(Na_2SO_4) and solvent was removed, the residue was subjected to kugelrohr distillation to give 1.11 g (7.0 mmol, 14% yield) of 2-(dimethylamino)octane: IR (neat) 1050, 1110, 1160, 1275, 1385, 1470, 2770, 2870, 2960 cm^{-1}; ^1H NMR (CCl_4) δ 2.13–2.70 (m, 1 H), 2.09 (s, 6 H), 1.24 (br s, 10 H), 0.63–1.20 (m, 6 H); methiodide, mp 232.3–233.1 °C (lit.[43] mp 240 °C).

Anal. Calcd for $C_{10}H_{23}N$: C, 76.36; H, 14.74; N, 8.90. Found: C, 76.18; H, 14.75; N, 8.94.

Synthesis and Decomposition of Sodium Benzylhydroxysulfinate (1a). Compound **1a** was synthesized by following Bazlen's method;[22b] IR (KBr pellet) 655, 690, 955, 1030, 2600–3700 cm^{-1} (no absorption due to benzaldehyde carbonyl could be detected). To 40 mL of a refluxing dioxane–H_2O (1:1) mixture was added **1a** (1.5 g, 8.7 mmol). After the mixture was refluxed for 1 h under nitrogen, a sample of the mixture was analyzed by GLC (Carbowax, vide supra) and ^1H NMR. Both benzyl alcohol and benzaldehyde were present in a 65:35 ratio. A solution of **1a** in cold dioxane–water did not contain benzyl alcohol, though a marked amount of benzaldehyde was found to be present in the solution upon GLC analysis; this comes from reversible formation of the α-hydroxy sulfinate.

Reduction of Phenacyl Bromide with $Na_2S_2O_4$. A solution of phenacyl bromide (400 mg, 2 mmol) in 7 mL of ether was added to a solution of 1.10 g of $NaHCO_3$ in 7 mL of H_2O; 2.00 g of $Na_2S_2O_4$ was added and the mixture was stirred under nitrogen for 6 h. The layers were separated and the aqueous layer was extracted with ether. The combined ethereal extracts were dried ($MgSO_4$) and the ether was evaporated. The residue was subjected to kugelrohr distillation to give acetophenone (108 mg, 0.9 mmol, 45% yield).

Reduction of methylphenacylphenylsulfonium tetrafluoroborate[44] was carried out as described above for phenacyl bromide. The sulfonium salt was added neat to the mixture because of its insolubility in ether. After 1.5 h the mixture was worked up as usual. The sulfonium salt (666 mg, 2.0 mmol) gave 486 mg of liquid residue, the sole constituents of which were acetophenone and thioanisole in a 1:1 ratio (maximum theoretical yield 488 mg). The products were identified by ^1H NMR and GLC (Carbowax, vide supra).

Attempted Reduction of Phenacyl Benzoate. Phenacyl benzoate (485 mg, 2.0 mmol) was subjected to the conditions described for the reduction of phenacyl bromide. After 6 h the reaction mixture was worked up as usual. Starting material was recovered (432 mg, 89%).

Attempted Reduction of Benzonitrile. Benzonitrile (200 mg, 2.0 mmol) was subjected to the conditions described for the reduction of aldehydes and ketones, except that the amount of $Na_2S_2O_4$ was doubled. Dioxane was used as cosolvent. After the usual workup benzamide (178 mg, 75% yield) was isolated. The identity of the product was verified by IR, ^1H NMR, melting point, and mixture melting point with an authentic sample.

Attempted Reduction of Benzoic Acid. Benzoic acid (245 mg, 1.9 mmol) was subjected to the conditions described for reduction of aldehydes and ketones. Extra $NaHCO_3$ was added to allow for neutralization of benzoic acid. Dioxane was used as cosolvent. After termination of the reaction the mixture was acidified by addition of sulfuric acid and was worked up as usual. Benzoic acid was recovered (232 mg, 95% yield); no benzyl alcohol could be detected in the reaction mixture by GLC (Carbowax, vide supra).

Attempted Reduction of *N*-Methylpyrrolidone. *N*-Methylpyrrolidone (200 mg, 2 mmol) was subjected to the conditions described for reduction of aldehydes and ketones. When the reaction was terminated the mixture was subjected to continuous extraction with ether. *N*-Methylpyrrolidone was recovered quantitatively.

Attempted Reduction of Diphenylacetylene. Diphenylacetylene (365 mg, 2.0 mmol) was subjected to the conditions described for the reduction of aldehydes and ketones with dioxane as cosolvent; thereafter the reaction mixture was analyzed by GLC (Carbowax, vide supra). The only peak present could be attributed to diphenylacetylene. Neither stilbene nor 1,2-diphenylethane was detected in the reaction mixture.

