Registry No.—**3a,** 54086-38-3; **3b,** 54086-39-4; **12a,** 61279-17-2; **12b,** 61279-18-3; **12c,** 61279-19-4; 1-chloro-2,2-dimethylpropane, 753-89-9.

Supplementary Material Available. Listing of the anisotropic temperature factors and hydrogen atom parameters (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Research Assistant, 1974–1975; (b) Research Associate, 1976, Oklahoma State University.
(2) (a) Research Assistant, 1972–1976, University of Oklahoma.
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Studies on the Syntheses of Heterocyclic Compounds. 696.[1] Stereochemistry of Four Isomeric 4a-Cyano-1,2,3,4,4a,9,10,10a-octahydro-7-methoxy-1-methoxycarbonyl-1-methylphenanthrenes

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Thermolysis of 1-cyano-4-methoxy-1-(4-methoxycarbonyl-4-vinylpentyl)benzocyclobutene gave four stereoisomers of 4a-cyano-1,2,3,4,4a,9,10,10a-octahydro-7-methoxy-1-methoxycarbonyl-1-methylphenanthrene, whose structures were revealed by the conversion of each octahydrophenanthrene into the known compounds. The structure elucidation and the chemistry of these compounds are presented.

There have been many reports on a discussion of the stereochemistry of stereoisomeric diterpenoids by physical and chemical means.[2,3] In general, naturally occurring diterpenoids have a trans A/B ring junction and are classified into podocarpic acid and abietic acid types of compounds depending upon the stereochemistry of C-1 substituents. Structures having a cis A/B ring junction are, however, possible and, in fact, there are several papers concerning the stereochemistry of four synthetic isomers.[4]

Previously, we have reported the synthesis of a key intermediate for diterpene alkaloids using the thermocyclization of a benzocyclobutene derivative.[5] In the course of investigation for this reaction, we could obtain four possible stereoisomeric octahydrophenanthrenes and reveal each structure using physical and chemical procedures.

As we have previously reported,[5] the thermolysis of 1-cyano-4-methoxy-1-(4-methoxycarbonyl-4-vinylpentyl)-benzocyclobutene (1) at 180–230 °C for 3 h gave 4aα-cyano-1,2,3,4a,9,10,10aα-octahydro-7-methoxy-1α-methoxycarbonyl-1β-methylphenanthrene (2) in a stereocontrolled manner, but the starting material was also recovered. Therefore, the benzocyclobutene 1 was treated under more

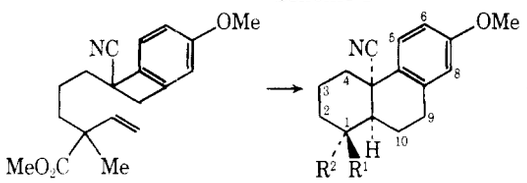
Table I. Chemical Shifts of Octahydrophenaenthrenes [a]

Compd	C_1 CH_3	C_5 H
2	1.26	7.35, J = 8 Hz
3	1.35	7.26, J = 8 Hz
4	1.72	7.36, J = 8 Hz
5	1.51	7.25, J = 8 Hz

[a] Determined on a JEOL PS-100 instrument and reported as δ values relative to Me_4Si (δ 0).

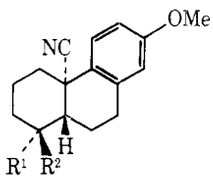
drastic conditions at 230 °C for 8 h to give four stereoisomeric octahydrophenanthrenes **2, 3, 4,** and **5** in a ratio of 17:4:10:1, which was calculated by the integration of C-1 methyl signals

Scheme I

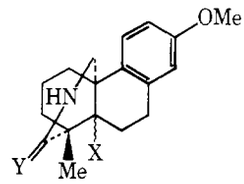


1

2, R^1 = Me; R^2 = CO_2Me
4, R^1 = CO_2Me; R^2 = Me
10, R^1 = Me; R^2 = CO_2H



3, R^1 = CO_2Me; R^2 = Me
5, R^1 = Me; R^2 = CO_2Me
11, R^1 = Me; R^2 = CO_2H

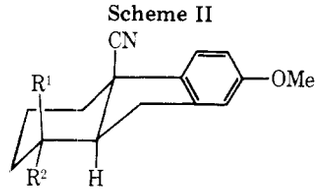


6, X = --H; Y = O
7, X = ◄H; Y = H_2

on the 100-MHz NMR, respectively, but all the octahydrophenanthrenes **2, 3, 4,** and **5** were actually isolated in a ratio of 20:2.5:5:1, respectively, after a purification on column chromatography and multiple recrystallization.

