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Registry No.—**2**, 67488-04-4; **3**, 67488-05-5; **4**, 67488-06-6; **4** methyl ester, 67488-07-7; **5**, 67488-08-08; **6**, 67488-09-9; 3-methoxy-5-methyldodecanoic acid, 67488-10-2.

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Notes

Cationic π Cyclizations.[1] Alkenes vs. Alkynes as the π Participant

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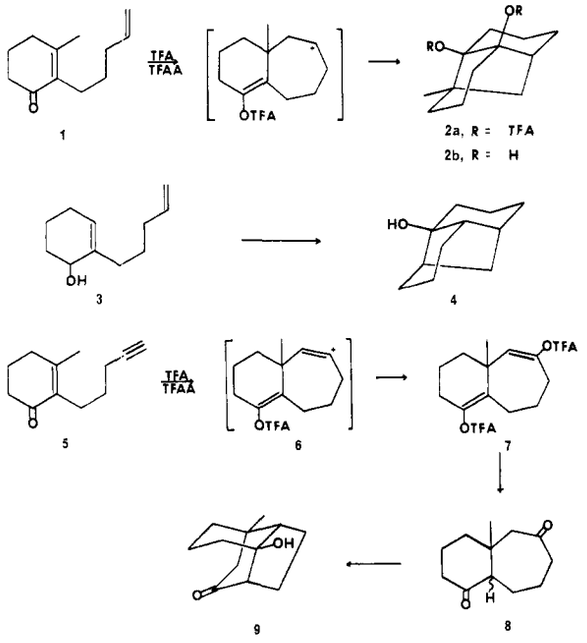
Terminal alkynes have been used as the π participant in a variety of cationic π cyclizations.[2] In those cases previously studied, the basic course of the cyclization has been the same as that observed with terminal alkenes. We now report a cyclization in which the change of π participant significantly affects the type of products observed. As part of our continuing studies on the synthetic utility of cationic π cyclizations of α,β-unsaturated enones[1,3] we investigated the cyclization of the enone **1**. Not surprisingly, treatment of enone **1**



with trifluoroacetic acid in trifluoroacetic anhydride[1,3b] led, in 71% yield, to a tricyclic diol assigned structure **2** in analogy with the known cyclization of alcohol **3** to tricyclic alcohol **4**.[4,5] Our interest in obtaining bicyclic products from this type of cyclization led us to examine the acetylenic enone **5**. Molecular models suggested that the geometry of the bicyclic vinyl cation **6** generated from cyclization of **5** would not favor further cyclization to a tricyclic product. In fact, the only product observed from TFA/TFAA cyclization of enone **5** was the bis(trifluoroacetate) **7**. Mild hydrolysis gave, in 85% yield, the diketone **8** as a mixture of cis and trans isomers. Based on the chemical shift of the angular methyl,[6] the major isomer is assumed to be the cis isomer. Mild base treatment of diketone **8** led to a tricyclic keto alcohol which is assigned the tricyclo[5.4.0.0^{4,8}]undecane structure **9**.[7]

These cyclization studies show that, in this system, use of the alkyne bond as the π participant allows isolation of bicyclic products rather than the tricyclic product obtained using an alkene bond as the π participant.[9] Application of this methodology to the synthesis of natural terpenoid systems is in progress.

Experimental Section

The ^{1}H NMR spectra were obtained on a Varian Associates HA-100 or T-60 spectrometer. The ^{13}C NMR spectra were obtained in the Fourier transform mode on a JEOL PFT-100 spectrometer system operating at 25.034 MHz (proton resonance frequency 99.539 MHz) and equipped with a Nicolet 1085 data system. High-resolution mass spectra were obtained on a CEC Model 21-110 spectrometer under the supervision of Dr. R. Grigsby.

The vapor phase chromatographic (VPC) analyses were performed using a $\frac{1}{8}$ in. × 6 ft 10% Carbowax on Chromosorb W column or a $\frac{1}{8}$ in. × 6 ft 1.5% OV-101 on Chromosorb G column. All percent-composition values are reported as relative peak areas without correction for relative detector response. Preparative VPC separations for MS analyses were performed using a $\frac{1}{4}$ in. × 6 ft 10% SE-30 on Chromosorb A column.

All distillations were conducted as bulb-to-bulb (Kugelrohr) short-path distillations. The temperatures cited for these distillations are the maximum temperature of the oven during the distillation. "Brine" refers to a saturated aqueous solution of sodium chloride. Anhydrous ether was stored over sodium. *tert*-Butyl alcohol was distilled from calcium hydride.