Acknowledgment. We are grateful to Dr. T. J. van Bergen for his advice at the beginning stages of this work.

Registry No. 1a, 14339-77-6; $Na_2S_2O_4$, 7775-14-6; 2-(dimethylamino)octane, 7378-97-4; phenacyl bromide, 70-11-1; methylphenacylphenylsulfonium tetrafluoroborate, 34881-63-5; thioanisole, 100-68-5; benzonitrile, 100-47-0; benzamide, 55-21-0; *n*-hexanal, 66-25-1; benzaldehyde, 100-52-7; 2-furyl aldehyde, 98-01-1; cyclohexanone, 108-94-1; 4-*tert*-butylcyclohexanone, 98-53-3; adamantanone, 700-58-3; camphor, 76-22-2; 4-heptanone, 123-19-3; 2-pentanone, 107-87-9; 2-octanone, 111-13-7; cyclopentanone, 120-92-3; 2-norbornanone, 497-38-1; cycloheptanone, 502-42-1; levulinic acid, 123-76-2; acetophenone, 98-86-2; benzophenone, 119-61-9; 4-bromobenzophenone, 90-90-4; ethyl phenylglyoxalate, 1603-79-8; *n*-hexanol, 111-27-3; benzyl alcohol, 100-51-6; 2-furyl alcohol, 22125-63-9; cyclohexanol, 108-93-0; *cis*-4-*tert*-butylcyclohexanol, 937-05-3; *trans*-4-*tert*-butylcyclohexanol, 21862-63-5; 2-adamantanol, 700-57-2; 4-heptanol, 589-55-9; 2-pentanol, 6032-29-7; 2-octanol, 123-96-6; cyclopentanol, 96-41-3; *exo*-2-norbornanol, 497-37-0; *endo*-2-norbornanol, 497-36-9; cycloheptanol, 502-41-0; 4-hydroxypentanoic 1,4-lactone, 108-29-2; 1-phenylethanol, 98-85-1; diphenylmethanol, 91-01-0; (4-bromophenyl)phenylmethanol, 29334-16-5; ethyl mandelate, 774-40-3; 2-(dimethylamino)pentane, 57303-85-2; dimethylcyclopentylamine, 18636-91-4.

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Reactions of the Cyclopropanone Hemiketal Magnesium Salt with Some Nucleophilic Reagents[1]

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Cyclopropanol (**5**), 1-(arylethynyl)cyclopropanol (**7**), 1-(3-hydroxypropyl)cyclopropanol derivative **10**, 1-(2-propynyl)cyclopropanol (**14**), cyclopropanone cyanohydrin (**19**), 1-(aminomethyl)cyclopropanol (**21**) derivatives, benzylidenecyclopropanes **32**, and ethyl cyclopropylideneacetate (**38**) have been prepared from the magnesium salt of cyclopropanone hemiketal **3**. 3-Cyclopropylidene-1-propanol (**12**) and 3-cyclopropylidene-1-propyne (**16**) have been obtained from the cyclopropanols **10** and **14**, respectively. Some reactions of this new synthon were specific. On the other hand, **3** did not undergo the nucleophilic addition of sulfur and nitrogen ylides; it underwent oxidizing ring opening with $BrZnCH_2COOEt$ and induced the decomposition of diazomethane.

The formation of cyclopropanone from ketene and diazomethane in inert solvent at −78 °C has been proven spectroscopically.[2,3] But, in spite of its considerable interest, this three-membered-ring ketone is not sufficiently

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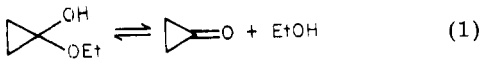
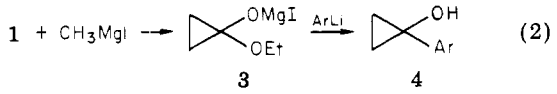
stable to permit useful synthetic applications. However, the ethyl hemiketal of cyclopropanone (1) can provide a convenient source of the parent ketone 2, on the basis of the equilibrium shown in eq 1.[4]



1 2 (1)

The stable hemiketal 1, obtained in the reaction of ketene and diazomethane in the presence of ethanol,[4] is now conveniently prepared on large scale from commercial ethyl 3-chloropropanoate.[5] It undergoes readily nucleophilic addition of Grignard reagents,[4,5] of azides,[4] and of amines[6] to provide 1-substituted cyclopropanols in high yields.

