are found per sodalite cage. There was no evidence suggesting any sodium ordering, such as supercell reflections. Models based on the "basic" sodalite structure[3,8] $Na_{8-\delta}(AlSiO_4)_6(OH)_{2-\delta}\cdot 4H_2O$ ($\delta > 0$) gave substantially poorer profile fits. Selected bond length data, with esd's in parentheses, for these phases are as follows: in the ZnPO system the Zn(1)–O(1), P(1)–O(1), Na(1)–O(1), and Na(1)–O_ω(1) contacts are 1.946 (6), 1.531 (3), 2.414 (8), and 2.397 (8) Å, respectively; in the ZnAsO system the Zn(1)–O(1), As(O)–O(1), Na(1)–O(1), and Na(1)–O_ω(1) bond lengths are 1.946 (6), 1.670 (6), 2.424 (11), and 2.431 (8) Å, respectively. O_ω(1) is the water molecule in each case. The Zn–O–X bond angle is 126.1 (3)° for ZnPO and 123.8 (3)° for ZnAsO, much smaller than the 136.2 (3)° found for the Al–O–Si bond angle in $Na_6(AlSiO_4)_6\cdot 8H_2O$.[3] The closest sodium–sodium contacts are 3.53 (3) Å for ZnPO and 3.56 (3) Å for ZnAsO (3.764 (8) Å for the sodium aluminosilicate[3]). The ZnAsO represents the largest cage size dimension observed to date in hydrated sodalite-type phases.

The results obtained to date have demonstrated that an extensive chemistry exists with respect to the room-temperature synthesis of novel non-aluminosilicate zeolitic-type materials. Synthetic and structural studies on other phases will be reported in subsequent publications.[9,10]

Acknowledgment. The support of the National Science Foundation (Grants NSFDMR 88-10430 and 88-21499) and the Quantum Electronic Studies Center (QUEST) at UCSB are acknowledged.

Supplementary Material Available: Table of atomic positional and thermal parameters for $Na_6(ZnPO_4)_6\cdot 8H_2O$ and $Na_6(ZnAsO_4)_6\cdot 8H_2O$ (1 page). Ordering information is given on any current masthead page.

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(8) Hassan, I.; Grundy, H. D. *Acta Crystallogr.* **1983**, *C39*, 3.
(9) Gier, T. E.; Stucky, G. D. *Nature*. In press.
(10) Harrison, W. T. A.; Gier, T. E.; Stucky, G. D. *Chem. Mater.* In press.

Solid-State Electrochemistry: Voltammetric Monitoring of Redox Transitions in Single Crystals of Silicotungstic Acid

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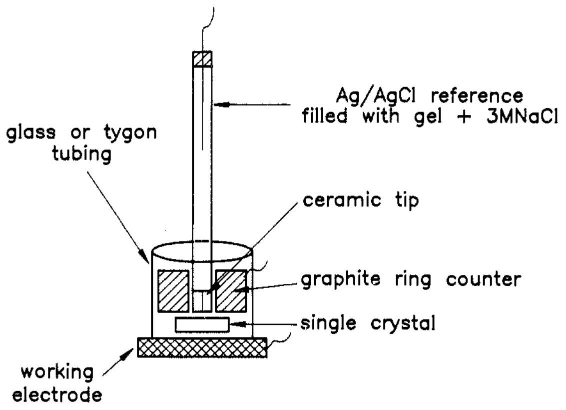

Figure 1. Illustration of a three-electrode cell arrangement for use in solid-state electrochemistry.

Recently there has been considerable interest in extending electrochemical methods to the study of solid-state redox transitions in thin polymeric films containing fixed redox sites,[1,2b] as well as in bulk mixed-valence and porous inorganic materials.[2] The eligible systems are ionically conducting solids having various accessible oxidation states and remaining capable of fast electron transfer between redox sites. A direct extension of normal electrochemical methods to the solid state would involve such crystalline molecular materials as heteropolyacids[3,4] and infinite colloidal oxides of tungsten,[3b,5] which possess distinct multiple valence states within their structures,[6] high protonic conductivities,[7] and semiconducting or semimetallic electronic properties.[3b-d,5e,6] They host mobile charged species, especially protons, at fairly large concentrations; and these can serve the same purpose as supporting electrolytes in conventional electrochemistry. Thus, the migration effects and electric fields within the material can become negligible.

