0.7 mL) for 1 h gave the product: 69.6 mg (63%); R_f = 0.46 (4:1 hexane-ether); IR 3086, 3063, 3028, 2943, 2186, 1949, 1874, 1805, 1718, 1604, 1497, 1454, 1413, 1369 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.299-7.207 (m, 2 H), 7.193-7.173 (m, 3 H), 2.903 (t, J = 7.6 Hz, 2 H), 2.734 (t, J = 7.7 Hz, 2 H), 2.403 (t, J = 7.2 Hz, 2 H), 1.029 (tt, $^3J_{HH}$ = 7.3 Hz, $^2J_{HD}$ = 2.0 Hz, 2 H); ^{2}H NMR (61.4 MHz, $CHCl_3$) δ 1.056 (s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 210.59, 141.09, 128.38, 128.22, 125.99, 43.80, 35.96, 29.74, 7.41 (t, $^1J_{CD}$ = 19.4 Hz); exact mass calcd for $C_{11}H_{13}DO$ 163.1108, found 163.1096 (64.4).

Crossover Experiment. Isomerization of a mixture of 3-deuterio-5-phenyl-1-penten-3-ol (**29**, 60.0 mg, 0.368 mmol) and 1-tetradecen-3-ol (**2**, 78.1 mg, 0.368 mmol) with **22** (26.6 mg, 36.6 μmol) and **33** (19.2 mg, 73.4 μmol) in dioxane (0.75 mL) for 1.5 h gave 5-deuterio-1-phenylpentan-3-one (20.9 mg, 35%; R_f = 0.40, 6:1 hexane-ether) and 3-tetradecanone (71.2 mg, 91%; R_f = 0.61, 6:1 hexane-ether). These compounds were characterized as described above.

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Communications to the Editor

A Convergent Synthetic Route to the Tunicamycin Antibiotics. Synthesis of (+)-Tunicamycin V

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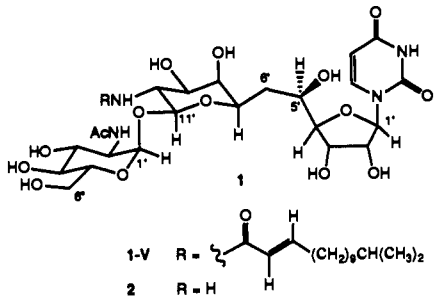
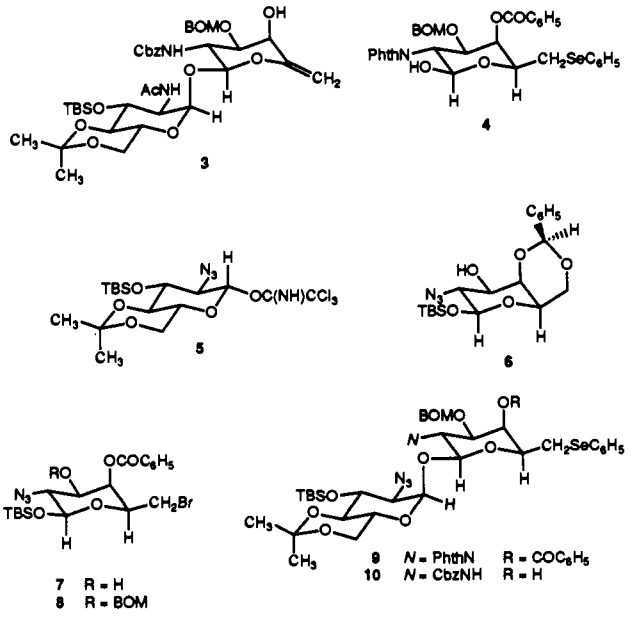
The tunicamycins are a family of natural products represented generally by structure **1**, wherein R indicates one of several long-chain branched, linear, saturated or unsaturated acyl substituents. They elicit a considerable range of biological responses including antimicrobial, antifungal, antiviral, and antitumor activities. Their ability to function as potent inhibitors of oligosaccharide synthesis in eukaryotic cells has established them as unique biochemical probes of the role of glycosylation on protein structure and function.[1] In this work, we describe a concise synthetic route to the tunicamycins, illustrated by the preparation of (+)-tunicamycin V (**1-V**).[2]



