dried over sodium sulfate, and distilled to give, besides ethyl propanoate (3 g) and triethyl phosphonoacetate (4.5 g), 600 mg (~10%) of crude ethyl cyclopropylideneacetate [bp 40 °C (0.08 mm)] which was purified by gas chromatography (Carbowax 20M, 10%, 115 °C): IR (CCl_4) 1770 ($\nu_{C=C}$), 1710 cm^{-1} ($\nu_{C=O}$); NMR δ (CCl_4) 1.10–1.40 (m, 7 H), 4.15 (q, 2 H), 6.18 (quintuplet, 1 H); mass spectrum, m/e (relative intensity) 126 (M^+, 2.1), 109 (11.8), 98 (100), 97 (24.1), 81 (32.6), 53 (48.4).

Registry No. 1, 13837-45-1; 3, 74592-24-8; 5, 16545-68-9; 7 (Ar = Ph), 57951-63-0; 9, 37494-03-4; 10, 74592-25-9; 10 tosylate, 74592-26-0; 11, 74592-27-1; 12, 72064-29-0; 14, 74592-28-2; 15, 74592-29-3; 15 trimethylsilyl ether, 74592-30-6; 15 tosylate, 74592-31-7; 16, 74592-32-8; 18, 6414-69-3; 19, 14743-56-7; 21, 74592-33-9; 21 THP ether, 74592-34-0; 21 *N*-benzoyl derivative, 74592-35-1; 22, 7677-24-9; 23, 27374-25-0; 28, 14633-95-5; 30, 7555-67-1; 31 (X = H), 16721-45-2; 31 (X = CH_3), 39110-21-9; 31 (X = OCH_3), 21960-26-9; 31 (X = NO_2), 6933-17-1; 32 (X = CH_3), 55088-80-7; 32 (X = OCH_3), 55088-84-1; 32 (X = NO_2), 73673-90-2; 34, 14114-06-8; 36, 867-13-0; 38, 74592-36-2; phenylacetylene bromide, 932-87-6; propargylic bromide, 106-96-7; ethyl bromoacetate, 105-36-2; (3-bromopropyl)triphenylphosphonium bromide, 3607-17-8; *p*-nitrobenzaldehyde, 555-16-8.

Preparation of β,γ-Unsaturated Methyl Esters from Allylic Alcohols[1]

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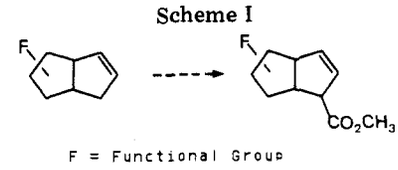
Received February 19, 1980

β,γ-Unsaturated esters are of interest for the synthesis of mono- and sesquiterpenes where the alkene linkage is destined for cleavage to a dialdehyde as well as for the synthesis of γ-butyrolactones. A general method for the preparation of deconjugated esters of this type from allylic alcohols is described. The method is useful for the construction of β,γ-unsaturated esters where the π bond is disubstituted and part of a cyclic array. The sequence works only poorly in acyclic systems.

For some time now we have been exploring the utility of bicyclo[3.3.0]octanes in the synthesis of mono- and sesquiterpenes.[2] During our efforts directed at the total synthesis of the iridoid monoterpene sarracenin[3] it became clear to us that efficient use of the more readily available [3.3.0] systems would depend on the development of a practical method for the introduction of a carbomethoxy group at the allylic position of an alkene with an overall net retention of the regiochemical relationships of the π bond (Scheme I).