On the other hand, the hemiketal 1 does not undergo the nucleophilic addition of organolithium reagents such as lithium cyanide,[7] ethynyllithium,[7] aryllithium,[8] etc. A simple solution to this difficulty was recently reported by Brown and Rao; thus, treatment of the 1-ethoxycyclopropanol (1), with an equimolar amount of methylmagnesium iodide converted it into a species, likely the magnesium salt 3, which was now able to react with aryllithium to give the expected 1-arylcyclopropanol (4) in satisfactory yields[8] (eq 2).

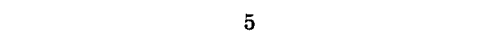


3 4 (2)

We report in this paper the behavior of the magnesium salt 3 in presence of some nucleophilic reagents including hydrides, organometallic reagents, cyanide carbanion, and phosphorus, sulfur, and nitrogen ylides, which we have investigated in order to determine the reactivity and the synthetic applications of the cyclopropanone hemiketal magnesium salt 3.

Reaction of the Magnesium Salt 3 with Lithium Aluminium Hydride. A New Synthesis of Cyclopropanol. Cyclopropanol 5 has been prepared either from the addition of magnesium bromide to epichlorohydrin and cyclization by means of ferric ion[9] or from the hydride reduction of cyclopropyl acetates.[10,11]

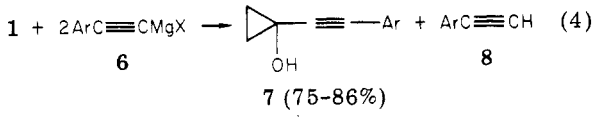
We have obtained 5 from the simple addition of lithium aluminium hydride to a suspension of the magnesium salt 3 in ether in 75% yield (eq 3) after refluxing the mixture



5 (3)

for 2 h, while, under the same conditions, addition of 2 equiv of $LiAlH_4$ to the cyclopropanone hemiketal 1 provided 5 in only 45% yield.

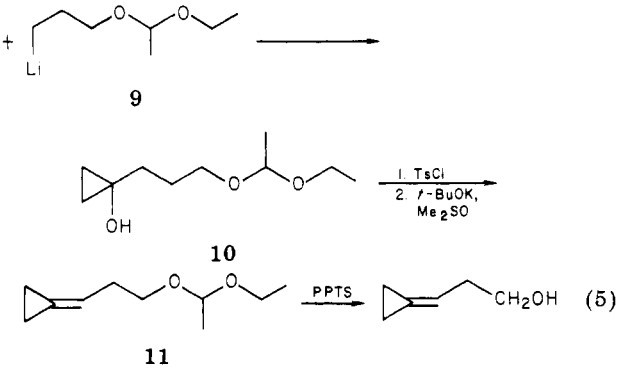
Reaction of the Magnesium Salt 3 with Organometallic Reagents. An Improved Synthesis of 1-Substituted Cyclopropanols. Due to the equilibrium hemiketal 1 ⇌ cyclopropanone 2 + ethanol (see eq 1), 2 equiv of the Grignard reagent are involved in the reaction with the cyclopropanone hemiketal 1. Thus, for instance, the reaction of 1 with 2 equiv of the arylacetylenic magnesium bromides 6 (X = Br) yielded 1-(*p*-arylethynyl)-cyclopropanols (7) and arylacetylenes (8) from ethanolysis[5] (eq 4)



6 7 (75-86%) 8 (4)

On the other hand, addition of only 1 equiv of the Grignard reagents 6 to the magnesium salt 3 provided the cyclopropanols 7 with comparable yields. So, the utilization of the magnesium salt 3 instead of the hemiketal 1 allows one both to save 1 equiv of the Grignard reagents 6 and to avoid further purification by a quite tedious separation of 7 and 8. Furthermore, addition of the corresponding organolithium derivatives ArC≡CLi to 3 yielded the expected cyclopropanols 7 in satisfactory yields.

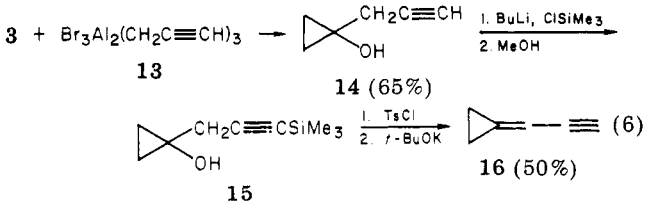
Some other challenging small-ring compounds have been prepared readily from the synthon 3. Thus, for instance, addition of the organolithium reagent 9[12] to the magnesium salt 3 led to the cyclopropanol 10 (eq 5). Tosylation of



9 10 11 (5)