Previous studies directed toward a synthesis of the undecose core of **1**, tunicaminyluracil (C1′-C11′),[2h] suggested that the complete antibiotic structure might be assembled in a highly convergent manner by the coupling of an allylic alcohol such as **3** with a suitably protected uridine 5′-aldehyde derivative to form the C5′-C6′ bond (vide infra). In the implementation of this strategy, it was first necessary to address the problem of formation of the "trehalose" glycosidic linkage within **3**. Prior work had established this to be a difficult bond formation;[2f,g] in a single reported success, Koenigs-Knorr methodology was found to produce the desired β,α-linkage, albeit in poor yield (18%).[2f] After an extensive investigation of the variables critical for successful coupling, we have developed an efficient synthesis of the desired trehalose linkage employing the galactosamine derivative **4** as nucleophile and the glucosamine derivative **5** as electrophile. Both



coupling partners were prepared in multigram quantities from simple carbohydrate precursors. Galactosamine derivative **4** was synthesized in six steps from the readily available precursor **6**.[3] Oxidative cleavage of the benzylidene acetal within **6** was achieved, without protection of the hydroxyl group, by irradiation of a solution of **6** in bromotrichloromethane (0.08 M, 0 °C, 2.5 h, 275-W sun lamp), providing the bromo alcohol **7** in 87% yield.[4] Bromo alcohol **7** was protected as its benzyloxymethyl (BOM) ether **8** with BOM chloride (5.0 equiv) and diisopropylethylamine

(1) Reviews: (a) Elbein, A. *Trends Biochem. Sci.* **1981**, 219. (b) *Tunicamycin*; Tamura, G., Ed.; Japan Scientific Press: Tokyo, Japan, 1982. (c) Echardt, K. *J. Nat. Prod.* **1983**, *46*, 544.

(2) Previous synthetic studies: (a) Suami, T.; Sasai, H.; Matsuno, K. *Chem. Lett.* **1983**, 819. (b) Corey, E. J.; Samuelsson, B.; Luzzio, F. A. *J. Am. Chem. Soc.* **1984**, *106*, 3682. (c) Corey, E. J.; Samuelsson, B. *J. Org. Chem.* **1984**, *49*, 4735. (d) Suami, T.; Sasai, H.; Matsuno, K.; Suzuki, N.; Fukuda, Y.; Sakanana, O. *Tetrahedron Lett.* **1984**, *25*, 4533. (e) Danishefsky, S.; Barbachyn, M. *J. Am. Chem. Soc.* **1985**, *107*, 7761. (f) Suami, T.; Sasai, H.; Matsuno, K.; Suzuki, N. *Carbohydr. Res.* **1985**, *143*, 85. (g) Danishefsky, S. J.; DeNinno, S. L.; Chen, S.; Boisvert, L.; Barbachyn, M. *J. Am. Chem. Soc.* **1989**, *111*, 5810. (h) Myers, A. G.; Gin, D. Y.; Widdowson, K. L. *J. Am. Chem. Soc.* **1991**, *113*, 9661.

(3) (a) Grundler, G.; Schmidt, R. R. *Liebigs Ann. Chem.* **1984**, 1826. (b) Lemieux, R. U.; Ratcliffe, R. M. *Can. J. Chem.* **1979**, *57*, 1244. (c) Shafizadeh, F. *Methods Carbohydr. Chem.* **1963**, *2*, 409.

(4) Chana, J. S.; Collins, P. M.; Farina, F.; Peacock, D. J. *J. Chem. Soc., Chem. Commun.* **1988**, 94.