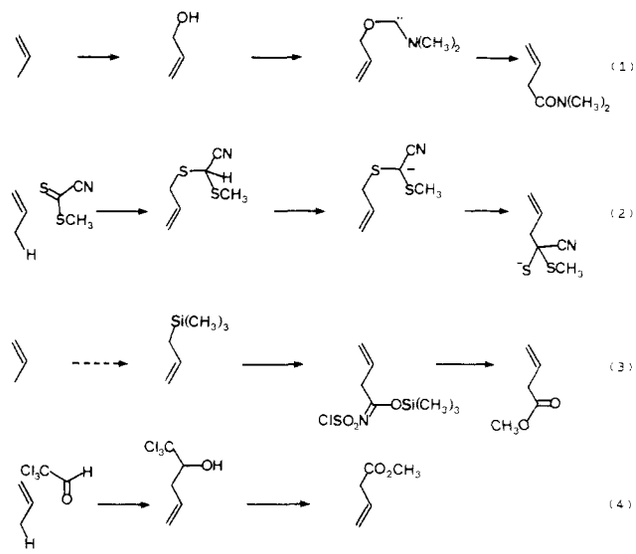
Several methods were known at that time for accomplishing this operation (eq 1–3, Scheme II), though each had inherent limitations that made their successful use in the present context appear improbable. Thus, the [2,3] sigmatropic rearrangement of the carbene intermediate in Büchi's sequence[4] works only poorly for disubstituted alkenes and with a model [3.3.0] system provided less than 15% of the β,γ-dimethylamidoyl group. The elegant sequence developed by Snider[5] also depends on a [2,3] rearrangement to establish the required new carbon–carbon bond but at present is limited by the lack of a method for degrading the α,α-dithiocyano group to the requisite carbomethoxy unit. Use of Fleming's sequence[6] for converting an allylsilane to the required functionality would merely beg the regiochemical question, requiring a sequence for the introduction of an allylsilane group without migration of the double bond. Finally, it should be noted that the Lewis acid catalyzed ene reaction of an alkene with chloral (eq 4)[7] provides a functionality that can be modified quite simply to form a β,γ-unsaturated ester, but this sequence effects a net migration of the double bond.

Scheme I

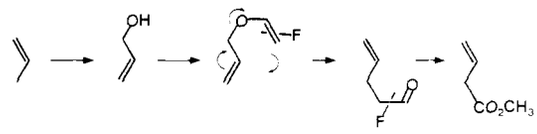


F = Functional Group

Scheme II



Scheme III

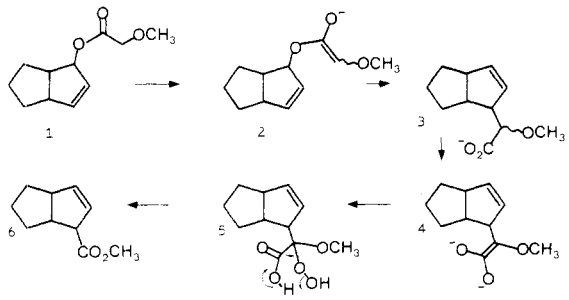


It occurred to us that establishment of the necessary carbon–carbon bond might be more readily accomplished by a [3,3] rather than a [2,3] rearrangement and that if the migrating unit was properly functionalized, then a facile degradation to remove the superfluous carbon re-

(1) A preliminary report of these results has appeared: Whitesell, J. K.; Helbling, A. M. *J. Chem. Soc., Chem. Commun.* **1977**, 594.
(2) See: Whitesell, J. K.; Matthews, R. S. *J. Org. Chem.* **1978**, *43*, 1650.
(3) Whitesell, J. K.; Matthews, R. S.; Helbling, A. M. *J. Org. Chem.* **1978**, *43*, 785.
(4) Büchi, G.; Cushman, M.; Wüest, H. *J. Am. Chem. Soc.* **1974**, *96*, 5563.
(5) Snider, B. B.; Hrib, N. J.; Fuzesi, L. *J. Am. Chem. Soc.* **1976**, *98*, 7115.
(6) Carter, N. J.; Fleming, I. *J. Chem. Soc., Chem. Commun.* **1976**, 679.
(7) Gill, G. B.; Wallace, B. *J. Chem. Soc., Chem. Commun.* **1977**, 380.

0022-3263/80/1945-4135$01.00/0

Scheme IV



quired for the [3,3] process might be achieved. When combined with the formation of the allylic alcohol from the epoxide, the two migrations would result in an overall retention of the regiochemical relationships of the π bond (Scheme III).

In fact, we have found that α-methoxyacetate esters of allylic alcohols serve nicely in this scheme. Thus, Claisen rearrangement of these esters (1) as the lithium enolates 2 (or as the enol silyl ethers) in analogy with the work of Ireland[8] afforded α-methoxy carboxylates 3 (Scheme IV). Degradation by one carbon was effected by the sequence of Wasserman[9] wherein the dianion 4 formed from the carboxylate was oxidized with molecular oxygen. The resulting α-methoxy-α-hydroperoxy carboxylic acid, 5, formed upon acidification spontaneously lost carbon dioxide and water to form the desired ester (6).

