vacuum and stored in sealed tubes saturated with pure, dry nitrogen. The aldehydes were commercially available reagents of the highest grade. They were used without further purification. Diglyme (Wako Junyaku Co.), used as a reaction solvent, was dried by being refluxed with sodium, distilled, and stored in a sealed glass tube.

The reaction was carried out under an atmospheric pressure of hydrogen in a glass reactor equipped with greaseless valves, which is described elsewhere.[13] After the catalyst precursor (0.1 mmol) was dissolved in 1% aqueous diglyme (50 mL) in a nitrogen atmosphere, nitrogen was replaced with hydrogen, the solution being aged for exactly 5 min under an atmospheric pressure of hydrogen, to yield the active hydrido complex. The aldehyde (10 mmol) was injected with a syringe through a silicon rubber stopper to start the reaction. The reaction was followed by gas chromatographic analysis (Yanako G180, column: polyethylene glycol (20 M), 2 m, polyethylene glycol 4000, 2 m) of a small portion of the reaction mixture (0.2 mL) which was sampled by the equipment[13] at appropriate intervals without any contact of the reaction system with air. The reaction under the higher pressure of hydrogen was carried out in an autoclave (200cc, Taiatsu Garasu Kogyo Co.).

^{13}C NMR of the aldehydes was measured with an FT NMR spectrometer (JEOL, FX-100).

Registry No. *n*-Butraldehyde, 123-72-8; benzaldehyde, 100-52-7; phenylacetaldehyde, 122-78-1; acetone, 67-64-1; methyl *n*-propyl ketone, 107-87-9; acetophenone, 98-86-2; phenylacetone, 103-79-7; crotonaldehyde, 4170-30-3; cinnamaldehyde, 104-55-2; hydrocinnamaldehyde, 104-53-0; methyl propenyl ketone, 625-33-2; methyl phenethyl ketone, 2550-26-7; PEt_3, 554-70-1; PMe_3, 594-09-2; PPh_3, 603-35-0; diphos, 1663-45-2; Rh, 7440-16-6.

(13) Fujitsu, H.; Matsumura, E.; Takeshita, K.; Mochida, I. *J. Org. Chem.* **1981**, *46*, 2287.

General Synthesis of ω-Acetylenic Vinyl Esters and Ethers

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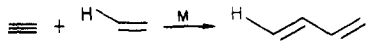
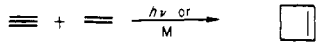
Received December 17, 1980

Vinyl ethers of the general structure $CH_2{=}CHO(CH_2)_nC{\equiv}CH$ and vinyl esters of the general structure $CH_2{=}CHOC(O)(CH_2)_nC{\equiv}CH$ have been prepared by mild elimination methods from the corresponding ω-acetylenic alcohols and acids. A two-step procedure involving addition of alcohol to (trimethylsilyl)oxirane followed by silanol elimination, and only slightly modified from the one developed by Hudrlik, provides the vinyl ethers in average overall yields of 45%. The vinyl esters must be prepared in three steps due to the unexpected lack of reactivity of the acid–oxirane adducts toward elimination. Vinyl 3-butynoate is not accessible at all via this route. Other vinyl esters are realized in overall yields of 40% or better. Several of these compounds exhibit high reactivity toward $Co_2(CO)_8$ in preliminary studies of possible cyclization reactions.

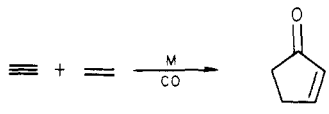
The versatility of the alkyne functional group makes its incorporation an important part of the design of many synthetic intermediates. In recent years a number of useful techniques for the linkage of alkyne and alkene groups have been developed, among these several that allow the direct construction of such important intermediates as 1,3-dienes,[1] cyclobutenes,[2] and cyclopentenones[3] (eq 1–3).



(1)



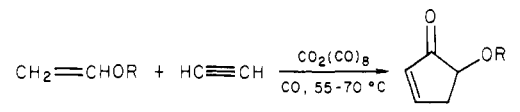
(2)

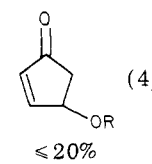


(3)

We are especially intrigued by the as yet unrealized potential of the cyclopentenone synthesis (eq 3) in the natural products field. The best conditions under which cocyclization of an alkene, an alkyne, and CO can be effected are those developed by Pauson and co-workers, who used $Co_2(CO)_8$ as a catalyst. Only strained alkenes (e.g., norbornene) are reactive under mild conditions (60–80 °C),[3] while simple alkenes participate only at much higher temperature (e.g., 140–150 °C) and usually produce only very low yields of cyclopentenones.[1b]

In a series of pilot experiments we have examined a variety of alkenes and discovered that the presence of electron-donor groups and intramolecularity are two key factors that can contribute to cyclization reactivity under mild conditions (eq 4 and 5).[4] These results have

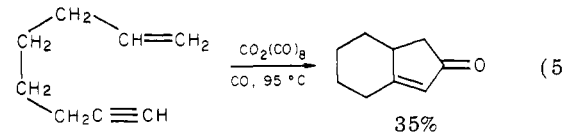




(4)

≤20%

R = CH_3CO, $(CH_3)_3C$



(5)

35%

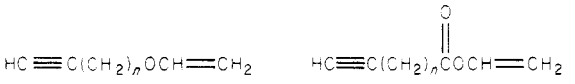
(1) For M = Co: (a) Khand, I. U.; Pauson, P. L. *J. Chem. Soc., Chem. Commun.* **1974**, 379. (b) Khand, I. U.; Pauson, P. L. *J. Chem. Res. (Miniprint)* **1977**, 0168. Moderate yields (e.g., 20%) are obtainable if the alkyne is aryl substituted. Unfortunately, the products obtained are not generally useful in natural product synthesis.

(2) For UV review: Coyle, J. D. In "The Chemistry of the Carbon–Carbon Triple Bond"; Patai, S., Ed., Wiley-Interscience: New York, 1978. For M = Al: Snider, B. B.; Hrib, N. J. *Tetrahedron Lett.* **1977**, 1725. Fienemann, H.; Hoffmann, H. M. R. *J. Org. Chem.* **1979**, *44*, 2802. Snider, B. B.; Roush, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1906. For M = Ti: Clark, R. D.; Untch, K. G. *J. Org. Chem.* **1979**, *44*, 248. For M = Ru: Mitsudo, T.; Kokuryo, K.; Takegami, Y. *J. Chem. Soc., Chem. Commun.* **1976**, 722. For M = Zn: Snider, B. B.; Brown, L. A.; Conn, R. S. E.; Killinger, T. A. *Tetrahedron Lett.* **1977**, 283.

(3) For M = Co: Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans. 1* **1973**, 977. Khand, I. U.; Pauson, P. L. *Ibid.* **1976**, 30. Khand, I. U.; Pauson, P. L. *J. Chem. Res. (Miniprint)* **1977**, 0153. Schore, N. E. *Synth. Commun.* **1979**, *9*, 41.

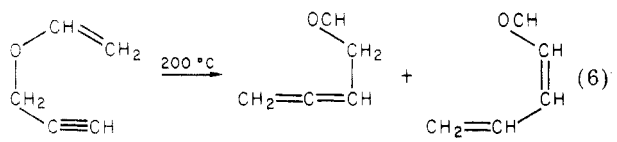
0022-3263/81/1946-5357$01.25/0

prompted us to undertake the development of convenient syntheses of vinyl ethers and esters **1** and **2** as potential substrates in cyclization processes that, if successful, would provide efficient entries to a variety of useful functionalized bicyclic systems.