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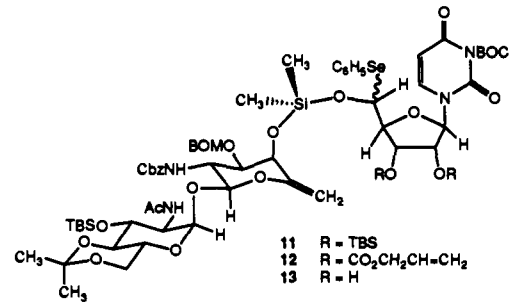
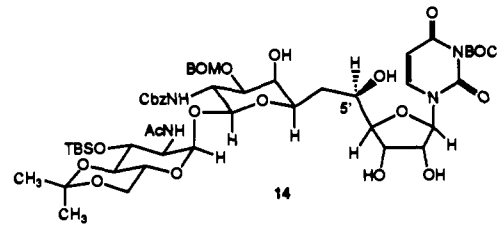
(5.5 equiv) in dichloromethane at reflux (15 h, quantitative).[5] Reduction of the azido group of **8** was accomplished with greatest efficiency utilizing a new procedure involving the treatment of **8** with benzeneselenol (3.0 equiv) in triethylamine at 60 °C for 2.5 h (98%). Protection of the resulting amino group with phthaloyl dichloride (2.0 equiv, Et_3N (4.0 equiv), CH_2Cl_2, 0 °C, 10 min; DBU, toluene, 100 °C, 1.5 h) afforded the corresponding phthalimide in 86% yield. Bromide displacement (Et_3N, C_6H_5-SeH, dimethoxyethane, reflux, 95%) and deprotection of the anomeric silyl ether ($Et_3N{\cdot}3HF$, acetonitrile, 23 °C, 97%) provided **4** as the β-anomer (>10:1 β:α, mp 69–71 °C). The electrophilic coupling partner, imidate **5**, was synthesized efficiently from glucose (see supplementary material).

Coupling reactions of **4** and **5** using trimethylsilyl trifluoromethanesulfonate as catalyst, as described in the protocol of Schmidt,[6] appeared to exhibit an induction period and did not proceed to completion. Reasoning that trifluoromethanesulfonic acid (TfOH) might function as the actual catalyst in this reaction,[7] a much more rapid and efficient coupling procedure was developed employing this reagent at the outset. Thus, addition of a solution of TfOH in toluene (5% v/v; 0.2 equiv total) in three equal portions over 2 h to a solution of the imidate **5** (1.5 equiv) and the hemiacetal **4** (1.0 equiv) in toluene at −20 °C afforded the disaccharide **9** in 70% yield (10.0 g **9**; smaller scale reactions are equally efficient) after purification by chromatography on silica gel. The α,α-diastereomeric disaccharide was isolated in a separate fraction in approximately 10% yield. One critical factor for efficient coupling is the control of β-orientation of the anomeric hydroxyl nucleophile. On the basis of experiments with alternative substrates in the coupling reaction, the 2-phthalimido group of **4** is believed to play an important role in this regard through steric destabilization of the α-anomer.[8]

The β,α-linked disaccharide **9** was transformed to the allylic alcohol **3** in six steps (56% total yield). Hydrazinolysis of **9** at 100 °C for 12 h (10% hydrazine hydrate in ethanol, sealed tube, 87%) produced an amino alcohol which, upon treatment with benzyl chloroformate (8.8 equiv) in pyridine at 0 °C for 30 min, afforded the crystalline carbamate **10** in 96% yield (mp 114–115 °C). To reduce the hindered azido group of **10**, it was necessary once again to employ the reagent benzeneselenol in triethylamine (55 °C, 12 h); the corresponding amino alcohol was produced in 91% yield as white needles (mp 172–174 °C). Acetylation of this product with acetic anhydride in pyridine at 60 °C provided the diacetyl derivative which, upon treatment with *m*-chloroperoxybenzoic acid (3.5 equiv) in carbon tetrachloride (−15 to 0 °C), addition of dimethyl sulfide (12 equiv) and triethylamine (3 equiv), and heating at 65 °C for 10 h followed by acetate hydrolysis with potassium carbonate (0.07 equiv) in methanol at 23 °C, afforded the allylic alcohol **3** in 74% yield for the three steps.

