Table I. ^{13}C Chemical Shifts (ppm from Me_4Si in $CDCl_3$)

compd[a]	C-1	C-2	C-3	C-4	C-5[b]	C-6[b]	C-7	C-8[b]	C-9	C-10	C-11[b]	C-12
3[c]	125.7, d	109.5, d	154.2, s	145.2, s	20.5, t	18.8, t	183.9, s	126.9, d	133.1, d	133.1, d	126.4, d	184.3, s
5	131.6, d	111.5, d	160.6, s	113.5, d	27.6, t	20.8, t	183.8, s	125.5, d	133.0, d	133.0, d	126.3, d	184.2, s

[a] The resonances of the bridgehead carbon atoms were not assigned but are listed as follows. Compound 3: 122.9, 131.9, 132.8, 133.0, 138.7, 141.5 ppm. Compound 5: 122.1, 131.8, 132.6, 138.4, 140.9, 140.9 ppm. [b] The 5- and 6-carbon atoms and the 8- and 11-carbon atoms were not unambiguously assigned. [c] Multiplicities in the off-resonance decoupled spectra are given below each chemical shift.

alkyl region are both triplets, dictating that two methylene carbons are present. These data exclude structures related to **2** and firmly establish structures such as **2a**.

In neither instance was a dihydro compound found which had a structure represented by **2**. It was evident that under the reaction conditions virtually complete conversion of **2** to **2a** was occurring.

Experimental Section

All melting points were determined by using a Fisher-Johns hot-stage apparatus and are uncorrected. Low-resolution mass spectra were taken on a Finnigan 3300 mass spectrometer equipped with a Finnigan 6000 data system. High-resolution mass spectra were obtained from a VG Micromass ZAB-2F mass spectrometer equipped with a VG 2000 data system. Magnetic resonance spectra were taken on a Varian XL-100 spectrometer using $CDCl_3$ (0.5% Me_4Si) as solvent, while IR spectra were obtained on a Perkin-Elmer 467 spectrophotometer as KBr pellets. Microanalyses were performed by Galbraith Laboratories.

Preparation of 5,6-Dihydro-3,4-dimethoxybenz[*a*]anthracene-7,12-dione (3) and 3,4-Dimethoxybenz[*a*]anthracene-7,12-dione (4). To 12 mL of toluene were added 400 mg (2.5 mmol) of 1,4-naphthoquinone, 610 mg (2.5 mmol) of chloranil, 1.5 g (9.1 mmol) of 2,3-dimethoxystyrene, and 30 mg of trichloroacetic acid. This mixture was heated in a 105 °C oil bath until no naphthoquinone could be observed by TLC on silica gel GF plates with benzene as the developing solvent (14 days). The mixture was then chromatographed on a Silicar CC-7 (Mallinckrodt) column employing a 20–50% benzene–hexane gradient as the eluting solvent system. The first red band yielded 95 mg (12%) of **4** as red crystals, mp 209–211 °C. Sublimation yielded analytically pure **4**: mp 210–211 °C; IR 1662 cm^{-1} (C=O), 1589, 1480, 1328, 1311, 1284, 1271, 1225, 1088; NMR δ 9.49 (d, J = 9.7 Hz, 1 H), 8.64–7.47 (m, aromatic, 7 H), 4.07 (s, 3 H), 4.02 (s, 3 H). Anal. Calcd for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43. Found: C, 75.37; H, 4.36.

The second red band yielded 120 mg (15%) of **3**: mp 173–175 °C; NMR δ 7.28–6.60 (m, aromatic, 6 H), 3.94 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 2.88 (br s, 4 H); mass spectroscopic molecular weight 320.1028 (calcd for $C_{20}H_{16}O_4$, 320.1049). Anal. Calcd for $C_{20}H_{16}O_4$: C, 74.98; H, 5.03. Found: C, 75.26; H, 4.84.

Preparation of 5,6-Dihydro-3-methoxybenz[*a*]anthracene-7,12-dione (5) and 3-Methoxybenz[*a*]anthracene-7,12-dione (6). The same conditions as above were used, with 3-methoxystyrene being substituted for 2,3-dimethoxystyrene and the reaction time being 12 days. Column chromatography employing a 10–30% benzene–hexane gradient yielded as the first major red band 137 mg (19%) of **6**, mp 168–169 °C (lit.[7] mp 169–169.5 °C).

The second band afforded 152 mg (21%) of **5**: mp 148–149 °C; NMR δ 8.25–6.74 (m, aromatic, 7 H), 3.82 (s, 3 H, OCH_3), 2.78 (s, 4 H); mass spectroscopic molecular weight 290.0934 (calcd for $C_{19}H_{14}O_3$, 290.0941).