Results and Discussion

(A) Ester Enolate Method. The sequence as originally developed by using the Claisen rearrangement of the ester enolates could be effected conveniently as a "one-pot" operation. Acceptable yields of β,γ-unsaturated esters were obtained from both a model and more complex bicyclo[3.3.0]octyl allylic alcohols as well as from 2-cyclohexen-1-ol and 2-cycloocten-1-ol (Table I, entries 1–5, column A). It was possible to interrupt the sequence immediately after the rearrangement and by spectral analysis to ascertain that both diastereomers of the α-methoxy acids were formed in roughly equal amounts. Thus it would appear that the internal solvation of the counterion that is possible only in the *Z* isomer of the anion is at the least unimportant in this kinetic deprotonation, if it operates at all.

Attempted extension of this method to systems wherein the allylic alcohol moiety was not contained within a carbocyclic ring or that involved migration from or to a quaternary center met with variable success (Table I, entries 7, 8, 10, 11, column A). Substantial amounts of starting allylic alcohol were obtained in many of those cases where little ester was produced. It would appear that fragmentation of the ester enolates was competing with the [3,3] rearrangement. Attempts to reduce the relative importance of the fragmentation by variations in the solvent polarity (from THF to DME, ether, hexane, or THF plus 20% HMPA) or in the cation (from lithium to potassium) invariably led to results that were inferior to the original THF–lithium system.

(B) Enol Silyl Ether Method. Following the analogy with the results reported by Ireland, we turned our attention to achieving the rearrangement via the enol silyl ethers, formed from the ester enolates, in order to reduce the tendency toward fragmentation. The intermediate α-methoxysilyl esters thus obtained could be isolated (Table I, column B) or converted in situ to the carboxylate by the addition of potassium fluoride and 18-crown-6. Continuation of the sequence by oxidative decarboxylation resulted in overall yields of β,γ-unsaturated esters superior in most cases to those obtained by using the ester enolate rearrangement. The intermediate α-methoxysilyl esters were obtained as diastereomeric mixtures, consistent with the conclusion above of low selectivity during the initial deprotonation. In addition, the intermediate α-methoxy carboxylic acids could be isolated and then, in a separate step, converted to the β,γ-unsaturated esters by the same sequence as before.

(C) Forcing Base Method. With the more hindered systems, we suspected that formation of the acid dianion with LDA was incomplete. In four cases an attempt was made to shift the equilibrium further toward the dianion by using additional *n*-butyllithium to consume the diisopropylamine formed during deprotonation. Though this technique was successful in providing low yields of the ultimate, unsaturated esters where none were otherwise obtained (Table I, entries 8, 10, 11), substantial amounts of *n*-butyl ketones resulted in these reactions from the addition of the alkyllithium to the lithium carboxylates.

In certain cases where the overall conversion to the unsaturated ester failed with all three methods, it was possible to interrupt the sequence at the α-methoxy acid stage (Table I, entries 12–14) and thereby to ascertain that responsibility for failure could be attributed to the oxidation–decarboxylation step. In each of these systems there are alternate acidic sites that may have suffered deprotonation during attempted formation of the dianion. It is interesting to note that **17** (see Experimental Section) was produced by a Claisen rearrangement involving the π system of a furan ring.

Experimental Section

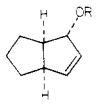
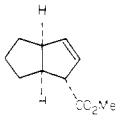
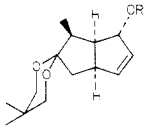
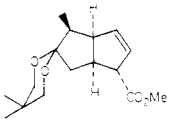
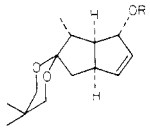
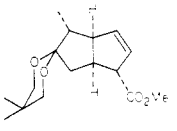
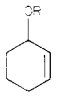
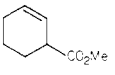
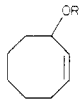
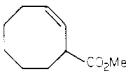
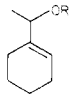
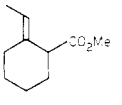
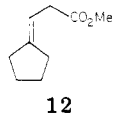
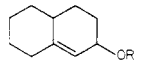
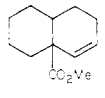
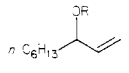
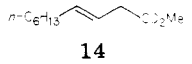
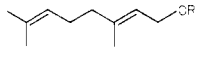
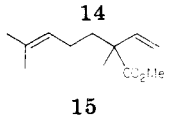
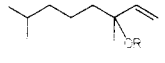
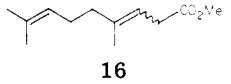
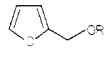
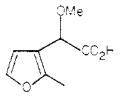
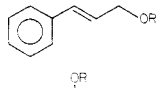
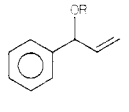
Materials. All reagents and solvents were obtained from commercial sources and used without further purification except for ether solvents which were dried with sodium–benzophenone and distilled before use.