In preparation for C5′–C6′ bond formation, the allylic alcohol **3** was coupled with an appropriately protected uridine 5′-aldehyde, using methodology previously described,[2h] to form an *O*-silyl hemiselenoacetal derivative such as **11** or **12**. Thus, dropwise addition of pyridine (3.0 equiv) to a solution of *N*-BOC-2′,3′-bis(allyloxycarbonate)-protected uridine 5′-aldehyde (2.0 equiv) and benzeneselenol (3.0 equiv) in toluene at 23 °C, addition of the resulting solution to dichlorodimethylsilane (20 equiv) in pyridine with stirring at 23 °C for 4.5 h, and concentration in vacuo followed by addition of toluene and a solution of allylic alcohol **3** (1 equiv) in pyridine (reaction for 5 min at 23 °C) produced the siloxanes **12** in 81% yield after purification by flash column chromatography. Free-radical cyclizations of hemiselenoacetal derivatives such as **11** and **13** were uniformly efficient in formation of the requisite C–C bond but differed markedly in





their selectivity for formation of the C5′ stereocenter. For example, the *tert*-butyldimethylsilyloxy-protected derivative **11** formed predominantly the undesired stereochemistry at C5′ under all conditions examined.[9] The observed preference for formation of the undesired stereochemistry at C5′ was rationalized as due to a destabilizing steric interaction between the glucosamine residue and the 3′-silyl ether in the transition state leading to the desired product. Accordingly, the diols **13** were prepared by cleavage of the allyloxycarbonate groups of **12** employing tributyltin hydride (3 equiv) and bis(triphenylphosphine)palladium(II) chloride (0.01 equiv) in dichloromethane saturated with water (23 °C, 7 min, 85% yield).[10] In addition to possessing a smaller 3′-substituent (versus **11**), alcohols **13** were viewed as favorable cyclization precursors by virtue of a low-energy, reactive conformation in which the C3′-hydroxyl group of the derived 5′-radical is hydrogen-bonded to the glucosyl amide oxygen. Free-radical cyclization of a solution of diols **13** (1 mM) with tributyltin hydride (2 mM) in deoxygenated toluene at 0 °C was induced by the addition of triethylborane[11] at 15-min intervals (3 additions, 0.1 equiv each), leading to a cyclic product with the desired configuration at C5′ (7.5:1 stereoselectivity); cleavage of the siloxane linker ($KF{\cdot}2H_2O$, CH_3OH) and careful column chromatography afforded the pure tetraol **14** in 60% yield from **13**. In support of the idea that hydrogen-bonding is important in producing the desired stereochemistry at C5′, it was found that cyclization of diols **13** in methanol proceeded with only 1.6:1 selectivity in favor of **14**. Complete deprotection of **14** was achieved by the following 3-step sequence: (1) transfer hydrogenolysis using palladium black as catalyst in 9:1 methanol:formic acid at 23 °C for 1 h; (2) BOC and acetonide removal with methanol and 90% aqueous formic acid (87:13) at 40 °C for 1.5 h; (3) TBS cleavage using excess 48% aqueous hydrofluoric acid in acetonitrile–methanol (1:1) at 23 °C. The resulting amino polyol **2** was purified by chromatography on reverse-phase silica gel (RP-18), eluting with a water–pyridine–methanol mixture (1.5:1:1). Selective N-acylation of **2** with (*E*)-13-methyl-2-tetradecenoic acid (supplementary material) and 1,3-dicyclohexylcarbodiimide (6 equiv each, added over 2 days) in methanol at 23 °C followed by column chromatography (RP-18, water–pyridine–methanol, 1:1:1) and trituration with chloroform provided pure tunicamycin V (**1-V**, 88 mg, 83% from tetraol **14**), identical in all respects (^1H and ^{13}C NMR, FTIR, mixed melting point,