1a, $n = 1$; b, $n = 2$; c, $n = 3$ — 2a, $n = 0$; b, $n = 1$; c, $n = 2$; d, $n = 8$

A limited number of preparations of ethers **1** have been reported involving either base-catalyzed eliminations[5] from halogenated precursors or thermal eliminations from acetals of acetylenic alcohols,[6] $CH_3CH[O(CH_2)_nC{\equiv}CH]_2$. The former methods are multistep processes of variable overall yield and limited generality while the latter, though more generally applicable, are inefficient in the use of the acetylenic precursor.[7] Only scattered mention of the corresponding vinyl esters is to be found in the literature,[8] and no generalizable synthetic route toward these compounds has been reported. In fact, the literature contains only a single example describing a chemical interaction between the alkyne and alkene portions of such a molecule: the Claisen rearrangement of vinyl propynyl ether (**1**, $n = 1$; eq 6).[9]



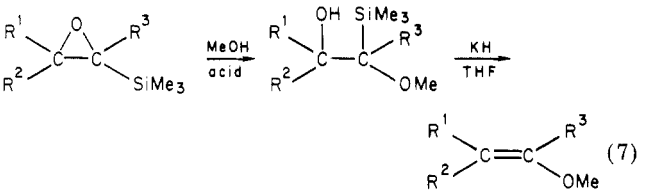
(6)

We report herein the results of investigations into the development of efficient and general new routes to **1** and **2** in detail and present some preliminary data concerning the reactivity of these compounds in transformations related to those described above.

Results and Discussion

The nature of the described compounds posed several immediate problems. Although many methods for the synthesis of alkynes and vinyloxy units exist, neither functional group is compatible with the majority of methods for introduction of the other into a molecule. For instance, vinyl ether and ester syntheses based on metal-catalyzed exchange processes[10] are unsuitable due to the interference of addition reactions at the triple bond. Furthermore, possible conjugate additions to **2** ($n = 0$) and isomerization reactions of the terminal triple bonds of **1** and **2** ($n \geq 1$) placed additional limitations on applicable synthetic routes of reasonable efficiency. Therefore, our efforts centered on methods that derive the alkyne function from readily available precursors and utilize mild elimination processes for introduction of the vinyl group.

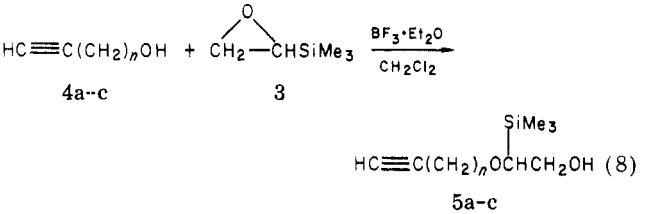
Synthesis of Vinyl Ethers 1. The sequence developed by Hudrlik and co-workers (eq 7)[11] was chosen for detailed



(7)

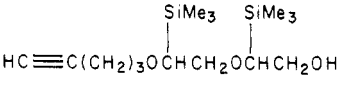
investigation. It was expected that procedural modifications would be necessary (1) because we wished to avoid the use of alcohol as solvent in the addition step since, in our cases, we required terminal alkynols as starting materials and (2) because the Hudrlik sequence had never been applied to the synthesis of simple unsubstituted vinyl ethers ($R^1 = R^2 = R^3 = H$), a fact that raised questions as to the likely facility of both the acid-catalyzed addition to the epoxide and the subsequent elimination reaction under mild conditions.

In fact, the addition of alcohols **4a–c** (**a**, $n = 1$; **b**, $n = 2$; **c**, $n = 3$) to epoxide **3** proceeded smoothly in CH_2Cl_2 at room temperature in the presence of catalytic amounts of boron trifluoride etherate (eq 8). Optimal conditions



(8)

for reaction involved addition of 1 drop of $BF_3{\cdot}Et_2O$ to a solution 0.55 M in alcohol and 0.5 M in epoxide. The small excess of alcohol was necessary to prevent addition of **5** to a second mole of epoxide, which gave rise to products such as **6**, isolated in 10% yield from the reaction of **4c** and **3** in a 1:1 ratio.

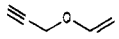
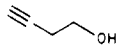
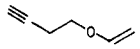
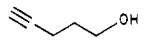
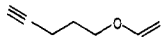
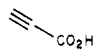
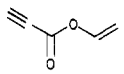
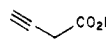
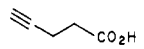
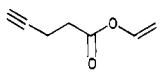
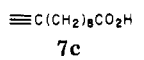
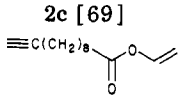


6

Hudrlik has found that substituted analogues of **5** eliminate readily to give vinyl ethers upon treatment with KH in THF; simple 2-(trimethylsilyl)-1-alkanols are similarly reactive, giving terminal alkenes in high yield.[12] The success of this elimination appears to be counterion dependent, as Chan and Chang have found that analogous silyl alkoxides of lithium or magnesium are unreactive, in accord with Peterson's early observations in the 1-(trimethylsilyl)-2-alkanol system.[13] In any event, slow addition of a suspension of KH in THF to a cooled solution of any of the adducts **5** in THF was carried out and was found to produce acetylenic vinyl ethers **1a–c** in about 40–45% yields, accompanied by some polymerization. A cleaner reaction and somewhat higher yields resulted from the use of diethyl ether as the solvent (eq 9 and Table I). Excess KH was used in the preparation of **1a** to de-

(4) Schore, N. E., Croudace, M. C. *J. Org. Chem.*, in press.
(5) For $n = 1$: (a) Eberly, K. C. U. S. Patent 2 537 643, 1951; *Chem. Abstr.* **1951**, *45*, P4261*h*. (b) Black, D. K.; Landor, S. R. *J. Chem. Soc.* **1965**, 5225.
(6) For $n = 1$: Shostakovskii, M. F.; Vlasov, V. M.; Balezina, G. G.; Emel'yanov, I. S. *Zh. Org. Khim.* **1969**, *5*, 212. For $n = 2$: Shostakovskii, M. F.; Vlasov, V. M.; Grenovskii, P. I. USSR Patent 165 447, 1964; *Chem. Abstr.* **1965**, *62*, P6398*a*.
(7) For $n = 3$ (mentioned without synthetic information): Sin'kina, N. I.; Kuznetsova, T. S. *Uch. Zap.—Yarosl. Gos. Pedagog. Inst. im. K. D. Ushinskogo* **1976**, *No. 161*, 42; *Chem. Abstr.* **1978**, *88*, 153043.
(8) For $n = 1$ and 2 (mentioned without synthetic information): Kuznetsova, T. S.; Shubnyakov, I. B.; Monakhova, G. A.; Vlasov, V. M. *Dokl. Vses. Konf. Khim. Atsetilena, 4th* **1972**, *1*, 325; *Chem. Abstr.* **1975**, *82*, 124659.
(9) Cresson, P. *C. R. Hebd. Seances Acad Sci.* **1965**, *261*, 1707.
(10) E.g.: Watanabe, W. H.; Conlon, L. E. *J. Am. Chem. Soc.* **1957**, *79*, 2828.
(11) Hudrlik, P. F.; Hudrlik, A. M.; Rona, R. J.; Misra, R. N.; Withers, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1993.
(12) Hudrlik, P. F.; Peterson, J.; Rona, R. J. *J. Org. Chem.* **1975**, *40*, 2263.
(13) Chan, T. H.; Chang, E. *J. Org. Chem.* **1974**, *39*, 3264. Peterson, D. J. *Ibid.* **1968**, *33*, 780.
(14) Mansfield, G. H.; Whiting, M. C. *J. Chem. Soc.* **1956**, 4761.