Procedures. Reactions were routinely effected under a dry nitrogen atmosphere with magnetic stirring. Oxygen was dried prior to use with 3-Å molecular sieves. Molecular sieves were also employed for drying of the organic layers before solvent removal. Lithium diisopropylamide solutions were prepared at 0 °C from the amine and commercial, salt-free *n*-butyllithium. Crude reaction products were routinely purified by "column filtration" through silica gel with an appropriate mixture of hexane and ethyl acetate (EtOAc). Samples thus treated were often homogeneous by thin-layer chromatographic (E. Merck precoated glass plates) and ^{1}H NMR analysis. Further purification of samples in large quantities was effected by using a Waters System 500 high-pressure liquid chromatograph while preparative gas chromatography (GC) was used to obtain analytical samples (Chemalytics, Inc.). Yields in several cases were estimated by external standard, gas chromatographic analysis. Nuclear magnetic resonance spectra were obtained on $CDCl_3$ solutions by using a Varian HA-100 spectrometer for ^{1}H NMR spectra and either a Brucker WD-90 or a Varian FT-80 spectrometer for ^{13}C NMR spectra and in both cases are reported in parts per million on the δ scale relative to tetramethylsilane as internal standard. Infrared spectra (Perkin-Elmer 237B, CH_2Cl_2 solutions) of the β,γ-unsaturated esters uniformly showed carbonyl adsorptions at 1730 cm^{-1} and are not otherwise reported here.

***exo*-4-[(Methoxyacetoxy)oxy]-*cis*-bicyclo[3.3.0]oct-2-ene (1).** To an ice cold solution of 4.35 g (35 mmol) of the allylic alcohol[10] in 30 mL of dichloromethane was added dropwise over a period of 5 min 4.8 mL (52 mmol) of methoxyacetyl chloride. The cooling bath was removed and the reaction permitted to proceed for 12 h at room temperature. The reaction mixture was washed with water, with three 30-mL portions of 2 N aqueous

(8) Ireland, R. E.; Mueller, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 5897. Ireland, R. E.; Mueller, R. H.; Willard, A. K. *Ibid.* **1976**, *98*, 2868.
(9) Wasserman, H. H.; Lipshutz, B. H. *Tetrahedron Lett.* **1975**, 4611; **1976**, 4613.

Table I[a]

entry	reactant	yield, % A	B	C	product
1		54	62		
2		45			**6** 
3		52			**7** 
4		51			**8** 
5		52	67		**9** 
6		40			**10** 
7		16	40		**11** 
8		0	0	14	**12** 
9		13			**13** 
10		0	0	23	**14** 
11		0	0	13	**15** 
12		0	27		**16** 
13		0	0		
14		0	0		**17**

[a] R = $OCCH_2OCH_3$.

HCl, and then with 30 mL of 5% aqueous sodium bicarbonate solution. The organic layer was dried, concentrated in vacuo, and purified by high-pressure LC (2:1 hexane–EtOAc) to afford 4.97 g (73%) of a colorless oil: ^1H NMR δ 3.46 (s, 3 H, OCH_3), 4.20 (s, 2 H, CH_2OMe), 5.46 (m, 1 H, C=CCHO), 5.74 (dt, J = 6, 2 Hz, 1 H, C=CH), 5.96 (dd, J = 2, 6 Hz, 1 H, CH=C).