Of particular interest are single crystals of tetragonal silicotungstic acid, $H_4SiW_{12}O_{40}\cdot 31H_2O$.[3f] They have a structure in which the rigid Keggin-type, molecular heteropolyanion[3b-d] $SiW_{12}O_{40}^{4-}$ is surrounded by a hydrated three-dimensional "pseudoliquid",[3c,8] which also hosts the protons[7] required for charge balance. These protons are known to be transported, virtually as fast as in aqueous solutions.[7a,c] Reduction of the rigid (het-

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(1) (a) Geng, L.; Reed, R. A.; Longmire, M.; Murray, R. W. *J. Phys. Chem.* **1987**, *91*, 2908. (b) Feldman, B. J.; Murray, R. W. *Inorg. Chem.* **1987**, *26*, 1702. (c) Chidsey, C. E.; Feldman, B. J.; Lundgren, C.; Murray, R. W. *Anal. Chem.* **1986**, *58*, 601. (d) Reed, R. A.; Wooster, T. T.; Murray, R. W.; Yaniv, D. R.; Tonge, J. S.; Shriver, D. F. *J. Electrochem. Soc.* **1989**, *136*, 2565. (e) Chao, S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 2197, 6627. (f) Grabner, E. W. Presented at the 88th Meeting of the Deutsche Bunsen-Gesellschaft, Siegen, FRG, 1989.

(2) (a) Rosseinsky, D. R.; Tonge, J. S.; Bertholt, J.; Cassidy, J. F. *J. Chem. Soc., Faraday Trans.* **1987**, *83*, 231. (b) Kulesza, P. J.; Galus, Z. *J. Electroanal. Chem.* **1989**, *269*, 455. (c) Kulesza, P. J. *J. Electroanal. Chem.* **1990**, *289*, 103; *Inorg. Chem.* **1990**, *29*, 2395. (d) Creasy, K. E.; Shaw, B. R. *J. Electrochem. Soc.* **1990**, *137*, 2353.

(3) (a) Day, V. W.; Klemperer, W. G. *Science* **1985**, *228*, 533. (b) McHardy, J.; Stonehart, P. *International Review of Science, Physical Chemistry Series Two, Electrochemistry*; Bockris, J. O'M., Ed.; Butterworths: London, 1976; Vol. 6, Chapter 4. (c) Pope, M. T. *Heteropoly and Isopoly Oxometallates*; Springer-Verlag: New York, 1983; Chapters 2 and 6. (d) Krebs, B. *Transition Metal Chemistry, Current Problems of General Biological and Catalytic Relevance*; Muller, A., Diemann, E., Eds.; Verlag: Weinheim, 1981: pp 91–105. (e) Barrows, J. N.; Pope, M. T. *Electron Transfer in Biology and Solid State*; Advances in Chemistry 226; American Chemical Society: Washington, DC, 1990; Chapter 21. (f) Evans, H. T. *Perspectives in Structural Chemistry*; Dunitz, J. D., Ibers, J. A., Eds.: Wiley: New York, 1971; Vol. IV, pp 8–21.

(4) (a) Keita, B.; Nadjo, L.; Krier, G.; Muller, J. F. *J. Electroanal. Chem.* **1987**, *223*, 287. (b) Keita, B.; Nadjo, L. *J. Electroanal. Chem.* **1985**, *191*, 441; **1987**, *227*, 265. (c) Toth, J. E.; Anson, F. C. *J. Am. Chem. Soc.* **1989**, *111*, 2444. (d) Kulesza, P. J.; Roslonek, G.; Faulkner, L. R. *J. Electroanal. Chem.* **1990**, *280*, 233. (e) Ingersoll, D.; Kulesza, P. J.; Faulkner, L. R., in preparation for *J. Electrochem. Soc.*

(5) (a) Reichman, B.; Bard, A. J. *J. Electrochem. Soc.* **1978**, *126*, 2133. (b) Jarman, R. H.; Dickens, P. G. *J. Electrochem. Soc.* **1982**, *129*, 2276. (c) Kulesza, P. J.; Faulkner, L. R. *J. Am. Chem. Soc.* **1988**, *110*, 4905; *J. Electroanal. Chem.* **1988**, *248*, 305; *Colloids Surf.* **1989**, *41*, 123. (d) Hagenmuller, P. *Comprehensive Inorganic Chemistry*, Trotman-Dickenson, A. F., Executive Ed.; Pergamon Press: Oxford, 1973; Vol. 4, Chapter 50, pp 541–563. (e) Crandall, R. S.; Faughnan, B. W. *Appl. Phys. Lett.* **1976**, *28*, 95.