2-(4-Pentenyl)-3-methyl-2-cyclohexen-1-one (1). Sodium hydride (176 mg, 7.4 mmol) was added to 80 mL of *tert*-butyl alcohol to generate sodium *tert*-butoxide. To this stirred solution was added 1.32 g (7.4 mmol) of 4-carbethoxy-3-methyl-2-cyclohexen-1-one (Hagemann's ester) in 10 mL of *tert*-butyl alcohol over a period of 20 min. Then 5-bromo-1-pentene (1 g, 6.7 mmol) in 10 mL of *tert*-butyl alcohol was added dropwise followed by 2 g of anhydrous powdered

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KI in one portion. The mixture was stirred for 22 h at room temperature and then at reflux for 2 h. The cooled solution was poured into 200 mL of 10% HCl overlaid with 200 mL of ether. The aqueous layer was separated and washed with ether. The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated to give 1.41 g of material. This material consisted of starting Hagemann's ester, the desired α-alkylated product, and some γ-alkylated material as shown by ^1H NMR. The mixture was stirred with 20 mL of 15% KOH in 95% ethanol for 12 h at 0 °C. The reaction was poured into 50 mL of water overlaid with 50 mL of ether. The separated aqueous layer was extracted twice with ether to remove unhydrolyzed material (primarily the γ-alkylated ester). The aqueous layer was acidified and extracted with ether until no color remained. The combined ether extracts were washed with brine, dried (Na_2SO_4), concentrated, and evaporatively distilled (130 °C (6.2 mm)) to give 710 mg (59% yield) of ketone **1**: IR (film) 1670 (C=O), 3100, 1625, 990, and 925 cm^{-1} (C=C); ^1H NMR (100 MHz, $CDCl_3$) δ 1.95 (bs, 3 H, CH_3) and 4.8–6.05 (m, 3 H, $CH=CH_2$); ^{13}C NMR ($CDCl_3$) δ 21.1 (C-3 methyl), 22.4, 24.8, 28.3 (C-2'), 32.9, 33.9 (C-3'), 37.9, 114.3 (C-4'), 135.6 (C-2), 138.7 (C-5'), 154.9 (C-3), and 198.3 (C-1). The ^{13}C spectrum and VPC analysis (OV-101, 130 °C) indicated a purity >95%. MS *m/e* calcd for $C_{12}H_{18}O$, 178.135760; found, 178.135076.

Cyclization of Enone 1. To 380 mg (2.1 mmol) of enone **1** was added 10 mL of trifluoroacetic acid and 5 mL of trifluoroacetic anhydride. The mixture was stirred for 2 h at room temperature. The TFA and TFAA were removed by concentration and the residue was distilled (115 °C (0.2 mm)) to give 650 mg of product: IR (film) 1780 cm^{-1} (trifluoroacetate C=O); ^1H NMR (60 MHz, CCl_4) δ 1.2 (angular methyl). This material was treated at room temperature with 20 mL of 10% KOH in methanol. After 20 min, the methanol was removed by concentration. Methylene chloride was added and salts were removed by filtration. The solution was dried (Na_2SO_4), concentrated, and distilled (125 °C (0.15 mm)) to give 310 mg (75% yield) of crystalline diol **2b** which was recrystallized from hexane: mp 133–135 °C; IR (KBr) 3400 and 1050 cm^{-1} (OH); ^1H NMR (100 MHz, $CDCl_3$) δ 0.94 (s, angular methyl); ^{13}C NMR (benzene-d_6) δ 18.6, 19.4, 20.5 (CH_3), 25.8, 30.3, 33.9, 34.0, 34.3, 39.6 (>C-H), 40.7 (>C<), 78.4 (>C-O-), and 78.8 (>C-O-); MS *m/e* calcd for $C_{12}H_{20}O_2$, 196.146320; found, 196.145711.

2-(4-Pentynyl)-3-methyl-2-cyclohexen-1-one (5). This material was prepared in a manner similar to that of enone **1** using 3.7 g (20 mmol) of Hagemann's ester and 3 g (20 mmol) of 5-bromo-1-pentyne.[11] In this case the crude alkylation product (3 g) was chromatographed on a silica gel column using methylene chloride to obtain 900 mg of starting ester and 2.0 g (52% yield based on recovered starting material) of pure α-alkylated product. Hydrolysis gave 1.3 g (91% yield) of enone **5**: IR (film) 3300 and 2150 (C≡CH), 1650 and 1630 cm^{-1} (C=CC=O); ^1H NMR (100 MHz, $CDCl_3$) δ 1.94 (s, 3 H, CH_3), 1.92 (t, J = 2 Hz, C≡CH); ^{13}C NMR ($CDCl_3$) δ 18.4 (C-3'), 21.2 (C-3 methyl), 22.3, 24.4, 27.9 (C-2'), 32.9, 37.8, 68.4 (C-5'), 84.5 (C-4'), 134.8 (C-2), 155.8 (C-3), and 198.4 (C-1). Analysis by VPC (OV-101, 130 °C) showed only one peak. MS *m/e* calcd for $C_{12}H_{16}O$, 176.120110; found, 176.119792.