***exo*-4-(Carbomethoxy)-*cis*-bicyclo[3.3.0]oct-2-ene (6). Method A.** To a solution of 12.2 mmol of lithium diisopropylamide (LDA) in 20 mL of tetrahydrofuran (THF) at −78 °C was added 1.56 g (7.96 mmol) of allylic ester 1 dropwise over 2 min. The clear solution was kept at −78 °C for another 5 min, warmed slowly to room temperature over 15 min, and then stirred at 60 °C for 30 min. The reddish solution was then cooled in a −5 °C ice–salt bath, and 1.0 mL of hexamethylphosphoramide (HMPA) was added followed by 12.8 mmol of LDA over a period of 15 min. After 90 min at −5 °C, the dark red, clear solution was cooled to −78 °C and treated with a stream of oxygen (large excess) over 10 min. A solution of 7.4 g (32 mmol) of camphorsulfonic acid

(CSA) in 20 mL of THF was added dropwise. The resulting clear orange solution was kept at room temperature for 2 h, diluted with 4 volumes of brine, and extracted with four 40-mL portions of ether. The organic phase was washed with 10% sodium sulfite solution and brine, dried, and concentrated in vacuo. There was thus obtained after simple chromatography 1.09 g (82%) of a clear oil with spectral properties very similar to those of an analytical sample. High-pressure LC purification of the bulk of the material afforded the product: 0.72 g (54%); ^{1}H NMR δ 1.5 (m, 6 H), 2.96 (m, 1 H), 3.24 (m, 2 H), 3.69 (s, 3 H, OCH_3), 5.58 and 5.72 (ddt, J = 2, 6 Hz, 2 H, CH=CH).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.95; H, 8.30.

Method B. A solution of the ester enolate was prepared as above from 1.18 g (6 mmol) of ester and was quenched after 1 min at −78 °C with 1.0 g (6.1 mmol) of *tert*-butyldimethylsilyl chloride dissolved in 1.0 mL of HMPA. After 5 min the solution was warmed to and kept at 60 °C for 30 min. At room temperature 0.175 g (0.66 mmol) of 18-crown-6 in 1.0 mL of THF was added followed by 1.4 g (24 mmol) of dry potassium fluoride. The heterogeneous mixture was stirred rapidly at 35 °C for 12 h. Oxidation of the resulting carboxylate as the dianion was effected exactly as in method A and afforded 1.13 g of crude ester. The yield was estimated at 62% by GC.

The intermediate α-methoxy acid could be isolated directly at the appropriate point in method A or by hydrolysis of the silyl ester formed in method B (2 equiv of 2 N HCl in THF–H_2O at 25 °C for 12 h). This material was converted to the corresponding methyl ester by using excess diazomethane in ether for the purpose of further purification and spectral analysis: ^{1}H NMR δ 3.38 (s, 3 H, H_3COCH), 3.77 (s, 3 H, H_3CO_2C); ^{13}C NMR δ 172.7, 137.7 and 137.4, 128.8, 84.5 and 84.2, 58.4, 57.6 and 57.4, 51.7, 50.5 and 50.4, 43.6, 35.0 and 34.7, 31.7, 25.2. (The ratio of diastereomers, as determined from the duplicate entries in the ^{13}C NMR data, was approximately 2:1. Not all of the diastereomeric carbons were resolved.)

6-*exo*-(Carbomethoxy)-2-*endo*-methyl-3,3-(2,2-dimethyl-1,3-propylenedioxy)-*cis*-bicyclo[3.3.0]oct-7-ene (7): method A; yield 45% after high-pressure LC purification (5:1 hexane–EtOAc); ^{1}H NMR δ 0.79 (s, 3 H), 0.94 (d, J = 8 Hz, 3 H), 1.10 (s, 3 H), 1.8–2.4 (m, 3 H), 3.05 (m, 1 H), 3.4 (m, 6 H), 3.70 (s, 3 H), 5.74 (m, 2 H); ^{13}C NMR δ 175.0, 134.3, 128.6, 108.6, 72.3, 71.6, 59.0, 52.0, 51.7, 42.9, 40.9, 35.8, 30.0, 22.6, 22.2, 10.4; high-resolution mass spectrum, calcd for $C_{16}H_{24}O_4$ m/e 280.1674, found m/e 280.1668.