(6) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry, A Comprehensive Text*: Wiley: New York, 1980. (b) Pope, M. T. *Mixed-Valence Compounds*; *Theory and Application in Chemistry, Physics, Geology and Biology*: Brown, D. B., Ed.; NATO Advanced Study Institute Series C; Reidel: Dordrecht, Holland, 1980; pp 365–386.

(7) (a) Clearfield, A. *Chem. Rev.* **1988**, *88*, 125. (b) Glasser, L. *Chem. Rev.* **1975**, *75*, 21. (c) Nakamura, D.; Kodama, T.; Ogiro, I.; Miyake, Y. *Chem. Lett.* **1979**, 17. (d) Tell, B.; Wagner, S. *Appl. Phys. Lett.* **1978**, *33*, 837.

(8) (a) Misono, M.; Okuhara, T.; Ichiki, T.; Arai, T.; Kanda, Y. *J. Am. Chem. Soc.* **1987**, *109*, 5535. (b) Misono, M.; Mizuno, N.; Katamura, K.; Kasai, A.; Konishi, Y.; Sakata, K.; Okuhara, T.; Yoneda, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 400.

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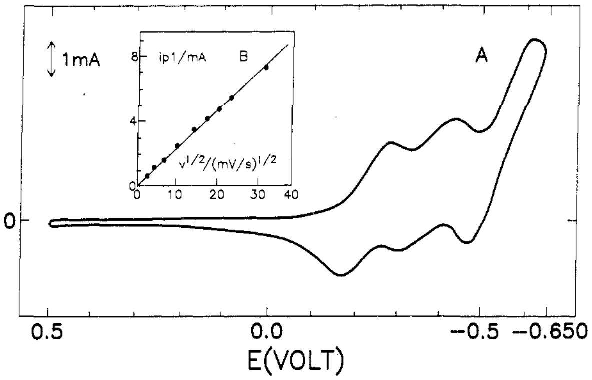

Figure 2. (A) Cyclic voltammetry of a silicotungstic acid single crystal (150 mg. weight; ca. 2–3 mm thick). Scan rate: 50 mV s^{-1}. Scan begins at 0.5 V vs Ag/AgCl and first moves negatively. Cathodic currents are up. (B) Inset: Cathodic peak current of first reduction peak vs square root of scan rate.

eropolyanion) portions of the structure is accompanied by the formation of well-defined, geometrically fixed W(VI)/W(V) redox sites, between which electron transfer is feasible.[3] We have demonstrated that single crystals of silicotungstic acid are characterized by reversible redox transitions in the solid state and that the overall mechanism of charge propagation is diffusional. To make this work possible, we have designed a three-electrode cell that permits voltammetric monitoring of redox transitions in bulk materials, including polyoxometalate single crystals.

Important to the cell (Figure 1) is an Ag/AgCl, 3 M NaCl (gel) reference electrode (Bioanalytical Systems, Inc.), which possesses a ceramic tip capable of forming an ion-permeable, but still basically dry, junction with the solid sample. The counter electrode, in the form of a fairly large graphite ring, surrounds the reference. Pressed against the opposite side of the crystal is the working electrode, a glassy carbon plate in most work described here. Instead of this electrode, an optically transparent SnO_2-coated glass or a Pt ultramicroelectrode was occasionally used. A key feature of this design is that it can handle substantial currents, while the voltage between the reference and working electrodes can be controlled as desired on a widely used potential scale (offset 0.197 V vs SHE). Care was exercised at all times to protect single crystals from evaporation, which would lead to loss of the crystalline character. The whole cell assembly was enclosed in Tygon or glass tubing and sealed with Parafilm or Teflon tape where necessary. Single crystals of silicotungstic acid were grown at ambient temperature (20 ± 2 °C) by slow evaporation of an aqueous saturated solution of the commercially available silicotungstic acid (Fluka).