Table I

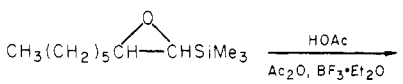
substrate	intermediate product(s) [yield, %][a]	final product [yield, %]
 4a	5a [68]	 1a [50]
 4b	5b [74]	 1b [55]
 4c	5c [73]	 1c [72]
 7a	8a [94], 9a [71]	 2a [56]
 7b	8b [30 (63)]	
 7c	8c [58 (96)], 9c [99]	 2c [69]
 7c	8d [51 (97)], 9d [91]	 2d [76]

[a] Yields in parentheses are based upon unrecovered starting material.

protonate the alkyne and prevent isomerization to the allene during elimination.

$$\underset{\textbf{5a–c}}{HC{\equiv}C(CH_2)_nOC(SiMe_3)HCH_2OH} \xrightarrow[\text{ether, 0 °C}]{KH} \underset{\textbf{1a–c}}{HC{\equiv}C(CH_2)_nOCH{=}CH_2} \quad (9)$$

Synthesis of Vinyl Esters 2. Successful syntheses of the two isomers of 1-octenyl acetate from the two 1-(trimethylsilyl)-1-hexene oxides have been described[11] (eq 10).



(10)

In these systems elimination of trimethylsilanol was found to occur *spontaneously* upon BF_3-catalyzed epoxide ring opening, thus yielding the vinyl ester in a single step. In the course of attempts to apply this chemistry directly to the synthesis of the required acetylenic vinyl esters, it was quickly determined that the acetylenic systems presented situations quite different not only from the above example but also from each other. The approaches used for each acetylenic carboxylic acid will therefore be described separately.

Vinyl propynoate (2a). The reaction of propynoic acid with epoxide **3** occurs spontaneously at room temperature without the assistance of Lewis acid catalysis, no doubt due to the substantially greater strength of propynoic acid (pK_a = 1.84) relative to nonconjugated carboxylic acids.[13] Remarkably, the product, isolated in 94% yield, is the *simple adduct* **8a** which not only fails to eliminate spontaneously to yield vinyl ester but also is completely resistant to elimination either thermally or in the presence of acidic or basic reagents. Treatment with either BF_3·Et_2O at 60 °C or saturated aqueous NH_4Cl afforded only uncharged starting material while stronger acid (e.g., H_2SO_4 in THF) led to decomposition. Strong bases (NaOMe, KO-*t*-Bu) gave products of conjugate addition while treatment with weaker or nonnucleophilic bases led only to reisolation of starting material upon workup.

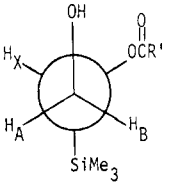


Figure 1. Likely favored conformation for compounds 8.

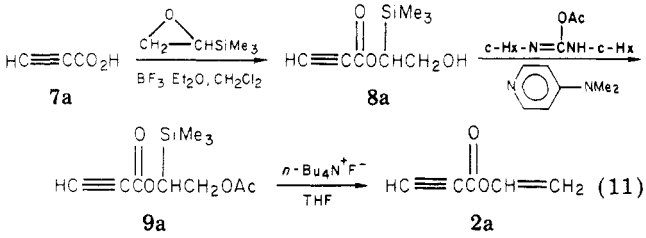
The lack of reactivity of this system toward acid-catalyzed elimination is presumably due to the difficulty associated with generating significant cationic character at the primary alcohol-bearing carbon, relative to internal, secondary systems. Eliminations of internal silyl hydroxy amides can be carried out successfully in the presence of base.[11] The failure of several kinds of bases to bring about elimination of the terminal silyl hydroxy ester appears to arise from a combination of problems including interference of undesired side reactions. In particular, no vinyl esters are observed on using KH in THF under the conditions found to succeed for the elimination of alcohols **5** to vinyl ethers **1**. A conformational factor may be partially responsible for the failure of this reaction as the elimination with base is a syn process and must proceed from a conformation in which the hydroxyl and trimethylsilyl groups bear a gauche relationship to one another. We have obtained spectroscopic evidence that suggests that the favored conformation of these compounds in solution places these groups in an anti relationship (Figure 1). NMR spectra for these hydroxy esters **8** display only broadened, complex multiplets for the methine and methylene protons in a nonpolar solvent at 60 MHz, while solutions in polar solvents display "deceptively simple" patterns (methine triplet and methylene doublet) that are equally uninformative. Acetylated derivatives of these compounds (vide infra) display ABX spectra at 360 MHz with J_{AX} = 2 Hz, J_{BX} = 9 Hz, and J_{AB} = 12 Hz, characteristic of one gauche vicinal coupling and one anti vicinal coupling.[15] The signal for H_B is ca. 0.2 ppm upfield relative to that for H_A. Thus the spectral data are most consistent with the conformation in Figure 1.[16] Should a similar situation obtain for the free alcohol and its alkali metal salts, the barrier to elimination would be increased by this unfavorable conformational preference. By way of contrast, in the Hudrlik hydroxy amide systems[11] either H_A or H_B becomes alkyl, thereby raising the energy of the conformation corresponding to that in Figure 1 relative to those favoring elimination.

Given these considerations together with the results of our initial studies, it appeared that the direct elimination process would not be feasible for generation of the terminal vinyl ester functionality. An alternative stepwise procedure was therefore employed involving acetylation followed by fluoride-promoted elimination (eq 11). Again, the interference of conjugate addition processes in the course of attempts to esterify the hydroxyl group by the usual methods (e.g., Ac_2O or AcCl/pyridine) necessitated the use of an alternative procedure. The method of Hassner, making use of the preformed reagent from acetic acid and dicyclohexylcarbodiimide,[17] gave high yields of acetate **9a**

(15) As predicted by normal Karplus correlations as described in, e.g.: Dyer, J. R. "Applications of Absorption Spectroscopy of Organic Compounds"; Prentice-Hall: Englewood Cliffs, NJ, 1965; Chapter 4. Karplus, M. *J. Chem. Phys.* **1959**, *30*, 11.

(16) Acetoxy groups exert a larger deshielding effect on anti β-protons than on gauche β-protons: Bhacca, N. S.; Williams, D. H. "Applications of NMR Spectroscopy in Organic Chemistry"; Holden-Day: San Francisco, 1964; Chapter 8.

(17) Hassner, A.; Alexanian, V. *Tetrahedron Lett.* **1978**, 4475.



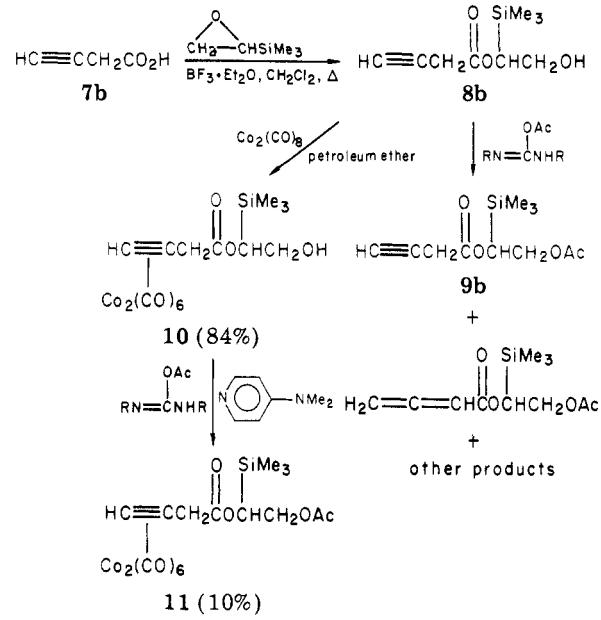
which could be readily purified chromatographically. Treatment of **9a** with anhydrous tetra-*n*-butylammonium fluoride in THF induced elimination[18] to the desired vinyl propynoate in satisfactory yield, accompanied by some acetaldehyde. The product was readily isolated and purified by distillation at reduced pressure. The overall yield for the three-step procedure was 45%.