6-*exo*-(Carbomethoxy)-2-*exo*-methyl-3,3-(2,2-dimethyl-1,3-propylenedioxy)-*cis*-bicyclo[3.3.0]oct-7-ene (8): method A; yield 52% after high-pressure LC purification (5:1 hexane–EtOAc); ^{1}H NMR δ 0.75 (s, 3 H), 1.08 (d, J = 8 Hz, 3 H), 1.16 (s, 3 H), 1.3 (m, 1 H), 1.7 (m, 1 H), 2.2 (m, 1 H), 2.9 (m, 3 H), 3.40 and 3.66 (dd, J = 10 Hz, 4 H), 3.70 (s, 3 H), 5.62 (m, 1 H), 5.94 (m, 1 H); ^{13}C NMR δ 174.9, 136.9, 126.8, 107.8, 72.8, 71.1, 58.0, 55.6, 51.8, 47.6, 40.7, 35.9, 30.1, 22.7, 22.1, 12.2; high-resolution mass spectrum, calcd for $C_{16}H_{24}O_4$ m/e 280.1674, found m/e 280.1676.

Methyl 2-cyclohexene-1-carboxylate (9): method A; yield 51% (GC). A sample for analysis was purified by preparative GC: ^{1}H NMR δ 1.1–2.2 (m, 6 H), 3.08 (m, 1 H), 3.68 (s, 3 H), 5.78 (br s, 2 H).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.27; H, 8.66.

Methyl 2-cyclooctene-1-carboxylate (10): method A, yield after high-pressure LC purification (5:1 hexane – EtOAc) 52%; method B, yield 67% (GC); ^{1}H NMR δ 1.2–2.32 (m, 8 H), 3.50 (m, 1 H), 3.71 (s, 3 H), 5.72 (m, 2 H); high-resolution mass spectrum, calcd for $C_{10}H_{16}O_2$ (M^+) m/e 168.1150, found m/e 168.1150.

Methyl 2-ethylidene-1-cyclohexanecarboxylate (11): method A; yield after high-pressure LC purification (4:1 hexane–EtOAc) 40%; ^{1}H NMR δ 1.26 (d, J = 6 Hz, 3 H), 1.22 (m, 8 H), 3.11 (m, 1 H), 3.70 (s, 3 H), 5.20 (br q, J = 6 Hz, 1 H); high-resolution mass spectrum, calcd for $C_{10}H_{16}O_2$ (M^+) m/e 168.1150, found m/e 168.1144.

Methyl β-cyclopentylidenepropionate (12): method A, 16% yield, plus 10% of the material was recovered as the original allylic alcohol; method B, 40% yield (GC). A sample for analysis was purified by preparative GC: ^{1}H NMR δ 1.64 (m, 4 H), 2.23 (m, 4 H), 3.02 (dt, J = 1.2, 6 Hz, 2 H), 3.69 (s, 3 H), 5.42 (tt, J = 2.5, 8 Hz, 1 H).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.03; H, 9.30.

Method C. 1-(Carbomethoxy)bicyclo[4.4.0]dec-2-ene (13). The crude acid obtained by hydrolysis of the appropriate silyl ester prepared by method B was treated as follows. To 1.64 g (7.3 mmol) of the methoxy acid in 20 mL of THF and 1.5 mL of HMPA was added at −78 °C 22 mmol of LDA in a THF solution. The temperature of the solution was raised to 0 °C, held there for 30 min, and then lowered again to −78 °C. A solution of *n*-butyllithium in hexane (14.6 mmol) was then added slowly, after which the reaction was stirred at 0 °C for 40 min. Oxidation and further treatment of the reaction mixture was identical with the procedure described under method B. Analysis of the crude product (GC) indicated the presence of two products, in 14 and 42% yields, and the minor component was determined to be the desired unsaturated ester. Preparative GC provided samples of each product.

For the minor component: ^{1}H NMR δ 1.15–2.43 (m, 13 H), 3.70 (s, 3H), 5.52 (br d, J = 12 Hz, 1 H), 5.80 (dt, J = 4, 12 Hz, 1 H); high-resolution mass spectrum, calcd for $C_{12}H_{18}O_2$ (M^+) m/e 194.1307, found m/e 194.1311.