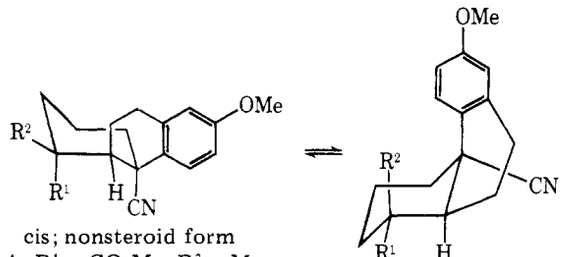
It has been widely known that decalin exists as a rigid trans conformer and a flexible cis conformer.[6] In the case of diterpenoid, the same subject could be also considered to exist as both trans and cis conformers. However, it has been also known that the compounds having a cis A/B ring junction were

Scheme II



trans

B, R^1 = CO_2Me; R^2 = Me
D, R^1 = Me; R^2 = CO_2Me



cis; nonsteroid form
A, R^1 = CO_2Me; R^2 = Me
C, R^1 = Me; R^2 = CO_2Me

cis; steroid form
E

classified into a steroidal conformer (E) and a nonsteroidal conformer (A and C).[4]

Four compounds, **2, 3, 4,** and **5,** which we obtained were elucidated to be a pair of trans conformers and a pair of nonsteroidal cis conformers by the following discussions.

NMR Studies. Proton chemical shifts of the C-1 methyl and C-5 proton of these hydrophenanthrenes are given in Table I.

In the 100-MHz NMR spectra of two octahydrophenanthrenes, **2** and **3**, the singlets at 1.26 and 1.35 ppm are ascribed to the C-1 methyl, respectively, whereas C-1 methyl signals of the compounds **4** and **5** appeared at 1.72 and 1.51 ppm, respectively. The resonances at abnormally low chemical shifts (1.72 and 1.51 ppm) in the latter compounds **4** and **5** are immediately recognized as the result of the strong deshielding due to the cyano function.[6] Therefore the compounds **4** and **5** should have a 1,3-diaxial relationship between C-1 methyl and C-4a cyano functions, that is, the structures should be nonsteroid form (C) and/or trans form (D). If either of **4** or **5** is the nonsteroid form (C), the C-5 proton should appear at lower field by the deshielding effect of the C-4a cyano group at the peri position. In fact, the C-5 proton of **4** was observed at 7.36 ppm with J = 8 Hz, whereas **5** appeared at 7.26 ppm as a normal chemical shift with J = 8 Hz. The same phenomena, that the C-5 protons of **2** and **3** appeared at 7.36 ppm with J = 8 Hz and 7.25 ppm with J = 8 Hz, respectively, have been found.

As mentioned above, we concluded that the octahydrophenanthrenes **2** and **4** were nonsteroid conformers (A and C) and **3** and **5** were natural trans conformers (B and D).

Chemical Studies. A relative configuration between C_{4a}-cyano and C_1-carbomethoxy groups in compound **2** was found to be cis by a high-pressure catalytic hydrogenation of **2** giving the lactam **6** as previously reported.[5] The compound **2** was also converted into **3** by way of four steps, namely, oxidation, bromination, dehydrobromination, and reduction, the structure of which was confirmed by a transformation into the known compound, 16,17-imino-13-methoxy-5α,10α-podocarpane-8,11,13-triene (**7**).[8,9]