When a single crystal of silicotungstic acid was introduced into the three-electrode assembly and subjected to potential cycling, the voltammetric pattern in Figure 2 was observed. In the potential range from −0.1 to −0.65 V, three well-defined, reversible redox transitions were observed, corresponding to the approximate electron ratios 1:1:2. These findings are consistent with those previously reported[3b–d,4a,b,6b] for silicotungstates, either dissolved in acid solutions or bound to electrode surfaces as modifiers. When the potential is sufficiently negative for the first electron transfer, corresponding to one of the hexavalent tungsten atoms in the lattice going to the pentavalent state, the most positive reduction peak is developed (Figure 2A). At scan rates up to 1000 mV s^{-1}, the height of this peak is proportional to the square root of scan rate (with 0 intercept; see inset in Figure 2), as expected for a diffusional process. Also, chronocoulometry involving the first reduction and reoxidation waves gives linear Anson plots over time scales as short as 50 ms. Apparently the electron transfer between chemically identifiable W(VI) and W(V) sites in the transition-metal cluster[6] is balanced rapidly by a flux of mobile protons; and diffusional gradients, rather than potential-driven gradients, are established in the material. Estimation of the apparent diffusion coefficient by the usual means, from the integrated Cottrell equation,[9] leads to values on the order of 10^{-7} cm^2 s^{-1}, i.e., somewhat lower than typically observed in aqueous solutions. On the basis of the crystal physicochemical parameters, the concentration of mixed-valence W(VI,V) redox sites was taken as 0.4 M in the above calculation.

Since the voltammetric response is analogous to that observed for silicotungstates dissolved in acid solutions (e.g., 0.5 M H_2SO_4),[3c,6b] the electrochemical charging of a silicotungstate anion in the crystal seems to correspond to

$$SiW_{12}O_{40}^{4-} + ze^- + zH^+ \rightleftharpoons H_zSiW_{12}O_{40}^{4-}$$

where $H_zSiW_{12}O_{40}^{4-}$ stands for a heteropolyanion and z can have values equal to 1, 2, and 4. Here protons originate from the "ionic budget"[1a–d] of structural H^+ in $H_4SiW_{12}O_{40}\cdot 31H_2O$. Upon consideration of the molecular weight, approximate volume (0.1 cm^3), and actual weight of the crystal, the population of protons is expected to be at the 1.5–2.0 M level, which makes the reaction feasible. To preserve electroneutrality during electroreduction, a side reaction, an oxidation, must take place at the counter electrode, presumably of water to hydrogen peroxide or oxygen. No effect of the reaction at the counter electrode manifested itself in the overall voltammetric behavior of the single crystal during at least 20 consecutive potential cycles within the potential limits of Figure 2; thus the side reaction products do not seem to diffuse into the bulk of the crystal. This stability and the reversibility of electron transfer also suggest that, as expected for the rapid formation of heteropoly blues,[3] the redox transitions are not accompanied by significant structural changes or intramolecular chemical reactions. Coloration, but no crystal degradation, is clearly visible when SnO_2-coated glass is used as the working electrode. Further reduction of heteropoly blues, though not shown here, can be accomplished at more negative potentials and leads irreversibly to "brown" species.[3b–d,6b] This behavior may result from structural reorganizations[3c,6b] or may reflect changes in the system's conductivity. As opposed to heteropoly blues, which are Robin–Day class III mixed-valence compounds,[6b] and which have metallic or semimetallic conductivities, the "brown" microstructures are class I insulators characterized by complete charge localization. Further discussion will be provided in our next communication.

Another important feature of the investigated system is that as long as it is not dried out and retains its crystalline character, strictly defined by the degree of hydration (31 H_2O),[3f] the voltammetric responses, as in Figure 2, are virtually insensitive to the humidity of the surrounding atmosphere. When a wet, freshly prepared silicotungstic acid single crystal (without visible droplets of the mother liquid on its surface) was introduced to the well-sealed cell, the material was stable and visually unchanged for at least 2 days.