10 followed by base-catalyzed elimination led to the methylenecyclopropane 11, and then, deketalization induced by pyridinium *p*-toluenesulfonate[13] (PPTS) gave the homoallyl alcohol 12 in 35% overall yield from 3. Recently the synthesis of 12 has been reported from 1-bromomethylenecyclopropane.[14]

The nucleophilic addition of the organoalane 13[15] to the magnesium salt 3 provided the homopropargylic cyclopropanol 14 in 65% yield (eq 6). Upon treatment with



13 14 (65%) 15 16 (50%) (6)

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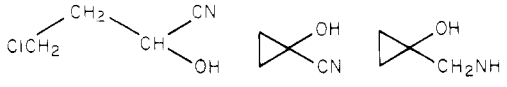
2 equiv of *n*-butyllithium and 2 equiv of trimethylsilyl chloride, **14** gave, after methanolysis, the cyclopropanol **15**. Tosylation of **15** followed by basic elimination led to 3-cyclopropylidene-1-propyne (**16**).

The formation of the cyclopropanol **17** could be expected from the nucleophilic addition of the Reformatsky reagent to the magnesium salt **3** (eq 7). Following the Rieke

18 (7) 17

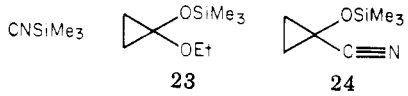
procedure,[16] addition of ethyl α-bromoacetate and activated zinc to **3** yielded, after hydrolysis, a mixture of hemiketal **1**, ethyl propanoate, and ethyl 3-iodopropanoate (**18**) from cyclopropane ring opening. Although it is known that 1-methoxycyclopropanol undergoes ring opening on treatment with oxidizing agents such as cupric, ferric, and ceric salts,[17] the formation of iodo ester **18** from the iodomagnesium salt **3** was quite unexpected.

Reaction of the Magnesium Salt 3 with Lithium Cyanide. A New Synthesis of Cyclopropanone Cyanohydrin. Cyclopropanone cyanohydrin (**19**) has been previously prepared either from the direct addition of hydrocyanic acid to cyclopropanone itself[18] or from the cyclization of 3-chloropropianaldehyde cyanohydrin (**20**) with the sodium salt of hexamethyldisilazane.[19]



20 19 21

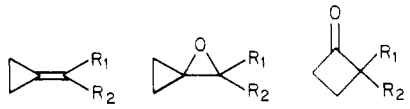
We have readily obtained the cyanohydrin **19** from the simple addition of lithium cyanide to the magnesium salt **3** in 75% yield; reduction of the cyano group of **19** with lithium aluminium hydride gave quantitatively 1-(aminomethyl)cyclopropanol (**21**). It has been reported that **21** undergoes ring enlargement into cyclobutanone upon treatment with nitrous acid.[19] It must be underlined that the reaction of the hemiketal **1** with lithium cyanide gave ethyl propanoate exclusively. The use of trimethylsilyl cyanide (**22**) as a reagent for the direct formation of stable cyanohydrin trimethylsilyl ethers from ketones has been recently reported.[20]



23 24

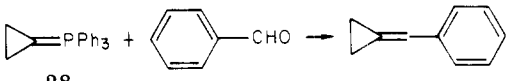
Treatment of the magnesium salt **3** with trimethylsilyl cyanide (**22**) in presence of zinc iodide in refluxing ether yielded only the 1-ethoxy-1-siloxy cyclopropane **23** instead of the expected cyclopropanone cyanohydrin trimethylsilyl ether (**24**). Likewise, **23** was obtained from the addition of silyl cyanide **22** to the hemiketal **1**.

Reaction of the Magnesium Salt 3 with Phosphorus Ylides. An Alternate Synthesis of Alkylidenecyclopropanes. Alkylidenecyclopropanes **25** provide a convenient key to enter the chemistry of small-ring compounds. Thus, for instance, epoxidation of **25** with peracids gave oxaspiropentanes **26** which underwent lithium salt induced ring enlargement into cyclobutanones **27**.[21]



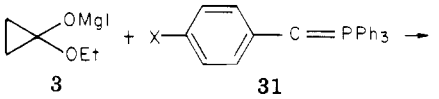
25 26 27

Alkylidenecycloalkanes are usually prepared by means of the Wittig reaction either between cycloalkylidenephosphoranes and alkanones or between alkylidenephosphoranes and cycloalkanones.[22] Owing to the lability of the cyclopropanone, the preparation of alkylidenecyclopropanes **25** had only been reported from the Wittig reaction of the cyclopropylidenephosphorane **28** with carbonyl compounds. In this way, the reaction of **28** with benzaldehyde (**29**) provided the benzylidenecyclopropane (**30**)[23] (eq 8).