Attempts to Prepare Vinyl 3-Butynoate (2b). With the exception of propynoic acid, all the ω-alkynoic acids react only extremely sluggishly with epoxide **3**. A variety of addition modes and conditions were attempted to overcome this problem and to also avoid the use of acid as solvent or in large excess, an obvious impracticality. In the case of 3-butynoic acid (**7b**), addition was found to proceed only upon slow addition of a concentrated CH_2Cl_2 solution of epoxide **3** to a refluxing CH_2Cl_2 solution containing 1.05 equiv of **7b** and a small amount of boron trifluoride etherate. This particular procedure was necessary to minimize BF_3-catalyzed reactions of **3** that did not involve addition of the acetylenic acid. In spite of these efforts, only a 30% yield of the adduct **8b** was obtained after purification, although more than half of the original quantity of acid could be recovered unchanged from the reaction mixture. The yield of **8b** based on unrecovered **7b** was 63%. With **8b** in hand, attempts were made to apply the same esterification–elimination sequence that succeeded for vinyl ester **2a**. Reaction with the DCC–acetic acid reagent led to some of the desired acetate **9b** (IR, NMR), but this and related sequences had to ultimately be abandoned due to the unexpected[19] sensitivity of **9b** toward isomerization to the allene during a variety of attempts at isolation of the pure product, including vacuum distillation, column chromatography (silica, alumina, florisil), GC (SE-30, Carbowax, DEGS), and HPLC (reverse phase). Although **9b** was clearly present in the product mixture, attempts at direct elimination without isolation also met with failure.

Protection of the terminal acetylene of **8b** with $Co_2(CO)_8$ was then carried out[20] to give the hexacarbonyldicobalt complex **10**. Acetylation of **10** was attempted by using the HOAc–DCC reagent. Although a very small amount of the impure complexed diester **11** was isolated (Scheme I), attempts to bring about the elimination with a stoichiometric amount of fluoride reagent were, again, unsuccessful. Further efforts to generate **2b** via methods of this general type were discontinued. Vinyl ester **2b** has been reported once in the literature without any information regarding its preparation.[8]

Vinyl 4-Pentynoate (2c) and Vinyl 10-Undecynoate (2d). With the higher homologues of ω-acetylenic acid, the overall sequence was again found to give rise to satisfactory results. Reaction of 4-pentynoic acid (**7c**) with **3** took place in the presence of boron trifluoride etherate at the melting point of **7c** to yield 58% of the corresponding adduct **8c**. Subsequent acetylation and elimination proceeded with an overall 68% yield to the desired

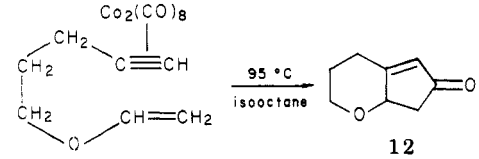
Scheme I



vinyl ester **2c**. In the case of 10-undecynoic acid (**7d**) the initial addition reaction proceeded well in CH_2Cl_2 solution, yielding 51% of adduct **8d** (97% based on unrecovered **7d**). Acetylation and elimination were similarly successful, proceeding in 91% and 76% yields, respectively (Table I). In summary, therefore, the general synthesis, with the modifications described, allows the two-step preparation of any vinyl ester of the general structure $HC{\equiv}C(CH_2)_nCO_2CH{=}CH_2$ for $n = 0$ and $n \geq 2$.

Reactions of Compounds 1 and 2 with $Co_2(CO)_8$. Each of the vinyl esters and ethers reacts rapidly and quantitatively with octacarbonyldicobalt in a hydrocarbon solvent at room temperature to yield the hexacarbonyldicobalt–alkyne complex. The reaction is accompanied by a color change from brown ($Co_2(CO)_8$) to deep reddish violet. The IR peak near 3300 cm^{-1} due to terminal acetylenic C–H stretch is replaced by a new band at 3045 cm^{-1} for the corresponding vibration of the complex, and the bridging carbonyl absorption of $Co_2(CO)_8$ at 1864 cm^{-1} disappears. The further transformations of the complexes derived from vinyl ethers **1a–c** have been investigated in the greatest detail. Preliminary results for the complex of vinyl ether **1c** are described below.

The hexacarbonyldicobalt complex of 4-pentynyl vinyl ether (**1c**) undergoes a thermal reaction in hydrocarbon solvent even at room temperature. Heating to 95 °C in isooctane causes rapid loss of the vinyl ether IR peaks at 1620 and 1640 cm^{-1} while a new absorption at 1715 cm^{-1} grows in. This transformation is accompanied by the appearance of a new absorption in the NMR at δ 5.75 and takes about 72 h to proceed to completion. Taken together, these observations are consistent with intramolecular cyclization of the complexed **1c** to yield cyclopentenone **12** (eq 12). Lending support to this interpre-



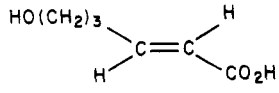
(12)

12

tation is the observation that analogous changes occur upon similar heating of a solution of the 3-butynyl vinyl ether complex, while the 2-propynyl vinyl ether complex, which would give rise to a compound containing a four-

(18) Chan, T. H.; Mychajlowskij, W. *Tetrahedron Lett.* **1974**, 171.
(19) Alcohol **8b** survives very similar procedures.
(20) Nicholas, K. M.; Pettit, R. *Tetrahedron Lett.* **1971**, 3475.

membered ring, is only slowly decomposed under identical conditions and fails to give rise to an IR band characteristic of a cyclopentenone when thermal decomposition takes place at 120 °C. To date, however, it has proved impossible to isolate ketone **12** from these reaction mixtures due to the occurrence of further thermal and hydrolytic processes that lead to a complex mixture. The hydrolyzed carbonylation product of **1c**, (*E*)-6-hydroxy-2-hexenoic acid (**13**),



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has been conclusively identified[21,22] as a component of this mixture. Further efforts to isolate and characterize the products of these reactions are currently underway and will be described separately along with the results of corresponding cyclization reactions in the all-carbon systems.

Experimental Section

Reagents. Dichloromethane was dried over 3-Å molecular sieves before use. Acetic acid was purified by treatment with acetic anhydride and CrO_3 and distillation. For procedures carried out under oxygen-free conditions, ethereal solvents were distilled from sodium–benzophenone ketyl. Propynoic acid (Aldrich), 10-undecynoic acid (Farchan), the three alkynols (Farchan), boron trifluoride etherate (Eastman), *m*-chloroperbenzoic acid (Aldrich), and vinyltrimethylsilane (Silar) were obtained commercially and used as received. 3-Butynoic[23] and 4-pentynoic[24] acids were prepared by literature procedures. Analytical samples of products were collected by gas chromatography with the columns and conditions indicated. All collections utilized a flow rate of 90 mL/min.