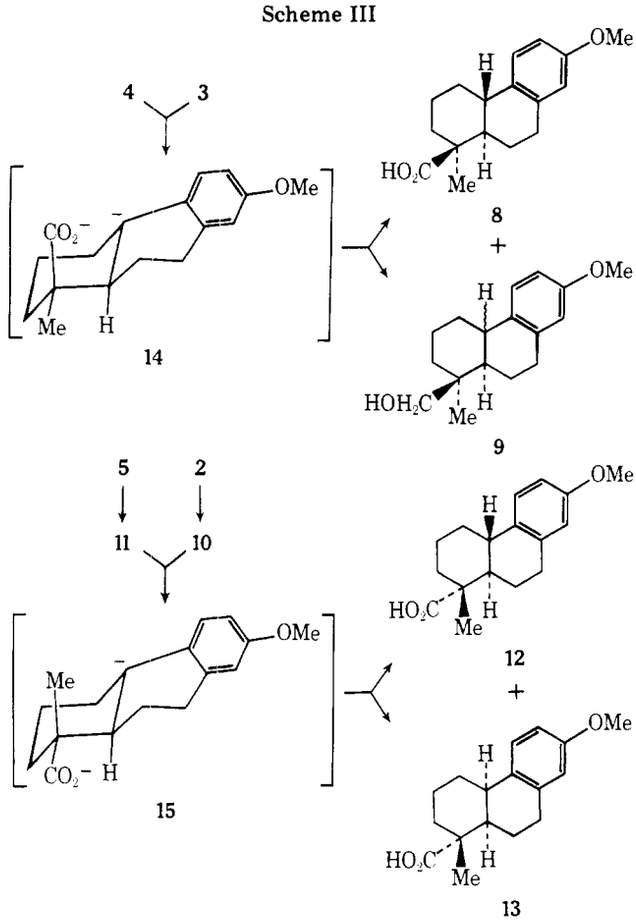
The structure determination of the compounds **4** and **5** was carried out by transformations using a decyanation reaction into the known carboxylic acids **8, 12,** and **13** which had already been prepared by Ghatak.[10]

In general, a cyano group located at the benzylic position is removed by reduction with sodium and liquid ammonia.[11] If four compounds **2, 3, 4,** and **5** were subjected to decyanation reaction, **2,** and **5** should give the same products which have a trans relationship between C-1 methyl and C-10a hydrogen, and **3** and **4** should afford cis products.

Wenkert[12] had proposed that podocarpic acid esters possessing less steric hindrance (*equatorial* methoxycarbonyl group) could be expected to be reduced to alcohol, while those having a steric hindrance (*axial* methoxycarbonyl group) should undergo reductive hydrolysis. If the decyanation reaction occurs first, the ester **3** and **4** should give the intermediate **14,** which have an *axial* methoxycarbonyl group, yielding predominantly the carboxylic acid, whereas the reduction of the ester **2** and **5** would afford the alcohol via a **15** type intermediate. In order to prevent a reduction of methoxycarbonyl group to hydroxymethyl function during decyanation with sodium and liquid ammonia[12] and to get the known compounds (**12** and **13**),[10] the carboxylic acids **10** and **11** have been used as substrates.

The reduction of **3** and **4** gave a mixture of an acid **8** and alcohols **9,** respectively, as expected. The acid obtained from **3** was identical with one prepared from **4** in several physical data and melting point (164–165 °C), whose IR and NMR spectra were superimposable upon those of Ghatak's sample **8**,[10] 1β-carboxy-1,2,3,4,4aβ,9,10,10aα-octahydro-7-me-

Scheme III



thoxy-1α-methylphenanthrene, mp 165–166 °C.

The esters of **2** and **5** were converted into carboxylic acids **10** and **11** by alkaline hydrolysis and the acids **10** and **11** were subjected to the following decyanation reaction. The reduction of the acid **10** with sodium in liquid ammonia gave surprisingly two nitrogen free acids (**12** and **13**), which were separated by chromatography and multiple recrystallization to afford 1α-carboxy-1,2,3,4,4aβ,9,10,10aα-octahydro-7-methoxy-1β-methylphenanthrene (**12**), mp 174–175 °C, and 1α-carboxy-1,2,3,4,4aα,9,10,10aα-octahydro-7-methoxy-1β-methylphenanthrene (**13**), mp 195–196 °C. The reduction of the acid (**11**) also gave the same products **12** and **13** which were completely identical with Ghatak's samples.[10]

Thus we could reveal the structures of octahydrophenanthrenes **2, 3, 4,** and **5** to be conformers A, B, C, and D, respectively.

Experimental Section

All melting points are uncorrected. NMR spectra were measured with a JNM-PMX-60 and JNM-PS-100 spectrometer (tetramethylsilane as an internal reference), IR spectra with a Hitachi 215 spectrophotometer, and mass spectra with a Hitachi RMU-7 spectrometer.