Conversion of Compound 3 to Compound 4. Oxygen was slowly bubbled for 3 h through a suspension of 75 mg of compound **3** in 25 mL of 5% ethanolic KOH. After neutralization with concentrated hydrochloric acid, the solvent was removed by evaporation and the crude material sublimed to afford 66 mg (89%) of **4**, mp 210–211 °C.

Conversion of Compound 5 to Compound 6. With use of the identical procedure as above, 70 mg of **5** gave 60 mg (87%) of **6**, mp 168–169 °C.

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Registry No. **3**, 72428-42-3; **4**, 72428-43-4; **5**, 72428-44-5; **6**, 63216-11-5; 1,4-naphthoquinone, 130-15-4; 2,3-dimethoxystyrene, 17055-36-6; 3-methoxystyrene, 626-20-0.

Isomerization of Internal Triple Bonds of Alkyn-1-ols with Sodium Hydride in 1,3-Diaminopropane[1]

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The "acetylenic zipper" reaction[2,3] offers a unique method for effecting the functionalization of the end of a long hydrocarbon chain. The reaction, which involves the base-mediated isomerization of an alkyne with an internal triple bond to the terminal alkyne, has been performed on both unsubstituted alkynes and alkyn-1-ols. The latter give ω-hydroxy alkynes:

$$HO(CH_2)_mC{\equiv}C(CH_2)_nH \rightarrow HO(CH_2)_{m+n}C{\equiv}CH$$

The mechanism is thought[2,4] to involve a random-walk process in which a series of allene–alkyne interconversions take place along the carbon chain until the terminal acetylide salt is formed.

The reaction is particularly useful in the synthesis of pheromones[5] and of long-chain fatty acid derivatives.[6] For instance, Pabon et al.[6] have obtained the 22-carbon acetylenic alcohol 21-docosyn-1-ol from 11-docosyn-1-ol in 87% yield—a transformation that involves a *minimum* of ten intermediate alkyn-1-ols.

We have experienced experimental difficulties using the "acetylenic zipper" reaction in work directed toward the synthesis of fatty acid derivatives. We, and others,[7] have encountered serious foaming problems in preparing the isomerization reagent, potassium 3-aminopropylamide

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Table I. Isomerization of Alkyn-1-ols with Sodium APA in DAP

starting alkyn-1-ol	time, h	product	yield,[a] %	mp,[b] °C
2-tetradecyn-1-ol	20	13-tetradecyn-1-ol	81	40–41 (34–36)[d]
5-hexadecyn-1-ol	2.5	15-hexadecyn-1-ol	63	52–54 (49–52)[e]
5-hexadecyn-1-ol	20	15-hexadecyn-1-ol	53	52–54 (49–52)[e]
2-nonadecyn-1-ol	20	18-nonadecyn-1-ol[c]	85	61–63
7-tetracosyn-1-ol	18	23-tetracosyn-1-ol[c]	47	77–78

[a] Yields reported are of crystalline material obtained after chromatography. Products are greater than 96% pure by GLC analysis. [b] Melting points are uncorrected. [c] Satisfactory analyses (C and H, ±0.3%) were obtained for all new products. [d] Reference 9. [e] Reference 3.

(KAPA). KAPA is prepared by the reaction of potassium hydride with 1,3-diaminopropane (DAP), the solvent of the reaction.

The foaming problem, which is particularly troublesome in larger scale work, along with the hazards of handling potassium hydride,[8] led us to search for an alternate method to prepare the isomerization reagent.

Working toward the same goal, Hommes and Brandsma[4] reported that an effective isomerization reagent could be obtained by the addition of DAP to freshly prepared potassium or sodium amide in liquid ammonia followed by evaporation of the ammonia. They stated that sodium hydride did not react with DAP.

We have developed a simpler, more convenient procedure to prepare the isomerization reagent. We have found that sodium hydride does, in fact, react with DAP at 70 °C with evolution of hydrogen, but no foaming, to give a clear brown solution which can be used to isomerize alkyn-1-ols.

Table I lists five isomerizations using our reagent (sodium APA). The starting materials we prepared in the standard manner[11] by reaction of the appropriate lithium (tetrahydropyranyloxy)acetylide with an alkyl bromide followed by deprotection with methanol and *p*-toluenesulfonic acid. The reactions were run with a fourfold excess of sodium APA (1 M in DAP) at 55 °C. Although reactions were usually complete within 2 h, they were normally allowed to proceed overnight.

With this procedure an "acetylenic zipper" reagent can routinely be prepared simply, quickly, and without foaming problems. Our modification should be particularly useful for large-scale experiments.