(Trimethylsilyl)oxirane (3). The literature procedure[25] was modified to use *m*-chloroperbenzoic acid (MCPBA) instead of perphthalic acid. In a typical preparation a solution of 50.0 g (0.25 mol) of 85% MCPBA in 150 mL of dichloromethane was added to a solution of 29.0 g (0.29 mol) of vinyltrimethylsilane in 45 mL of dichloromethane at 0 °C dropwise with stirring over a period of 2 h. The mixture was allowed to come to room temperature, stirred for an additional 2 h, and then neutralized by careful treatment with saturated aqueous $NaHCO_3$, after which the organic layer was dried over Na_2SO_4. The solution was then distilled at room temperature and under high vacuum into a liquid nitrogen cooled receiver. Redistillation at atmospheric pressure allowed isolation of pure **3**: bp 106–110 °C; typical yield 13.0 g (51%). Yields were invariably lower if the crude reaction mixture was not vacuum transferred prior to atmospheric pressure distillation.

2-(3-Butynyloxy)-2-(trimethylsilyl)ethanol (5b). To a stirred solution of 1.75 g (0.0250 mol) of 3-butyn-1-ol and 2.63 g (0.0227 mol) of (trimethylsilyl)oxirane in 5 mL of CH_2Cl_2 was added 1 drop of $BF_3{\cdot}Et_2O$. An exothermic reaction took place, and the originally colorless solution turned brown. The reaction mixture was stirred for 1 h, poured into 20 mL of saturated aqueous $NaHCO_3$, and extracted with portions (3 × 20 mL) of ethyl ether. The extracts were dried ($MgSO_4$), and the solvent was removed in vacuo. Chromatography (silica gel/hexane) yielded 3.12 g (74%) of **5b**. An analytical sample was isolated by GC (10 ft × $^3/_8$ in. column, 10% SE-30 on Chromasorb W, 170 °C): IR (neat) 1250, 2120, 2850–2950, 3300, 3450 (br) cm^{-1}; NMR (CCl_4) δ 0.09 (s, 9 H), 2.05 (t, *J* = 2.5 Hz, 1 H), 2.47 (dt, *J* = 2.5, 7 Hz, 2 H), 3.15 (m, 1 H), 3.2 (br m, 1 H, OH), 3.71 (br m, 4 H); mass spectrum, *m/e* (relative intensity) 169 (26, M – OH), 157 (5), 143 (12), 117 (41, Me_3SiCH_2CHOH), 73 (100, Me_3Si), 67 (37, $HC{\equiv}CCH_2CH_2O$). All peaks give satisfactory high-resolution mass spectral values, e.g.: calcd for $C_9H_{17}OSi$ *m/e* 169.0731, found *m/e* 169.0712. Anal. Calcd for $C_9H_{18}O_2Si$: C, 58.06; H, 9.68. Found: C, 57.69; H, 9.53.

2-(2-Propynyloxy)-2-(trimethylsilyl)ethanol (5a). This compound was prepared and isolated as for **5b** from 0.74 g (0.0131 mol) of 2-propyn-1-ol and 1.37 g (0.0118 mol) of (trimethylsilyl)oxirane; yield 1.38 g (68%). For the sample collected by GC (10 ft × $^3/_8$ in. column, 10% SE-30 on Chromasorb W, 160 °C): IR (neat) 1250, 2120, 2850–2950, 3300, 3450 (br) cm^{-1}; NMR (CCl_4) δ 0.09 (s, 9 H), 2.36 (t, *J* = 2.2 Hz, 1 H), 2.60 (s, 1 H, OH), 3.50 (m, 3 H), 4.20 (d, splitting = 2.2 Hz, 2 H); mass spectrum, *m/e* (relative intensity) 172 (1, M), 117 (4), 73 (100); high-resolution mass spectrum calcd for $C_8H_{16}O_2Si$ *m/e* 172.0950, found *m/e* 172.0955. Anal. Calcd for $C_8H_{16}O_2Si$: C, 55.81; H, 9.30. Found: C, 55.98; H, 9.28.

2-(4-Pentynyloxy)-2-(trimethylsilyl)ethanol (5c). This compound was prepared and isolated as for **5b** from 2.57 g (0.0318 mol) of 4-pentyn-1-ol and 2.77 g (0.0239 mol) of (trimethylsilyl)oxirane; yield 3.40 g (73%). For the sample collected by GC (10 ft × $^3/_8$ in. column, 10% SE-30 on Chromasorb W, 190 °C); IR (neat) 1250, 2120, 2850–2950, 3300, 3450 (br) cm^{-1}; NMR (CCl_4) δ 0.09 (s, 9 H), 1.87 (m, 2 H), 1.98 (t, *J* = 2 Hz, HC≡C), 2.15 (br s, 1 H, OH), 2.32 (dt, *J* = 2, 6 Hz, 2 H), 3.06 (dd, *J* = 3, 6 Hz, 1 H), 3.5–4.2 (m, 4 H); mass spectrum, *m/e* (relative intensity) 183 (56, M – OH), 155 (26), 177 (90), 82 (60, $HC{\equiv}CCH_2CH_2CHO$), 67 (62, $HC{\equiv}CCH_2CH_2CH_2$), 73 (100); high-resolution mass spectrum calcd for $C_{10}H_{19}OSi$ *m/e* 183.1205, found *m/e* 183.1205. Anal. Calcd for $C_{10}H_{20}O_2Si$: C, 59.93; H, 10.08. Found: C, 59.86; H, 9.87.

Reactions carried out as above but starting with a 1:1 ratio of reactants give rise to a second product, isolated in 10% yield by GC (conditions as described for **5c** above) and identified spectroscopically as 2-[2-(pentynyloxy)-2-(trimethylsilyl)ethoxy]-2-(trimethylsilyl)ethanol (**6**): IR (neat) 1250, 2120, 2850–2950, 3320, 3200–3600 (br) cm^{-1}; NMR (CCl_4) δ 0.04 (br s, 18 H), 1.8 (m, 3 H), 2.3 (br m, 2 H), 3.0–3.3 (m, 2 H), 3.70 (m, 7 H) ppm.

4-(Ethenyloxy)-1-butyne (Vinyl 3-Butynyl Ether)[6] (1b). The mineral oil was washed from 1.10 g of 22.5% KH–mineral oil dispersion (0.0062 mol) with several portions of dry petroleum ether. The dry KH was then suspended in 10 mL of anhydrous ether, and this suspension added dropwise via syringe to a solution of 1.21 g (0.0065 mol) of **5b** in 10 mL of anhydrous ether under N_2 at 25 °C. After the initial exothermic reaction, the mixture, now yellow-brown, was stirred for 1 h and then poured into 20 mL of water. The crude product was extracted with ether (3 × 25 mL) which was dried over anhydrous K_2CO_3. The ether was removed by distillation (spinning band) leaving a mixture of vinyl ether **1b** and hexamethyldisiloxane which could not be readily separated by distillation [hexamethyldisiloxane, bp 101 °C; **1b**, bp 102 °C (720 mmHg[6])]. Purification by preparative GC was easily accomplished, however (10 ft × $^3/_8$ in column, 3% SE-30 on Chromasorb W in glass, 35 °C): yield 0.33 g (55%); IR (neat) 1620, 1640, 2115, 3320 cm^{-1}; NMR (C_6D_6) δ 1.90 (t, *J* = 2 Hz, 1 H), 2.18 (m, 2 H), 3.52 (m, 2 H), 3.89 (dd, *J* = 2, 7 Hz, 1 H), 4.15 (dd, *J* = 2, 14 Hz, 1 H), 6.40 (dd, *J* = 7, 14 Hz, 1 H); mass spectrum, *m/e* (relative intensity) 96 (5, M), 69 (83, $HC{\equiv}CCH_2CH_2O$), 53 (100, $HC{\equiv}CCH_2CH_2$). All peaks give satisfactory high-resolution mass spectral values, e.g.: calcd for C_6H_8O *m/e* 96.0558, found *m/e* 96.0566.