Thermolysis of 1-Cyano-1-(4-methoxycarbonyl-4-vinylpentyl)-5-methylbenzocyclobutene (1). A solution of benzocyclobutene **1** (1.0 g) in dry toluene (400 ml) was heated at 230 °C in a sealed tube for 8 hr. The solvent was evaporated to give a pale brown solid (0.98 g), which was chromatographed on silica gel (50 g). The first eluate with benzene gave mainly **5** together with **4**, which were subjected to fractional recrystallization from methanol to afford 4aβ-cyano-1,2,3,4,4a,9,10,10aα-octahydro-7-methoxy-1α-methoxycarbonyl-1β-methylphenanthrene (**5**, 19 mg) as colorless fibers: mp 160–161 °C; IR ($CHCl_3$) 2230 (CN) and 1720 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.51 (3 H, s, C_1 CH_3), 3.72 (3 H, s, CO_2CH_3), 3.80 (3 H, s, OCH_3), 6.59 (1 H, d, J = 3 Hz, C_8 H), 6.72 (1 H, dd, J = 8 and 3 Hz, C_6 H), and 7.25 ppm (1 H, d, J = 8 Hz, C_5 H); mass spectrum m/e 313 (M^+).

Anal. Calcd for $C_{19}H_{23}NO_3$: C, 72.82; H, 7.40; N, 4.47. Found: C, 72.54; H, 7.42; N, 4.40.

The second eluate with benzene gave mainly **4** together with **5.** It was subjected to fractional recrystallization from methanol to afford 4aα-cyano-1,2,3,4,4a,9,10,10aα-octahydro-7-methoxy-1β-methoxycarbonyl-1α-methylphenanthrene (**4,** 103 mg) as colorless fibers: mp 199–200 °C; IR ($CHCl_3$) 2225 (CN) and 1720 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.72 (3 H, s, C_1 CH_3), 3.76 (3 H, s, CO_2CH_3), 3.80 (3 H, s, OCH_3), 6.53 (1 H, d, J = 3 Hz, C_8 H), 6.74 (1 H, dd, J = 8 and 3 Hz, C_6 H), and 7.36 ppm (1 H, d, J = 8 Hz, C_5 H); mass spectrum m/e 313 (M^+).

Anal. Calcd for $C_{19}H_{23}NO_3$: C, 72.82; H, 7.40; N, 4.47. Found: C, 72.69; H, 7.53; N, 4.67.

The third eluate with benzene gave mainly **2** together with **3,** which were subjected to fractional recrystallization from methanol to afford 4aα-cyano-1,2,3,4,4a,9,10,10aα-octahydro-7-methoxy-1α-methoxycarbonyl-1β-methylphenanthrene (**2,** 410 mg) as colorless fibers; mp 150–151 °C.

The fourth eluate with benzene gave mainly **3** together with **2,** which were subjected to fractional recrystallization from methanol to afford 4aβ-cyano-1,2,3,4,4a,9,10,10aα-octahydro-7-methoxy-1β-methoxycarbonyl-1α-methylphenanthrene (**3,** 52 mg) as colorless fibers: mp 157–158 °C; IR ($CHCl_3$) 2230 (CN) and 1720 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.35 (3, H, s, C_1 CH_3), 3.74 (3 H, s, CO_2CH_3), 3.78 (3 H, s, OCH_3), 6.57 (1 H, d, J = 2 Hz, C_8 H), 6.71 (1 H, dd, J = 8 and 2 Hz, C_6 H), and 7.26 ppm (1 H, d, J = 8 Hz, C_5 H); mass spectrum m/e 313 (M^+).

Anal. Calcd for $C_{19}H_{23}NO_3$: C, 72.82; H, 7.40; N, 4.47. Found: C, 73.30; H, 7.61; N, 4.83.

The combined methanolic mother liquor during the recrystallization of **2** and **3** was evaporated to give a colorless solid (175 mg), which is a mixture of **2** and **3** (1:1).