(5) Zoretic, P. A.; Soja, P.; Conrad, W. E. *J. Org. Chem.* **1975**, *40*, 2962.
(6) (a) Schmidt, R. R.; Grundler, G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 781. (b) Review: Schmidt, R. R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 212.
(7) For related observations, see: Evans, D. A.; Kaldor, S. W.; Jones, T. K.; Clardy, J.; Stout, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 7001.
(8) Lemieux, R. U.; Takeda, T.; Chung, B. Y. *ACS Symp. Ser.* **1976**, *39*, 90.
(9) Each cyclization product was subjected to limited acidic hydrolysis followed by acetylation; comparison with authentic samples of peracetyltunicaminyluracil and its 5′-epimer then secured the assignment of stereochemistry at C5′.[2h]
(10) Guibe, F.; Dangles, O.; Balavoine, G. *Tetrahedron Lett.* **1986**, *27*, 2365.
(11) (a) Furukawa, J.; Tsuruta, T.; Inoue, S. *J. Polym. Sci.* **1957**, *26*, 234. (b) Ashikari, N.; Nishimura, A. *J. Polym. Sci.* **1958**, *31*, 249. (c) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987**, *109*, 2547. We thank Professor David Bergbreiter for making us aware of refs a and b.

HPLC, HRMS, optical rotation) with an authentic sample.

In summary, an efficient synthetic route to the aminopolyol **2** is described. This compound may be selectively N-acylated to provide any of the homologous tunicamycin antibiotics in pure form as well as a series of related structures of potential utility as biological probes.

Acknowledgment. This research was generously supported by the National Science Foundation, ICI Americas Inc., and Glaxo Inc. D.Y.G. acknowledges a doctoral fellowship from the Natural Sciences and Engineering Research Council of Canada.

Supplementary Material Available: Procedures for the synthesis of **5**, *N*-BOC-2′,3′-bis(allyloxycarbonate)-protected uridine 5′-aldehyde, and (*E*)-13-methyltetradecenoic acid and a summary of spectral and analytical data for all synthetic intermediates (42 pages). Ordering information is given on any current masthead page.

Transformation of an Alkynyl Thioether into a Disubstituted Acetylene by Combination with a Chromium Carbene

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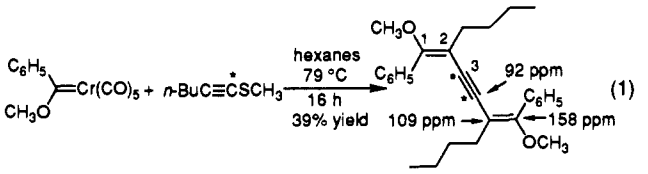
Although the combination of acetylenes with metal carbenes like **1** is a wellspring of organic structures,[1] few of the acetylenes previously studied have been substituted at their triple bonds by atoms other than carbon or hydrogen. Alkynyl ethers give the *p*-methoxyphenol products of the Dötz reaction.[2] Ynamines give pentacarbonyl (1-amino-2-propenylidene)chromiums,[3] and, after heating, indenes.[3c,4] Bis(diphenylphosphino)acetylene after heating also gives indenes.[5] (Trimethylsilyl)acetylene gives the normal Dötz product and bis(trimethylsilyl)acetylene a ketene.[6] We report here that, as pictured in eq 1, when the acetylene is an alkynyl thioether, a precursor easily obtained,[7] the structure of the product, despite the enormous variety previously formed from metal carbenes and acetylenes,[1] is of a kind not seen before.[8,9]



(1)

1 2

The structure of **2** (analyzed as $C_{28}H_{34}O_2$) is revealed by its NMR spectra,[10] showing equal numbers of phenyl, methoxyl, and butyl groups, and four quaternary carbons, the phenyl (resonating at δ 134.51) and three others (resonating at δ 158.23, 108.94, and 92.20). These last are assigned to C-1, C-2, and C-3 on the basis of analogies.[11] The experiment that identified the structure is one in which C-1 of the precursor (starred in eq 1) is replaced by ^{13}C. The only resonance in the product that intensifies is the one at 92 ppm, and the only ones split by coupling to the ^{13}C are those at 109 and 158 ppm. The split peaks appear as AA′X "triplets", the separations of the outer lines (which should equal $J_{AX} + J_{A'X}$) being 102.5 Hz for the former resonance and 10.5 Hz for the latter. For there to be only one major splitting, the labeled carbons in **2** must be acetylenic. That they are is also demonstrated by the magnitude of the 102.5 Hz splitting, which identifies a bond between carbons that are sp and sp^2 hybridized.[16] That the butyl and phenyl groups are not interchanged is shown by the 5.6 Hz coupling (collapsed by irradiating δ_H 2.25) between the allylic methylene protons and C-3. This is considerably larger than that of known four-bond *H*CC=C*C* couplings.[20,21] The stereochemistry about the double bond is shown by the 5% NOE of the carbon resonance at 92 ppm when either δ_H 7.55 (the *o*-phenyl protons) or 2.25 is irradiated and the lack of NOE when the resonance irradiated is δ_H 3.37 (the OCH_3).[22]