The major component was identified as the α-methoxy-*n*-butyl ketone: ^{1}H NMR δ 0.8–2.2 (m, 20 H), 2.4–2.66 (m, 2 H), 3.28, 3.34, 3.35 (3 s, 1:2:6, 3 H total), 3.70, 3.84, 3.96 (3 s, 2:6:1, 1 H total), 5.34–5.86 (m, 2 H).

While the butyl ketone was obtained as a mixture of diastereomers about the ring fusion, the β,γ-unsaturated ester apparently was not. We have no evidence bearing on the stereochemistry of the ring fusions in these compounds.

Methyl 3-decenoate (14): method A; yield 13% (GC), plus 15% of material recovered as the original allylic alcohol: ^{1}H NMR δ 0.8–1.6 (m, 11 H), 1.9–2.15 (m, 2 H), 3.05 (br d, J = 5 Hz, 2 H), 3.70 (s, 3 H), 5.54 (m, 2 H); high-resolution mass spectrum, calcd for $C_{11}H_{20}O_2$ (M^+) m/e 184.1463, found m/e 184.1465.

This material appeared to be a single geometric isomer, but because of the low yields obtained here and with other acyclic systems we did not pursue this point.

Methyl 2,6-Dimethyl-2-vinylhept-5-enoate (15). None of this material was formed by either method A or B. Modification of the procedure to force formation of the dianion as described above for **13** (method C) afforded 23% (GC) of **15** and 19% of the *n*-butyl ketone: ^{1}H NMR δ 1.30 (s, 3 H), 1.59 (s, 3 H), 1.68 (s, 3 H), 1.4–2.1 (m, 4 H), 3.70 (s, 3 H), 5.12 (m, 3 H), 6.07 (dd, J = 9.5, 18 Hz, 1 H); high-resolution mass spectrum, calcd for $C_{12}H_{20}O_2$ (M^+) m/e 196.1463, found m/e 196.1467.

Methyl 4,8-Dimethylnona-3,7-dienoate (16). None of this ester could be obtained by either method A or B. Method C afforded a low yield (13%, GC) of a 1:1 *E* to *Z* mixture with ^{1}H NMR and mass spectral data consistent with the assigned structures, but this material was not analyzed in detail.

Methyl Methoxy(2-methyl-3-furyl)acetate (17). Method B was interrupted before the oxidation, and the silyl ester thus obtained was converted to the acid with aqueous 2 N HCl. The crude acid was converted to the methyl ester with diazomethane for purification and analysis: ^{1}H NMR δ 2.34 (s, 3 H), 3.38 (s, 3 H), 3.77 (s, 3 H), 4.74 (s, 1 H), 6.39 (d, J = 1.8 Hz, 1 H), 7.28 (d, J = 1.8 Hz, 1 H).

Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.07; H, 6.34.

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Registry No. **1**, 65656-64-6; 1 alcohol, 27141-89-5; **6**, 65656-67-9; **7**, 74563-33-0; **8**, 74609-33-9; **9**, 25662-37-7; **10**, 4984-96-7; **11**, 74563-34-1; **12**, 74563-35-2; **13**, 74563-36-3; **14**, 21994-74-1; **15**, 74563-37-4; (*E*)-**16**, 56051-73-1; (*Z*)-**16**, 74380-60-2; **17**, 74563-38-5; methoxyacetyl chloride, 38870-89-2; (3′α,3′aβ,4′β,6′aβ)-3′,3′a,4′,6′a-tetrahydro-3′,5,5-trimethylspiro[1,3]dioxane-2,2′(1′*H*)-pentalen-4′-ol methoxyacetate ester, 74609-34-0; (3′α,3′aα,4′α,6′aα)-3′,3′a,4′,6′a-tetrahydro-

3′,5,5-trimethylspiro[1,3]dioxane-2,2′(1′*H*)-pentalen-4′-ol methoxyacetate ester, 74609-35-1; cyclohex-2-en-1-ol methoxyacetate ester, 74563-39-6; cyclooct-2-en-1-ol methoxyacetate ester, 74563-40-9; α-methylcyclohex-1-enemethanol methoxyacetate ester, 74563-41-0; 1-ethenylcyclopentanol methoxyacetate ester, 74563-42-1; 2,3,4,4a,5,6,7,8-octahydronaphthalen-2-ol methoxyacetate ester, 74563-43-2; non-1-en-3-ol methoxyacetate ester, 74563-44-3; 3,7-dimethylocta-2,6-dien-1-ol methoxyacetate ester, 74563-45-4; 3,7-dimethylocta-1,6-dien-3-ol methoxyacetate ester, 74563-46-5; 2-furanmethanol methoxyacetate ester, 74563-47-6; 3-phenylprop-2-en-1-ol methoxyacetate ester, 74563-48-7; 1-phenylprop-2-en-1-ol methoxyacetate ester, 74563-49-8.