Decyanation of Esters 3 and 4. To a stirred solution of each ester (100 mg) in dry tetrahydrofuran (3 ml) and redistilled liquid ammonia (30 ml) was added sodium (80 mg) and the stirring was continued for 5 min. An excess of ammonium chloride (2 g) was added in small portions to the reaction mixture and ammonia was allowed to evaporate. The residue was acidified with 10% hydrochloric acid (10 ml) and extracted with ether. The ethereal layer was washed with water and extracted with 10% sodium hydroxide aqueous soution. The ethereal layer was washed with water and dried over anhydrous sodium sulfate. The solvent was evaporated to give an alcohol. After acidification of the alkaline layer the corresponding acid was isolated by extraction with ether. The results are shown below.

The ester **3** gave 1β-carboxyl-1,2,3,4,4aβ,9,10,10aα-octahydro-7-methoxy-1α-methylphenanthrene (**8**), which was recrystallized from methanol to give colorless fibers (37 mg) [mp 164–165 °C (lit.[10] 165–166 °C); IR (KBr) 1690 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.32 (3 H, s, C_1 CH_3), 3.75 (3 H, s, OCH_3), 6.58 (1 H, d, J = 2 Hz, C_8 H), 6.67 (1 H, dd, J = 9 and 2 Hz, C_6 H), and 7.16 ppm (1 H, d, J = 9 Hz, C_5 H)] and alcohol **9** (22 mg).

The ester **4** gave the same acid **8** (38 mg) and alcohol **9** (34 mg). This alcohol [ir ($CHCl_3$) 3620 cm^{-1} (OH)] is a diastereoisomeric mixture of **9,** which could not be separated in pure state.

Saponification of Ester 2. A mixture of the ester **2** (300 mg), diethylene glycol (30 ml), potassium hydroxide (1.5 g), and water (10 ml) was heated under reflux for 1 h. An unsaponified ester was extracted with ether after dilution with saturated sodium chloride solution (100 ml). After acidification of the alkaline aqueous layer, the resulting mixture was extracted with chloroform. The extract was washed with saturated aqueous sodium chloride solution and dried over anhydrous sodium sulfate. The solvent was removed by evaporation to give a colorless solid, which was recrystallized from methanol to afford 1α-carboxy-4aα-cyano-1,2,3,4,4a,9,10,10aα-octahydro-7-methoxy-1β-methylphenanthrene (**10,** 240 mg) as colorless fibers: mp 223–224 °C; IR ($CHCl_3$) 2240 (CN) and 1700 cm^{-1} (C=O).

Anal. Calcd for $C_{18}H_{21}NO_3$: C, 72.21; H, 7.07; N. 4.68. Found: C, 72.34; H, 7.24; N, 4.58.

Saponification of Ester 5. A mixture of the ester **5** (150 mg), ethanol (20 ml), potassium hydroxide (750 mg), and water (20 ml) was heated under reflux for 3 h. The unsaponified ester was extracted with ether after dilution with saturated sodium chloride solution (50 ml). After acidification of the resulting alkaline layer, the mixture was extracted with chloroform. The extract was washed with saturated sodium chloride solution and dried over anhydrous sodium sulfate. The solvent was removed to give a colorless solid, which was recrystallized from methanol to afford 1α-carboxy-4aβ-cyano-1,2,3,4,4a,9,10,10aα-octahydro-7-methoxy-1β-methylphenanthrene (**11,** 110 mg) as colorless needles: mp 239–240 °C; IR ($CHCl_3$) 2230 (CN) and 1700 cm^{-1} (C=O).

Anal. Calcd for $C_{18}H_{21}NO_3$: C, 72.21; H, 7.07; N, 4.68. Found: C 72.11; H, 7.35; N, 4.46.

Decyanation of Acids 10 and 11. To a stirred solution of each acid (100 mg) in dry tetrahydrofuran (3 ml) and redistilled liquid ammonia (30 ml) was added sodium (80 mg) and the stirring was continued for 5 min. An excess of ammonium chloride (2 g) was added in small portions to the reaction mixture and ammonia was allowed to evaporate. The residue was acidified with 10% hydrochloric acid (10 ml) and extracted with ether. The ethereal layer was washed with water and extracted with 10% sodium hydroxide. After acidification of the above alkaline layer the acid was isolated by extraction with ether. The results are shown below.