(1) Leading references: (a) McCallum, J. S.; Kunng, F.-A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346. (b) Bos, M. E.; Wulff, W. D.; Miller, R. A.; Chamberlin, S.; Brandvold, T. A. *J. Am. Chem. Soc.* **1991**, *113*, 9293. (c) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 5, p 1065 ff. (d) Katz, T. J.; Yang, G. X.-Q. *Tetrahedron Lett.* **1991**, *32*, 5895. (e) Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737. (f) Hoye, T. R.; Rehberg, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 2841. (g) Harvey, D. F.; Lund, K. P.; Neil, D. A. *Tetrahedron Lett.* **1991**, *32*, 6311. (h) Herndon, J. W.; Tumer, S. U.; Schnatter, W. F. K. *J. Am. Chem. Soc.* **1988**, *110*, 3334. (i) Grotjahn, D. B.; Dötz, K. H. *Synlett* **1991**, 381. (j) Schwindt, M. A.; Miller, J. R.; Hegedus, L. S. *J. Organomet. Chem.* **1991**, *413*, 143. (k) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422.

(2) (a) Yamashita, A.; Toy, A. *Tetrahedron Lett.* **1986**, *27*, 3471. Other metal carbenes behave similarly: (b) Yamashita, A. *J. Am. Chem. Soc.* **1985**, *107*, 5823. (c) Yamashita, A.; Scahill, T. A.; Toy, A. *Tetrahedron Lett.* **1985**, *26*, 2969. (d) Yamashita, A.; Toy, A.; Ghazal, N. B.; Muchmore, C. R. *J. Org. Chem.* **1989**, *54*, 4481. The tungsten analogue with ethoxyacetylene is said to give the pentacarbonyl (1-ethoxy-3-phenyl-2-propenylidene)tungsten: (e) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282.

(3) (a) Dötz, K. H.; Kreiter, C. G. *Organomet. Chem.* **1975**, *99*, 309. (b) Dötz, K. H. *Chem. Ber.* **1977**, *110*, 78. (c) Dötz, K. H.; Pruskil, I. *Chem. Ber.* **1978**, *111*, 2059. (d) Fischer, H.; Dötz, K. H. *Chem. Ber.* **1980**, *113*, 193. (e) Dötz, K. H.; Kreiter, C. G. *Chem. Ber.* **1976**, *109*, 2026.

(4) (a) Dötz, K.-H.; Neugebauer, D. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 851. (b) Review: Dötz, K. H. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1986; Vol. 1, Chapter 4.

(5) (a) Dötz, K. H.; Pruskil, I.; Schubert, U.; Ackermann, K. *Chem. Ber.* **1983**, *116*, 2337. (b) Cambie, R. C.; Rutledge, P. S.; Tercel, M.; Woodgate, P. D. *J. Organomet. Chem.* **1986**, *315*, 171.

(6) Dötz, K. H.; Fügen-Köster, B. *Chem. Ber.* **1980**, *113*, 1449.

(7) 1-Alkyne + *n*-BuLi in THF at −78 °C, followed by $(MeS)_2$. Brandsma, L. *Preparative Acetylene Chemistry*, 2nd ed.; Elsevier: New York, 1988; p 132.

(8) 1-(Methylthio)-1-propyne and pentacarbonyl [ethoxy(phenylethynyl)methylene]tungsten, the only alkynyl thioether and metal carbene previously combined, at 40 °C inserted the acetylene into the C=M bond. Fischer, H.; Meisner, T.; Hofmann, J. *J. Organomet. Chem.* **1990**, *397*, 41.