3-(Ethenyloxy)-1-propyne (Vinyl 2-Propynyl Ether)[5,6] (1a). Use of only 1 equiv of KH causes some isomerization, producing allenyl vinyl ether [(ethenyloxy)propadiene]: NMR (CCl_4) δ 4.03 (dd, *J* = 2, 7 Hz, 1 H), 4.53 (dd, *J* = 2, 14 Hz, 1 H), 5.38 (d, *J* = 5 Hz, 2 H), 6.34 (dd, *J* = 7, 14 Hz, 1 H), 6.62 (t, *J* = 5 Hz, 1 H). The procedure given effectively protects the terminal alkyne. A mixture of 3.00 g of pentane-washed 22.5% KH dispersion (0.0168 mol) and 5 mL of THF was cooled to −78 °C and a solution of 1.11 g (0.0064 mol) of **5a** in 5 mL of THF, also cooled to −78 °C, was added dropwise. The mixture was stirred for 3 h at −78 °C, allowed to warm slowly, and stirred at room temperature for 1 h. The solution, now yellow, was cooled again to −78 °C and treated with 10 mL of hexane followed by a cooled solution of 5 mL of water in 10 mL of THF. The hexane layer was separated, washed with H_2O (5 × 25 mL), and dried (K_2CO_3). Distillation

(21) Dolezal, S. *Collect. Czech. Chem. Commun.* **1972**, *37*, 3117.
(22) For related reactions see: Pino, P.; Miglierina, A. *J. Am. Chem. Soc.* **1952**, *74*, 5551. Heck, R. F. "Organotransition Metal Chemistry"; Academic Press: New York, 1974; pp 238–247.
(23) Heilbron, I.; Jones, E. R. H.; Sondheimer, F. *J. Chem. Soc.* **1949**, 606.
(24) Holland, B. C.; Gilman, N. W. *Synth. Commun.* **1974**, *4*, 203.
(25) Bazant, V.; Matousek, V. *Collect. Czech. Chem. Commun.* **1959**, *24*, 3758. See also: Wilt, J. W.; Kolewe, O.; Kraemer, J. F. *J. Am. Chem. Soc.* **1969**, *91*, 2624.

afforded 0.256 g (48% yield) **1a**: bp 90 °C [lit. bp 79 °C (746 mmHg),[5a] 90–92 °C (760 mmHg),[5b] 40–42 °C (150 mmHg)[6]]; IR (THF) 1620, 1640, 2115, 3320 cm^{-1}; NMR (CCl_4) δ 2.33 (t, J = 2 Hz, 1 H), 4.17 (dd, J = 2, 7 Hz, 1 H), 4.32 (d, J = 2 Hz, 2 H), 4.53 (dd, J = 2, 14 Hz, 1 H), 6.34 (dd, J = 7, 14 Hz, 1 H).

5-(Ethenyloxy)-1-pentyne (Vinyl 4-Pentynyl Ether)[7] (1c). This compound was prepared as for **1b** from 8.0 g of 22.5% KH dispersion (0.0450 mol) and 6.0 g (0.0300 mol) of **5c**: yield 2.40 g (72%). For the sample collected by GC (10 ft × $^3/_8$ in. column, 3% SE-30 on Chromasorb W in glass, 55 °C): IR (neat) 1620, 1640, 2115, 3320 cm^{-1}; NMR (C_6D_6) δ 1.51 (m, 2 H), 1.85 (t, J = 2 Hz, 1 H), 2.15 (m, 2 H), 3.48 (m, 2 H), 3.98 (dd, J = 2, 7 Hz, 1 H), 4.17 (dd, J = 2, 14 Hz, 1 H), 6.40 (dd, J = 7, 14 Hz, 1 H); NMR (CCl_4) δ 1.87 (m, 3 H), 2.29 (dt, J = 2, 6 Hz, 2 H), 3.73 (t, J = 6 Hz, 2 H), 3.89 (dd, J = 2, 7 Hz, 1 H), 4.09 (dd, J = 2, 15 Hz, 1 H), 6.36 (dd, J = 7, 15 Hz, 1 H); mass spectrum, m/e (relative intensity) 110 (16, M), 83 (32, $HC{\equiv}CCH_2CH_2CH_2O$), 67 (100, $HC{\equiv}CCH_2CH_2CH_2$); high-resolution mass spectrum calcd for $C_7H_{10}O$ m/e 110.0748, found m/e 110.0740. Anal. Calcd for $C_7H_{10}O$: C, 76.36; H, 9.09. Found: C, 75.86; H, 9.00.

2-Hydroxy-1-(trimethylsilyl)ethyl Propynoate (8a). To a stirred solution of 3.11 g (0.0045 mol) of propynoic acid in 5 mL of CH_2Cl_2 at 0 °C was added a solution of 4.7 g (0.0041 mol) of (trimethylsilyl)oxirane with 2 mL of CH_2Cl_2 over a period of 30 min. The reaction was allowed to come to room temperature and stirred an additional 2 h. Solvent was removed by rotary evaporation and the residue chromatographed (silica gel, 3:1 hexane–ether) to yield 7.50 g (94%) **8a**. An analytical sample was isolated by GC (5 ft × $^1/_4$ in. column, 1.5% OV-101 on Chromasorb G, 140 °C); IR (neat) 1250, 1715, 2140, 3340, 3450 (br) cm^{-1}; NMR (CCl_4) δ 0.08 (s, 9 H), 2.82 (d, J = 3 Hz, 1 H), 2.98 (br s, OH, 1 H), 3.75 (m, 2 H), 4.77 (m, 1 H); mass spectrum, m/e (relative intensity) 169 (26, M − OH), 116 (65, $Me_3SiC_2H_3O$), 73 (100, Me_3Si), 54 (10, $HC{\equiv}CCO$). Anal. Calcd for $C_8H_{14}O_3Si$: C, 51.61; H, 7.53. Found: C, 51.10; H, 7.70.

2-Acetoxy-1-(trimethylsilyl)ethyl Propynoate (9a). A stirred mixture of 6.15 g (0.0298 mol) of dicyclohexylcarbodiimide, 0.35 g (0.0029 mol) of 4-(dimethylamino)pyridine, and 20 mL of anhydrous ether was treated with 1.65 g (0.0275 mol) of acetic acid under dry N_2.[17] A white precipitate of the *O*-acetylisourea formed almost immediately. To this suspension was added 5.96 g (0.0298 mol) of **8a**, and the reaction was stirred 18 h. Solid material was removed by filtration and the ether layer washed in turn with water (3 × 50 mL), 5% acetic acid (3 × 50 mL), water (3 × 50 mL), and 50 mL of saturated aqueous NaCl. The solution was dried (K_2CO_3) and stripped, and the residue was chromatographed (silica gel, hexane) to yield 5.65 g (85%) of **9a**. Analytically pure material may be obtained by distillation [bp 110–112 °C (1 mmHg)] although recovery is poor. Distillation at 0.1 mmHg (bath temperature 65 °C) does not significantly improve the purity of the chromatographed product, which is ≥95%, and results in losses approaching 50%; therefore, the chromatographed product was used as obtained for further reaction: IR (neat) 1250, 1705, 1740, 2110, 2960, 3300 cm^{-1}; NMR (CD_3CN) δ 0.08 (s, 9 H), 1.97 (s, 3 H), 2.77 (s, 1 H), 4.18 (m, 2 H), 4.97 (dd, J = 3, 8 Hz, 1 H). Anal. Calcd for $C_{10}H_{16}O_4Si$: C, 52.63; H, 7.07. Found: C, 52.26; H, 7.12.