Experimental Section

All isomerizations were run under similar conditions. The reactions were carried out under a positive pressure of dry nitrogen in flame-dried glassware. The 1,3-diaminopropane (corrosive!) was distilled at reduced pressure from BaO and stored over 4A molecular sieves. The general procedure employed is described in detail for the case of the reaction of 2-nonadecyn-1-ol.

18-Nonadecyn-1-ol was synthesized as follows. To NaH (Ventron Corp., 57% in mineral oil, 720 mg, 17 mmol, washed free of oil three times with hexane) was added DAP (15 mL). The mixture was stirred in a constant-temperature oil bath at 70 °C. After 10 min gas evolution was noted and after 1 h a clear brown solution resulted. The reagent was cooled to ambient temperature, and a solution of 2-nonadecyn-1-ol (600 mg, 2.15 mmol) in DAP (8 mL) was added. The reddish brown mixture was stirred at 55 °C overnight and then cooled, water was added, and the organic product was extracted four times with ether. The combined ether phases were washed successively with water, dilute HCl, and NaCl solutions and then dried over Na_2SO_4. Filtration and evaporation of the solvent yielded 580 mg of crude product which was chromatographed over silicic acid (Bio-Rad, 200–400 mesh) to give 18-nonadecyn-1-ol: 510 mg; 85% yield; mp 61–63 °C (hexane); IR ($CHCl_3$) 3605, 3450 (OH), 3300, 2110 cm^{-1} (C≡CH); ^1H NMR (100 MHz, $CDCl_3$, internal Me_4Si) δ 1.2–1.7 (br m, 31 H, CH_2, OH), 1.88 (t, J = 2.75 Hz, 1 H, C≡CH), 2.18 (m, $w_{1/2}$ = 15 Hz, 2 H, $CH_2C{\equiv}C$), 3.59 (t, J = 6.0 Hz, 2 H, OCH_2); ^{13}C NMR (25.16 MHz, $CDCl_3$) 84.86 (C-18), 68.07 (C-19), 63.10 (C-1), 32.90 (C-2), 28.84 (C-15), 28.58 (C-16), 25.82 (C-3), 18.46 (C-17) (from Me_4Si);[10] purity by GLC (FID, 1 m × 3 mm stainless-steel column packed with 80–100 mesh acid-washed silanized Chromosorb W coated with 1.5% Dexsil 300) 97%. The analysis was performed by Microanalysis Laboratories Ltd. Anal. Calcd for $C_{19}H_{36}O$: C, 81.36; H, 12.94. Found: C, 81.36; H, 12.75.

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Registry No. 1,3-Diaminopropane, 109-76-2; sodium hydride, 7646-69-7; 2-tetradecyn-1-ol, 51309-22-9; 5-hexadecyn-1-ol, 72443-47-1; 2-nonadecyn-1-ol, 72443-48-2; 7-tetracosyn-1-ol, 72443-49-3; 13-tetradecyn-1-ol, 18202-12-5; 15-hexadecyn-1-ol, 62914-53-8; 18-nonadecyn-1-ol, 72443-50-6; 23-tetracosyn-1-ol, 72443-51-7.

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Metabolites of the Marine Sponge *Dercitus* sp.

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The tryptophan derivative aplysinopsin (**1**) has previously been reported from the sponges *Thorecta* (≡ *Aplysinopsis*?)[1] sp. and *Verongia spengelii*.[2] In the former report, Wells et al.[1] suggested the presence of a monobromo analogue which they were unable to isolate. In this note, we describe the isolation and identification of the related compounds 2′-de-*N*-methylaplysinopsin (**2**) and 6-bromo-2′-de-*N*-methylaplysinopsin (**3**).

The marine sponge *Dercitus* sp. was collected at Lighthouse Reef, Belize, and stored in methanol for 6 months. Soxhlet extraction of the sponge with methanol produced a brownish yellow extract which was fractionated on a Sephadex LH-20 column to yield aplysinopsin (**1**) (2.7% dry weight) as the major metabolite, 2′-de-*N*-methylaplysinopsin (**2**) (1.0% dry weight), and 6-bromo-2′-de-*N*-methylaplysinopsin (**3**) (1.0% dry weight).

The ^1H NMR spectrum of the monomethyl compound **2** was very similar to that of aplysinopsin (**1**) and showed signals at δ 3.06 (s, 3 H) attributed to the *N*-methyl, at δ 6.81 (s, 1 H) due to the olefinic proton attached to the glycocyamidine side chain, and at δ 7.11 (m, 2 H), 7.43 (d, 1 H, J = 6 Hz), 7.93 (d, 1 H, J = 6 Hz), and 8.52 (s, 1 H) due to the protons at C-5, C-6, C-4, C-7, and C-2, respec-

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