In conclusion, we have shown that electrochemical methodology can be extended to the investigation of the protonically conducting, crystalline mixed-valence molecular materials. Such studies provide information about thermodynamics and kinetics of redox processes in these materials. Our additional results,[10] with thin films and powders of silicotungstic acid and related oxide systems, clearly suggest that solid-state electrochemical responses are very sensitive to the degree of hydration, which probably controls the protonic mobility. We have been able to perform useful solid-state electrochemical measurements on other powdered materials, including Prussian blue analogues and metalloproteins, by essentially the same methodology. The approach may also prove useful in the further structural characterization of the reduced forms, heteropoly "blues" and "browns". Apart from the fundamental significance, applications to the construction of miniature batteries, electrochromic devices, and sensors and in microelectronics can be envisioned.

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(9) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; pp 199–204.

(10) Kulesza, P. J.; Faulkner, L. R. Abstract 730, The 177th Electrochemical Society Meeting Extended Abstracts, Vol. 90-1, Montreal, Canada, May 6–11, 1990; Abstract 401, 17th Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Cleveland, OH, Oct 7–12, 1990.

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Stereoselective, One-Step Assembly of the Strained Protoilludane Framework by Cobalt-Mediated Cyclization of an Acyclic Enediyne Precursor. A Total Synthesis of Illudol

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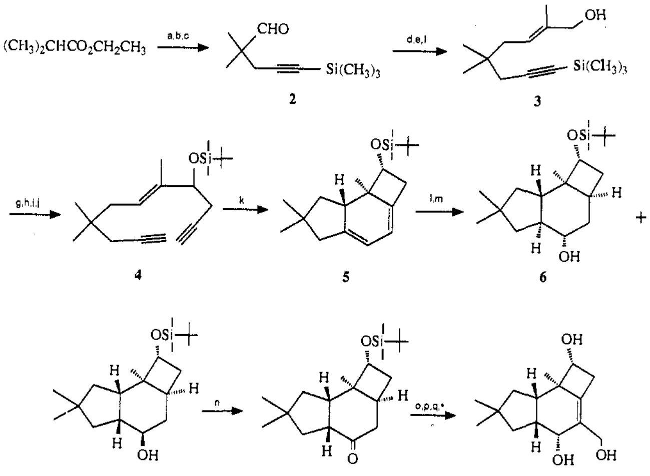
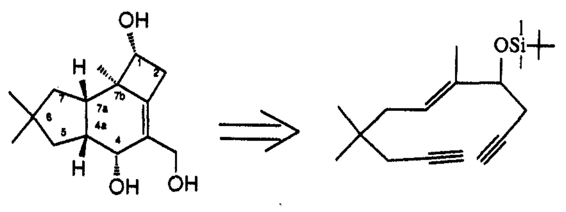
A number of basidiomycete sesquiterpenoids exhibit considerable toxic, antibiotic, and antitumor activity, including members of the protoilludane, illudane, marasmane, and sterpurane families.[1] The first type is considered to play an important biogenetic role with respect to the remainder.[1a,f,j,k,2] Among the synthetically most challenging protoilludanes ranks illudol (**1**), because it combines the task of constructing the unusual angular and strained hydrocyclobutaindane nucleus with that of controlling five contiguous stereocenters. Isolated by Anchel and co-workers some time ago,[1g,h,l,m] the molecule has seen only two total syntheses in the past two decades.[3,4] Like most other approaches to complex oligocycles, they relied on a stepwise strategy for ring formation.[5] Compared to these, a topologically more profound retrosynthetic disconnection envisions enediyne **4** as the direct precursor to the basic skeleton of **1**. Thus, it was hoped that stoichiometric $CpCo(CO)_2$ would convert **4** to CpCo-complexed **5** by intramolecular [2 + 2 + 2] cycloaddition,[6] the ligand **5** possessing the necessary functionality to allow its elaboration to **1** (Scheme I). This anticipation notwithstanding, there was considerable concern about the lack of precedence for such a transformation, featuring internal double bonds flanked by two alkynes, all previous examples leading to unstrained systems and suffering much lesser encumbrance by substituents.[6] Moreover, related terminal enediyne cyclizations were shown to be complicated by isomerizations involving hydrogen shifts.[7] We now report the realization of Scheme I, incorporating the stereoselective assembly of **5** and its conversion to racemic illudol (**1**).[8]