Ethenyl Propynoate[8] (2a). A solution of 0.93 g (0.0041 mol) of **9a** in 10 mL of anhydrous THF was treated under N_2 with 14.1 mL of 1.0 M tetra-*n*-butylammonium fluoride (0.0041 mol) over a 15-min period. The reaction mixture was stirred for 1 h. All volatile materials were then collected by high-vacuum distillation at room temperature into a −196 °C trap. Analysis of the distillate by NMR indicated the presence of acetaldehyde as well as the desired product, which was isolated and purified by redistillation; bp 44–46 °C (81 mmHg) [lit.[26] bp 31 °C (35 mmHg)]. For **2a**: yield 0.22 g (56%); IR (THF) 1625, 1650, 1750 cm^{-1}; NMR (CD_3CN) δ 2.55 (s, 1 H), 4.48 (dd, J = 2, 6 Hz, 1 H), 4.78 (dd, J = 2, 13 Hz, 1 H), 7.16 (dd, J = 6, 13 Hz, 1 H).

2-Hydroxy-1-(trimethylsilyl)ethyl 3-Butynoate (8b). A solution of 1.37 g (0.0163 mol) of 3-butynoic acid and 1 drop of $BF_3{\cdot}Et_2O$ in 5 mL of CH_2Cl_2 was heated to reflux and treated over a period of 30 min with a solution of 2.38 g (0.0205 mol) of (trimethylsilyl)oxirane in 5 mL of CH_2Cl_2, added dropwise. The reaction was stirred for an additional hour at reflux, cooled, and extracted with saturated aqueous $NaHCO_3$. The organic layer was dried (K_2CO_3) and stripped, and the residue was chromatographed (silica gel, chloroform) to yield 0.98 g (30%) **8b**. Final purification was by GC (5 ft × $^1/_4$ in. column, 1.5% OV-101 on Chromasorb G, 165 °C); IR (neat) 1250, 1720, 2140, 2910, 3320, 3450 (br) cm^{-1}; NMR ($CDCl_3$) δ 0.08 (s, 9 H), 2.25 (t, J = 3 Hz, 1 H), 3.20 (br s, OH, 1 H), 3.38 (d, J = 3 Hz, 2 H), 3.83 (d, splitting = 5 Hz, 2 H), 5.03 (t, splitting = 5 Hz, 1 H). Acidification of the basic extracts allowed isolation of 0.72 g (52% recovery) of unreacted acid, making the yield of **8b** based on unrecovered material 63%.

Attempts were made to acetylate **8b** according to the procedure established for **8a**. Thus *O*-acetyl-*N,N'*-dicyclohexylisourea was prepared from 0.58 g (0.0028 mol) of dicyclohexylcarbodiimide, 0.04 g (0.003 mol) of 4-(dimethylamino)pyridine, and 0.15 g (0.0026 mol) of acetic acid in 3 mL of anhydrous ether and treated with 0.56 g (0.0028 mol) of **8b**. After a workup procedure similar to that used for **9a**, a crude product was obtained that exhibited IR and NMR signals suggestive of both the desired product and an allene derivative (presumably the 2,3-butadienoic acid ester). A variety of separation techniques were attempted with this product mixture without success (see text).

Treatment of this crude product mixture with tetra-*n*-butylammonium fluoride in either THF or CH_3CN gave no evidence for formation of a vinyl ester.

2-Hydroxy-1-(trimethylsilyl)ethyl 3-Butynoate–Hexacarbonyldicobalt (10). A solution of 0.20 g (0.0010 mol) of **8b** in 5 mL of petroleum ether under N_2 was treated with 0.40 g (0.0012 mole) of $Co_2(CO)_8$. After the mixture was stirred overnight, the solvent was removed in vacuo, leaving a brown residue which was chromatographed on silica gel. Unreacted $Co_2(CO)_8$ was eluted first (petroleum ether) followed by purple complex **10**, eluted with ether. Removal of the solvent left 0.35 g (71%) **10**: IR (neat) 1250, 2030, 2070, 2110 (ν_{CO}), 3060 (complexed HC≡C), 3300 (OH) cm^{-1}; NMR (C_6D_6) δ 0.08 (s, 9 H), ~3.5 (br m, 5 H), 5.03 (m, 1 H), 5.73 (m, complexed HC≡C, 1 H). This air-sensitive material was used without further purification.

O-Acetyl-*N,N'*-dicyclohexylisourea was prepared from 0.16 g (0.0005 mol) of dicyclohexylcarbodiimide, 0.0065 g (0.000 05 mol) of 4-(dimethylamino)pyridine, and 0.028 g (0.000 47 mol) of acetic acid in 5 mL of ether. Then 0.25 g (0.0005 mol) of **10** was added and the reaction mixture allowed to stir overnight. Solvent was removed in vacuo, and the residue was chromatographed on silica gel (petroleum ether–ether) to yield 0.15 g of product contaminated with dicyclohexylurea. Analysis by NMR of the material obtained indicated the presence of a 10% yield of the acetate of **10** (**11**): IR (neat) 1250, 1375, 1730, 2030, 2070, 2110, 3070 cm^{-1}; NMR (C_6D_6) δ 0.08 (s, 9 H), 1.90 (s, 3 H), 3.68 (br m, 4 H), 5.00 (m, 1 H), 5.78 (m, 1 H).

An attempt to bring about elimination by reaction of **11** with equimolar tetra-*n*-butylammonium fluoride in THF instead caused disruption of the acetylene–hexacarbonyldicobalt complex (loss of IR bands at 2030, 2070, and 2110 cm^{-1} and reappearance of uncomplexed C–H stretching band at 3250 cm^{-1}). It did not prove possible to isolate the acetate of uncomplexed **8b** from this mixture.

2-Hydroxy-1-(trimethylsilyl)ethyl 4-Pentynoate (8c). A mixture of 2.92 g (0.029 mol) of 4-pentynoic acid and 5 drops of $BF_3{\cdot}Et_2O$ were heated to the melting point of the acid. Then 3.40 g (0.029 mol) of neat (trimethylsilyl)oxirane was added dropwise over a period of 1 h. The reaction was allowed to proceed for 2 h, whereupon the mixture was poured directly into 50 mL saturated aqueous $NaHCO_3$. After extraction with ether and drying (K_2CO_3), the solvent was removed and the residue chromatographed (silica gel, chloroform) to yield 3.63 g (58%) of **8c**. Final purification was by GC (5 ft × $^1/_4$ in. column, 1.5% OV-101 on Chromasorb G, 180 °C). Unreacted acid (1.17 g) was recovered, bringing the yield of **8c** based on unrecovered starting material to 96%. For **8c**: IR (neat) 1250, 1715, 2140, 3340, 3450 (br) cm^{-1}; NMR (CCl_4) δ 0.08 (s, 9 H), 1.82 (br s, 1 H), 2.46 (br s, 4 H), 2.85 (br s, OH, 1 H), 3.67 (d, splitting = 5 Hz, 2 H), 4.63 (t, splitting = 5 Hz, 1 H); mass spectrum, m/e (relative intensity) 197 (48, M − OH), 116 (58), 81 (100, $HC{\equiv}CCH_2CH_2CO$), 73 (97). All peaks give satisfactory high-resolution mass spectral values, e.g.: calcd

(26) Shostakovskii, M. F.; Kamarova, L. I.; Filippova, A. K. H.; Ratovoskii, G. V. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1967**, 2526.

for $C_{10}H_{17}O_2Si$ m/e 197.1022, found m/e 197.0969.