(9) The reaction of 1-(methylthio)-1-octyne analogous to eq 1 is described in the supplementary material.

(10) ^1H NMR ($CDCl_3$, 300 MHz): δ 0.88 (t, 7.1 Hz, 6 H), 1.34 (m, 8 H), 2.25 (t, 7.4 Hz, 4 H), 3.37 (s, 6 H), 7.27 (m, 6 H), 7.54 (m, 4 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.01, 22.49, 29.94, 30.79, 58.22, 92.20, 108.94, 127.75, 128.18, 128.95, 134.51, 158.23.

(11) C-1: calcd is 160.3 ppm (ref 12); the analogous carbon in the lactone of 4-methoxy-4-*p*-tolyl-2-(3-hydroxypropyl)-but-3-enoic acid resonates at 157.0 ppm (ref 1a) and in (*Z*,*Z*)-1,6-diphenyl-1,6-bis(phenylthio)hexa-1,5-dien-3-yne at 147.5 ppm (ref 13). This last compound also provides analogies for the resonance of C-3 (96.4 ppm) and the UV spectrum. Its λ_{max} in CH_3CN (372 nm, log ϵ = 4.45) plus increments for replacing RS by RO (48 nm, ref 14) and adding two alkyls (+10 nm) implies that λ_{max} for **2** should be 334 nm. Found (in 95% EtOH) is 328 nm (log ϵ = 4.20). C-2: 101 ppm is calculated by adding to the chemical shift of α-methoxystyrene (81.71 ppm) increments for the butyl and ethynyl substituents (ref 12) and 14.9 ppm for the deconjugating effect of a substituent cis to methoxyl (ref 15).

(12) Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. *Tables of Spectral Data for Structure Determination of Organic Compounds*, 2nd ed.; Springer-Verlag: New York, 1989; p C85 ff.

(13) Zschunke, A.; Mügge, C.; Hintzsche, E.; Schroth, W. *J. Prakt. Chem.-Chem. Z.* **1992**, *334*, 141.

(14) Scott, A. I. *Interpretation of the Ultraviolet Spectra of Natural Products*; Pergamon Press: New York, 1964; Table 2.2.

(15) (a) Taskinen, E. *Tetrahedron* **1978**, *34*, 425. (b) Strobel, M. P.; Andrieu, C. G.; Paquer, D.; Vazeux, M.; Pham, C. C. *Nouv. J. Chim.* **1980**, *4*, 101.

(16) Equations for J_{AX} (ref 17) and for $J_{A'X}$ (ref 18) when summed imply that $(\%s_A)(\%s_X) = 1617$, similar to the ideal $(50)(33^1/_3) = 1667$. In two phenylacetylenes $J_{AX} + J_{A'X}$ is 104 Hz (ref 19), while a substitution of *t*-Bu for Ph reduces the sum to 77 Hz (ref 19b).

(17) Frei, K.; Bernstein, H. J. *J. Chem. Phys.* **1963**, *38*, 1216.

(18) Lambert, J.; Klessinger, M. *Magn. Reson. Chem.* **1987**, *25*, 456.

(19) (a) Hansen, P. E.; Poulsen, O. K.; Berg, A. *Org. Magn. Reson.* **1975**, *7*, 405. (b) Kamieńska-Trela, K.; Biedrzycka, Z.; Machinek, R.; Knieriem, B.; Lüttke, W. *J. Organomet. Chem.* **1986**, *314*, 53.

(20) Hansen, P. E. *Prog. Nucl. Magn. Reson. Spectrosc.* **1981**, *14*, 175, Table 10.

(21) Three-bond H–C couplings are this size. (a) Karabatsos, G. J.; Orzeck, C. E., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 560. (b) Vogeli, U.; von Philipsborn, W. *Org. Magn. Reson.* **1975**, *7*, 617. (c) Hansen, M.; Jakobsen, H. J. *J. Magn. Reson.* **1975**, *20*, 520.

(22) Neuhaus, D.; Williamson, M. P. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH Publishers: New York, 1989.

0002-7863/93/1515-2038$04.00/0