Scheme I^a



^{a}(a) (i) $[(CH_3)_2CH]_2NLi$ (1.0 equiv), THF, −78 °C, 2 h; (ii) 3-bromo-1-(trimethylsilyl)propyne (1.0 equiv), −78 to 23 °C, 12 h, 94%; (b) $LiAlH_4$ (0.5 equiv), $(CH_3CH_2)_2O$, 23 °C, 4 h, 100%; (c) (i) $(COCl)_2$, DMSO, −78 °C, 1.5 h; (ii) $(CH_3CH_2)_3N$, −78 to 23 °C, 4 h, 97%; (d) (i) $CH_3S(O)CH_2Li$ (1.4 equiv), $(C_6H_5)_3p^+CH_2OCH_3Cl^-$ (1.5 equiv), THF, 0 °C for 5 h, 23 °C for 1 h; (ii) **2** (1.0 equiv), 0–23 °C, 4.5 h; (iii) 1 N HCl, 23 °C, 18 h, 86%; (e) $(C_6H_5)_3P{=}C(CH_3)CO_2CH_2CH_3$ (1.2 equiv), CH_2Cl_2, 23 °C, 48 h, 92%; (f) $[(CH_3)_2CHCH_2]_2AlH$ (2.05 equiv), CH_2Cl_2, −78 °C, 2 h, 99%; (g) (i) $(COCl)_2$, DMSO, −78 °C, 1.5 h; (ii) $(CH_3CH_2)_3N$, −78 to 23 °C, 3.5 h, 98%; (h) propynylmagnesium bromide (2.5 equiv), $(CH_3CH_2)_2O$, 0 °C, 15 min, 89%; (i) K_2CO_3 (1.2 equiv), CH_3OH, 23 °C, 24 h, 100%; (j) $[(CH_3)_3C](CH_3)_2SiCl$ (1.8 equiv), imidazole, DMF, 23 °C, 36 h, 99%; (k) (i) $CpCo(CO)_2$ (1.1 equiv), toluene, 110 °C, *hν*, 6 h; (ii) $CuCl_2{\cdot}2H_2O$ (2.5 equiv), 1,2-dimethoxyethane, 23 °C, 3 h, 92%; (l) (i) Li (excess), NH_3–$(CH_3)_3COH$–THF (8:2:3), 33 °C, 5 min; (ii) NH_4Cl (20 equiv), −33 °C, 62%; (m) (i) B_2H_6 (3.0 equiv), THF, 23 °C, 3 h; (ii) H_2O_2 (5.0 equiv), K_2CO_3 (1.2 equiv), 65 °C, 1.5 h, 77% (**6**:**7**, 2:3); (n) (i) $(COCl)_2$, DMSO. −78 °C, 2 h; (ii) $(CH_3CH_2)_3N$, −78 to 23 °C, 3 h; (iii) K_2CO_3 (1.5 equiv), CH_3OH, 23 °C, 4.5 h, 79%; (o) (i) $[(CH_3)_2CH]_2NLi$ (2.0 equiv), THF, 23 °C, 3.5 h; (ii) CO_2 (excess), −78 °C, 5 min; (iii) 1 N HCl (2.0 equiv), −78 to 0 °C; (iv) CH_2N_2 (10 equiv), $(CH_3CH_2)_2O$, 0–23 °C, 2 h, 56%; (p) (i) NaH (1.2 equiv), THF, 0 °C, 2.5 h; (ii) C_6H_5SeCl (0.95 equiv), −78 °C, 0.5 h; (iii) H_2O_2 (excess), NH_4Cl (20 equiv), CH_2Cl_2, 0 °C, 1.5 h, 40%; (q) $NaH_2Al(OCH_2CH_2OCH_3)_2$ (5.0 equiv), C_6H_6, 23 °C, 24 h, 54% (17:37 β:α); (r) $(CH_3CH_2CH_2CH_2)_4N^+F^-$ (1.0 equiv), THF, 23 °C, 12 h, 74%.