Cyclization of Enone 5. A mixture of 10 mL of trifluoroacetic acid and 5 mL of trifluoroacetic anhydride was added to 650 mg (3.7 mmol) of enone **5**. The mixture was stirred at room temperature for 2.5 h. The TFAA and TFA were removed by concentration and the residue was distilled (115 °C (0.1 mm)) to give 1.23 g (86% yield) of bis(enoltrifluoroacetate) **7**: IR (film) 1785 (trifluoroacetate C=O) and 1680 (C=C); ^1H NMR (100 MHz, CCl_4) δ 1.29 (s, angular methyl), 5.24 (bs, C=CH). This ester was treated with 25 mL of saturated sodium bicarbonate in methanol for 20 min at room temperature. The methanol was removed by concentration and methylene chloride and $MgSO_4$ were added. The solution obtained after filtration was concentrated and distilled (125 °C (0.15 mm)) to give 600 mg (85% overall yield) of diketone **8** as a 6:1 mixture of cis and trans isomers: IR (film) 1725 cm^{-1} (C=O); ^1H NMR (100 MHz, $CDCl_3$) δ 1.07 (s, cis angular methyl) and 0.78 (s, trans angular methyl); ^{13}C NMR ($CDCl_3$) (major isomer) δ 20.9, 21.3, 26.6, 27.4 (C-1 methyl), 37.6, 39.0 (C-1), 39.5, 43.3, 53.3 (C-2), 60.4 (C-7), 212.0 (C-3 or C-8), 212.6 (C-3 or C-8). Analysis by VPC (Carbowax, 200 °C) showed one major peak with a shoulder for the trans isomer. MS *m/e* calcd for $C_{12}H_{18}O_2$, 194.130670; found, 194.130136.

Hydrolysis of bis(enoltrifluoroacetate) **7** under more vigorous conditions or treatment of diketone **8** with methanolic hydroxide led to a tricyclic aldol product. A 220-mg sample of diketone **8** was treated with 10 mL of 15% KOH in methanol at room temperature for 1 h. The mixture was poured into water and extracted with ether. The combined ether extracts were washed with brine, dried (Na_2SO_4), concentrated, and distilled (130 °C (0.2 mm)) to give 200 mg (90% yield) of a solid keto alcohol assigned structure **9**: mp 146–148 °C (from hexane); IR (CCl_4) 1715 (C=O) and 3450 cm^{-1} (OH); ^1H NMR (100 MHz, $CDCl_3$) δ 1.00 (s, angular methyl); ^{13}C NMR ($CDCl_3$) δ 19.9 (C-10), 22.7, 27.2 (C-1 methyl), 27.4, 34.5, 37.0 (C-1), 39.6, 46.2 (C-2), 52.4 (C-7), 60.9 (C-4), 81.1 (C-8), and 214.2 (C-3).[11]

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Registry No.—**1**, 67425-72-3; **2a**, 67425-73-4; **2b**, 67425-74-5; **5**, 67425-75-6; **7**, 67425-76-7; *cis*-**8**, 67425-77-8; *trans*-**8**, 67425-78-9; **9**, 67463-82-5; Hagemann's ester, 487-51-4; 5-bromo-1-pentene, 1119-51-3; trifluoroacetic acid, 76-05-1; 5-bromo-1-pentyne, 28077-72-7.

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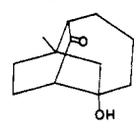
(7) The alternative tricyclo[5.4.0.0^{3,9}]undecane (4-homotwistane) aldol product **i** appears much less favorable. Calculations[8] indicate that tricyclo[5.4.0.0^{4,8}]undecane is significantly more stable than tricyclo[5.4.0.0^{3,9}]undecane.



i

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(9) It should be noted that the differences observed are a result of the different allowable geometries for the bicyclic cationic intermediates in these two cyclizations and are not necessarily applicable to all alkyne cyclizations. In particular, tricyclic products have been observed in cases involving an internal alkyne as the π participant.[5b,5c]
(10) Prepared from 4-pentyn-1-ol using PBr_3 in pyridine.
(11) This ^{13}C NMR spectrum correlates well with the spectrum of an isomeric tricyclic alcohol, 8-methyltricyclo[5.4.0.0^{4,8}]undecan-3-on-1-ol: K. E. Harding and J. L. Cooper, unpublished results.

Carbon–Carbon Bond Formation. 6.[1] Alkyl Halide Coupling from an Electrochemically Generated Iron Promoter

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The use of transition metal complexes to promote organic reactions has been well-established. However, the nature of

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