The acid (**10**) formed a colorless oil which was chromatographed on silica gel (5 g) using benzene–*n*-hexane (4:1) to give 1α-carboxy-1,2,3,4,4aα,9,10,10aα-octahydro-7-methoxy-1β-methylphenanthrene (**13**), which was recrystallized from methanol to give colorless needles (33 mg): mp 195–196 °C (lit.[10] 197–198 °C); IR (KBr) 1690 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.23 (3, H, s, C_1 CH_3), 3.75 (3 H, s, OCH_3), 6.60 (1 H, d, J = 2 Hz, C_8 H), 6.67 (1 H, dd, J = 8 and 3 Hz, C_6 H), and 6.96 ppm (1 H, d, J = 8 Hz, C_5 H).

Further elution with benzene gave 1α-carboxy-1,2,3,4,4aβ,9,10,10aα-octahydro-7-methoxy-1β-methylphenanthrene (**12**), which was recrystallized from methanol to give colorless prisms (29 mg): mp 174–175 °C (lit.[10] 175 °C); IR (KBr) 1685 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.20 (3 H, s, C_1 CH_3), 3.74 (3 H, s, OCH_3), 6.57 (1 H, d, J = 3 Hz, C_8 H), 6.66 (1 H, dd, J = 9 and 3 Hz, C_6 H), and 7.17 ppm (1 H, d, J = 9 Hz, C_5 H).

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Registry No.—1, 61243-63-8; **2,** 61259-31-2; **3,** 61259-32-3; **4,** 61259-33-4; **5,** 61259-34-5; **8,** 61259-35-6; α-**9,** 61259-36-7; β-**9,** 61259-37-8; **10,** 61259-38-9; **11,** 61259-39-0; **12,** 61259-40-3; **13,** 61259-41-4.

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A Method for the Synthesis of Unsaturated Carbonyl Compounds

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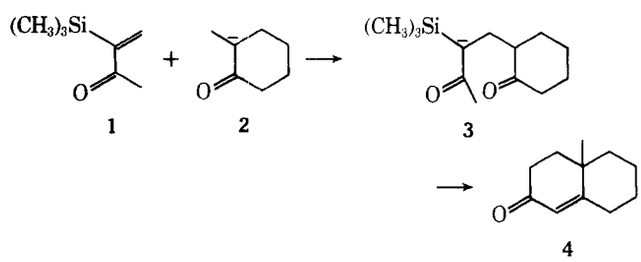
Unsaturated carbonyl compounds can be prepared by a three-step procedure involving (1) formation of an ethyloxalyl derivative **14**; (2) reaction with an aldehyde to give a diketolactone **15**; and (3) base cleavage to product **16**. Twenty-five examples are reported. Ketones, esters, lactones, lactams, and nitriles all undergo the reaction, although esters and lactones appear to work best. The method has been found to be particularly efficient in preparing α-methylenecyclohexanone (87%), α-methylenebutyrolactone (83%), and α-methylenevalerolactone (93%).

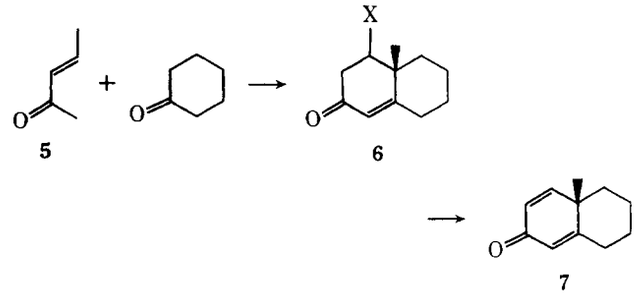
One of the more valuable recent contributions to the methodology of organic synthesis is the work of Stork[1] and Boeckmann[2] in which Robinson annelation reactions are carried out by reacting equivalent amounts of enolate ions with methyl (α-trimethylsilyl)vinyl ketone. Cyclization and desilylation of the initial Michael adducts are then effected by base treatment.



1 2 3 4

The great advantage of this method is that the anion adduct **3** is stable under reaction conditions and does not polymerize the vinyl ketone. This low reactivity of **3** is presumed[1] to be due to the stabilizing effect of silicon on the neighboring carbanion, although steric effects may also play a large role.

For some time, we have been interested in developing general methods of enone synthesis and have reported,[3] for example, the use of β-carboxy ketones as enone equivalents. Our basic idea was to effect Robinson annelation with a substituted vinyl ketone such as **5** and then unmask the enone at



5 6 7

an appropriate time (by oxidative decarboxylation when X = CO_2H).

Combining the Stork–Boeckmann work with our own in-