Mechanism of the Liquid-Phase Catalytic Hydrogenolysis on Palladium/Carbon of Cyclohexene Epoxides

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Heterogeneous catalytic hydrogenolysis of cyclohexene epoxides on 10% Pd/C was studied in different solvents. The principal products were found to be alcohols, formed by cleavage of one epoxide C–O bond. In addition, simultaneous cleavage of both C–O bonds gave hydrocarbons, and isomerization on the catalyst gave ketones as byproducts. The deuterolysis of *cis*- and *trans-tert*-butylcyclohexene epoxides and kinetic studies with cyclohexene epoxides carrying an axial methyl group in position 3 or 5 showed that hydrogenolysis gives preferentially axial alcohols and trans hydrogen addition, after a "roll over" on the catalyst. If one epoxide carbon carries a methyl group, conformational and steric factors come into play. C–O bond cleavage at the more substituted carbon, leading to equatorial alcohols, becomes competitive with preferential formation of axial alcohols, and steric hindrance to molecular reorientation on the catalyst causes cis as well as trans hydrogen addition.

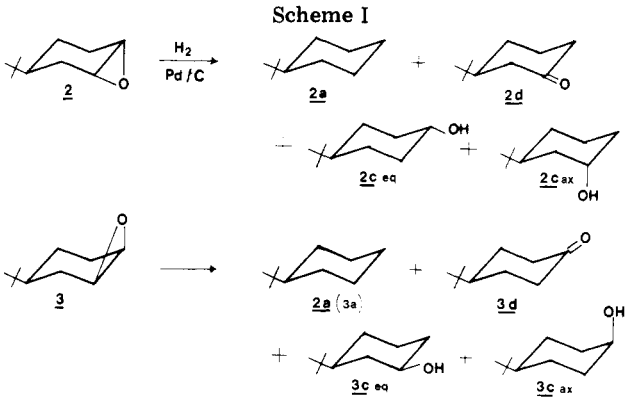
Heterogeneous catalytic hydrogenations are often accompanied by some degree of hydrogenolysis, depending on factors like the metal or solvent.[1] For example, catalytic hydrogenation of carbonyl derivatives (to alcohols) often leads to, besides the alcohols, the formation of hydrocarbons via hydrogenolysis of the alcoholic C–O bond. Epoxides show the same behavior and are particularly well suited for adsorption studies of the C–O bond. In this case, opening of one C–O bond gives alcohols, simultaneous cleavage of both C–O bonds leads to hydrocarbons,[2-5] and intramolecular rearrangements on the catalyst give rise to the formation of ketones.[6-8] While homogeneous acid- or base-catalized epoxide ring opening is well understood,[9] no model has yet been found which explains all stereochemical results of heterogeneous catalytic studies in the liquid[5-10] and gas phase.[2,3,8] We therefore decided to study the hydrogenolysis of some cyclohexene epoxides, since the conformations of both the initial and final products (alcohols, hydrocarbons, and ketones) are well-defined in these systems. Palladium on charcoal was chosen as the catalyst, since it proved to be more active in the liquid phase and at ordinary pressure than platinum, nickel, or rhodium.

Table I. Hydrogenolysis of 1,2-Epoxycyclohexane[a]

solvent	% 1a	% 1d	% 1c	% solvolysis
cyclohexane		18	82	
ether	20	12	68	
2-propanol	32	10	58	traces
ethanol[b]	15	5	65	15
methanol[b]	14	5	61	20

[a] P_{H_2} = 1 atm; T = 20 °C. [b] The use of these solvents leads to the trans 1,2-diaxial ether-alcohol.

Scheme I



Results and Discussion

Hydrogenolysis of cyclohexene epoxide (1) on palladium in various solvents (Table I) gives predominantly cyclo-

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