2-Acetoxy-1-(trimethylsilyl)ethyl 4-Pentynoate (9c). This compound was prepared and isolated as for **9a** from 1.44 g (0.0070 mol) of dicyclohexylcarbodiimide, 0.09 g (0.0007 mol) of 4-(dimethylamino)pyridine, 0.38 g (0.0063 mol) of acetic acid, and 1.50 g of **8c**: yield 1.60 g [99%; purified by vacuum distillation (bath temperature 115 °C at 0.10 mmHg); IR (neat) 1250, 1705, 1740, 2110, 2960, 3300 cm^{-1}; NMR (CCl_4) δ 0.08 (s, 9 H), 1.82 (br s, 1 H), 1.98 (s, 3 H), 2.45 (m, 4 H), 4.15 (m, 2 H), 4.82 (m, 1 H). Anal. Calcd for $C_{12}H_{20}O_4Si$: C, 56.25; H, 7.81. Found: C, 56.60; H, 7.89.

Ethenyl 4-Pentynoate (2c). This compound was prepared as for **2a** from 1.60 g (0.0063 mol) of **9c** and 6.6 mL of 1.0 M tetra-*n*-butylammonium fluoride (0.0066 mol). Vacuum transfer into a −196 °C trap was followed by GC collection (10 ft × $^3/_8$ in. column, 3% SE-30 on Chromasorb W in glass, 50 °C): yield 0.54 g (69%); IR (neat) 1620, 1640, 1755, 2940, 3320 cm^{-1}; NMR (CCl_4) δ 1.96 (br s, 1 H), 2.64 (br s, 4 H), 4.67 (dd, J = 2, 6 Hz, 1 H), 4.97 (dd, J = 2, 14 Hz, 1 H), 7.48 (dd, J = 6, 14 Hz, 1 H); mass spectrum, m/e (relative intensity) 124 (0.1, M), 123 (0.2, M − 1), 81 (97), 53 (100, $HC{\equiv}CCH_2CH_2$), 43 (3, C_2H_3O), 39 (8, $HC{\equiv}CCH_2$); high-resolution mass spectrum calcd for $C_7H_8O_2$ m/e 124.0310, found m/e 124.0323.

2-Hydroxy-1-(trimethylsilyl)ethyl 10-Undecynoate (8d). Prepared as for **8b** from 7.66 g (0.0421 mol) of 10-undecynoic acid (**7d**) and 5 drops of $BF_3{\cdot}Et_2O$ in 10 mL of CH_2Cl_2 plus 5.16 g (0.0445 mol) of oxirane in 5 mL of CH_2Cl_2. Unreacted acid was not removed by base extraction due to its potential surfactant properties. Instead, the crude product after removal of solvent was dissolved in a minimum amount (ca. 25 mL) hexane, and cooled to 0 °C to precipitate out the acid. The process was repeated twice with successively smaller portions of hexane to return 3.65 g of acid. A total of 6.34 g of **8d** was isolated from the hexane solutions after solvent removal (51% yield, 97% based on unrecovered **7d**). The material, a colorless oil, was shown to be >95% pure by NMR and was used directly in the following reaction: IR (film) 1355, 1729, 2130, 3330, 3100–3600 (br) cm^{-1}; NMR (CCl_4) δ 0.04 (s, 9 H), 1.35 (m, 12 H), 1.78 (t, J = 3 Hz, 1 H), 2.20 (m, 4 H), 3.03 (m, 1 H), 3.65 (m, 2 H), 4.72 (m, 1 H).

2-Acetoxy-1-(trimethylsilyl)ethyl 10-Undecynoate (9d). This compound was prepared and isolated as for **9a** from 3.46 g (0.0168 mol) of dicyclohexylcarbodiimide, 0.21 g (0.0016 mol) of 4-(dimethylamino)pyridine, 0.87 g (0.0145 mol) of acetic acid, and 5.00 g (0.0168 mol) of **8d**; yield 4.50 g (91%). This material was used directly in the next reaction. Analytically pure material was collected by GC (10 ft × $^3/_8$ in. column, 10% SE-30 on Chromasorb W, 200 °C); IR (film) 1355, 1730, 3330 cm^{-1}; NMR (CCl_4 + $CDCl_3$, 360 MHz) δ 0.04 (s, 9 H), 1.34 (m, 8 H), 1.45 (m, 2 H), 1.58 (m, 2 H), 1.81 (t, J = 2 Hz, 1 H), 1.99 (s, 3 H), 2.12 (dt, J = 2, 7 Hz, 2 H), 2.25 (m, 2 H), 4.09 (dd, J = 9, 12 Hz, 1 H), 4.27 (dd, J = 2, 12 Hz, 1 H), 4.91 (dd, J = 2, 9 Hz, 1 H). Anal. Calcd for $C_{18}H_{32}O_4Si$: C, 63.49; H, 9.47. Found: C, 63.55; H, 9.57.

Ethenyl 10-Undecynoate (2d). This compound was prepared as for **2a** from 1.00 g (0.0029 mol) of **9d** and 2.94 mL of 1.0 M tetra-*n*-butylammonium fluoride (0.0029 mol) in THF. After removal of solvent, the viscous product was purified by GC (10 ft × 0.5 in. column 3% SE-30 on Chromasorb W in glass, 120 °C): yield 0.46 g (76%); NMR (CCl_4 and acetone-d_6, 360 MHz) δ 1.33 (m, 8 H), 1.49 (m, 2 H), 1.63 (m, 2 H), 1.96 (t, J = 2 Hz, 1 H), 2.13 (dt, J = 6, 2 Hz, 2 H), 2.34 (m, 2 H), 4.52 (dd, J = 2, 6 Hz, 1 H), 4.79 (dd, J = 2, 14 Hz, 1 H), 7.22 (dd, J = 6, 14 Hz, 1 H). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.71. Found: C, 75.16; H, 10.29.

Reaction of Vinyl 4-Pentynyl Ether with $Co_2(CO)_8$. A mixture of 6.33 g (0.0185 mol) of $Co_2(CO)_8$ and 2.34 g (0.0185 mol) of **1c** in 50 mL of toluene was allowed to stir under N_2 for 2 h at room temperature, during which time CO evolution was observed and a violet color developed. The reaction mixture was then heated to 95 °C under 1 atm of CO for 96 h. IR analysis showed the loss of vinyl ether related bands at 1640 and 1660 cm^{-1} and the appearance of a new band at 1715 cm^{-1}. NMR of the crude product mixture after removal of solvent showed a broad singlet at δ 5.75 accompanied by broad complex absorption upfield of δ 3. Chromatography of the mixture (silica gel) gave rise to a major polar fraction displaying IR absorption at 1060, 1635, 1700, and 3100–3600 (br) cm^{-1} and NMR signals at δ 3.6 and 4.9, as well as unresolved absorptions to higher field. HPLC (reverse phase) yielded a small quantity of a material subsequently identified as (*E*)-6-hydroxy-2-hexenoic acid:[21] IR (CCl_4) 1285, 1310, 1425, 1650, 1700 (br), 3465 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 1.26 (br s, 1 H, OH), 1.73 (tt, J = 6, 7 Hz, 2 H), 2.34 (ddt, J = 1, 7, 7 Hz, 2 H), 3.68 (t, J = 6 Hz, 2 H), 5.85 (dt, J = 15, 1 Hz, 1 H), 7.07 (dt, J = 15, 7 Hz, 1 H), 11.89 (br s, 1 H, CO_2H).

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