1 **4**

Alkylation of the enolate of ethyl 2-methylpropanoate with 3-bromo-1-(trimethylsilyl)propyne, followed by reduction of the ester function to the corresponding alcohol and subsequent oxi-

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(1) (a) Ayers, W. A.; Browne, L. M. *Tetrahedron* **1981**, *37*, 2199. (b) Donnelly, D. M. X.: Coveney, D. J.; Fukuda, N. *J. Nat. Prod.* **1986**, *49*, 111. (c) Arnone, A.: Cardillo, R.: Nasini, G. *Phytochemistry* **1986**, *25*, 471. (d) Donnelly, D. M. X.; Coveney, D. J.; Polonsky, J. *Tetrahedron Lett.* **1985**, *26*, 5343. (e) Donnelly, D. M. X.: Abe, F.; Coveney, D. J.: Fukuda, N.; O'Reily, J. *J. Nat. Prod.* **1985**, *48*, 10. (f) Ayers, W. A.; Nakashima, T. T.; Saeedi-Ghomi, M. H. *Can. J. Chem.* **1984**, *62*, 531. (g) McMorris, T. C.; Nair, M. S. R.; Anchel, M. *J. Am. Chem. Soc.* **1967**, *89*, 4562. (h) McMorris, T. C.; Nair, M. S. R.; Singh, P.; Anchel, M. *Phytochemistry* **1971**, *10*, 1611, 3341. (i) Parker, W.; Roberts, J. C.; Ramage, R. *Q. Rev.* **1967**, *21*, 331. (j) Morisaki, N.; Furukawa, J.: Kobayashi, H.; Iwasaki, S.; Nozoe, S.; Okuda, S. *Tetrahedron Lett.* **1985**, *26*, 4755. (k) Nozoe, S.; Kobayashi, H.; Urano, S.; Furukawa, J. *Tetrahedron Lett.* **1977**, 1381. (l) Nair, M. S. R.; Anchel, M. *Tetrahedron Lett.* **1975**, 1267. (m) Anchel, M.; Hervey, A.; Robbins, W. J. *Proc. Natl. Acad. Sci. U.S.A.* **1950**, *36*, 300; **1952**, *38*, 927.

(2) (a) Hanson, J. R.; Marten, T. *J. Chem. Soc., Chem. Commun.* **1973**, 171. (b) Cane, D. E.; Nachbar, R. B. *J. Am. Chem. Soc.* **1978**, *100*, 3208; **1979**, *101*, 1908. (c) Anchel, M.; McMorris, T. C.: Singh, P. *Phytochemistrry* **1970**. *9*. 2339. (d) Hanson. J. R.; Marten, T.; Nyfelder, R. *J. Chem. Soc., Perkin Trans. 1* **1976**, 876. (e) Hayano, K.; Ohfune, Y.; Shirahama, H.; Matsumoto, T. *Helv. Chim. Acta* **1981**, *64*, 1347. (f) Misumi, S.; Ohtsuka, T.; Ohfune, Y.; Sugita, K.; Shirahama, H.; Matsumoto, T. *Tetrahedron Lett.* **1979**, 31. (g) Ohfune, Y.; Misumi, S.; Furusaki, A.; Shirahama, H.; Matsumoto, T. *Tetrahedron Lett.* **1977**, 279. (h) Misumi, S.; Ohfune, Y.; Furusaki, A.; Shirahama. H.: Matsumoto, T. *Tetrahedron Lett.* **1976**, 2865. (i) Shirahama. H.: Osawa, E.: Matsumoto, T. *Tetrahedron Lett.* **1978**, 1987. (j) Shirahama, H.; Osawa. E.; Matsumoto, T. *J. Am. Chem. Soc.* **1980**, *102*, 3208.

(3) (a) Matsumoto, T.; Miyano, K.; Kagawa, S.; Yü, S.; Ogawa, J.-I.; Ichihara, A. *Tetrahedron Lett.* **1971**, 3521. (b) Kagawa, S.; Matsumoto, S.; Nishida, S.; Yü, S.; Morita, J.; Ichihara, A.; Shirahama, H.; Matsumoto, T. *Tetrahedron Lett.* **1969**, 3913.

(4) (a) Semmelhack, M. F.; Tomoda, S.; Nagaoka, H.; Boettger, S.; Hurst, K. M. *J. Am. Chem. Soc.* **1982**, *104*, 747. (b) Semmelhack, M. F.; Tomoda, S.; Hurst, K. M. *J. Am. Chem. Soc.* **1980**, *102*, 7567.

(5) Ho, T.-L. *Carbocycle Construction in Terpene Synthesis*; VCH: New York, 1988.

(6) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539; *Lect. Heterocycl. Chem.* **1987**, *9*, 59.

(7) Duñach, E.; Halterman, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1985**, *107*, 1664.

(8) All new compounds gave satisfactory spectral and analytical data.

0002-7863/91/1513-381$02.50/0