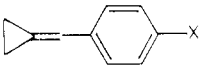


28 29 30 (50%) (8)

In the field of our investigation, it was interesting to test the alternate pathway to the cyclopropylidene derivatives **25** from the reaction of the cyclopropanone hemiketal magnesium salt **3** with nucleophilic alkylidene phosphoranes. As expected, the addition of the phosphoranes **31** prepared from the corresponding benzyltriphenylphosphonium chlorides and *n*-butyllithium to a suspension in ether of the magnesium salt **3** led, after refluxing of the mixture for 40 h to complete the discharge of the yellow-orange color of the phosphoranes, to the benzylidenecyclopropanes **32** (eq 9); while, under the same conditions the hemiketal **1** was not reactive.[24]



3 31



32 (34-51%) (9)

X = H, CH_3, OCH_3

On the other hand, the addition of (*p*-nitrobenzylidene)triphenylphosphorane (**31**, X = NO_2) to the magnesium salt **3** did not give **32** (X = NO_2). Likewise, in spite of considerable experimental effort, attempts to obtain the Wittig reaction of some other alkylidenephosphoranes with **3** have failed. Thus, for example, although on addition to the magnesium salt **3** the deep red color of the phosphorane **33**, prepared from cyclohexyltriphenylphosphine iodide,[25] was completely discharged when the mixture was heated at 40 °C for 40 h, the olefin **34** was not obtained (eq 10). The crude white suspension obtained from the reactions of **3** with **33** gave a NMR

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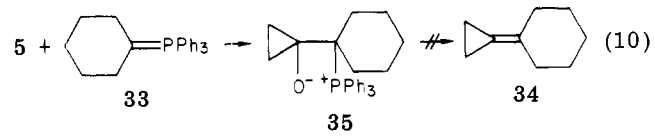
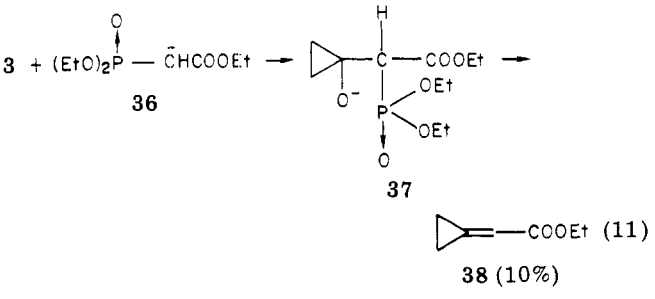


(10)

33 35 34

spectrum in accordance with the betaine **35** (15 aromatic protons at δ ($CDCl_3$) 7.15 vs. 14 methylenic protons at δ 0.6–2.1); but, the olefin **34** was not obtained on further heating of **35** in refluxed tetrahydrofuran, benzene, toluene, or xylene for days. It was confirmed that cyclopropylidenecyclohexane (**34**), unequivocally prepared from cyclohexanone and phosphorane **28**,[23] is stable under these conditions.

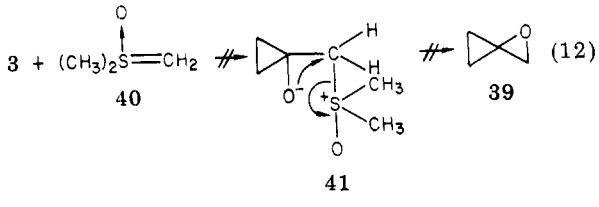
Addition of the phosphonate carbanion **36**[26,27] to the magnesium salt **3** gave the ester **38**, via the oxyanion **37**, in low yield (eq 11), while the alternate pathway, i.e., the Wittig reaction of the cyclopropylidenephosphorane **28** with ethyl glyoxylate,[28] did not lead to the ester **38**.



(11)

36 37 38 (10%)

Reactions of the Magnesium Salt 3 with Sulfur and Nitrogen Ylides. Oxaspiropentane (**39**)[21] could be expected from the nucleophilic addition of dimethyloxosulfonium methylide **40**[29] to the magnesium salt **3** via the intermediate betaine **41** (eq 12).



(12)

40 41 39

However, upon treatment with 1 equiv of ylide **40** in refluxing tetrahydrofuran for 16 h, **3** gave, after the usual workup, a mixture of cyclopropanone hemiketal **1** and ethyl propanoate. Likewise, attempts to add dimethylsulfonium methylide [$(CH_3)_2S{=}CH_2$][29] and nucleophilic diazomethane[30,31] to **3** have failed.

Experimental Section

Synthesis of 1-ethoxycyclopropanol (1) from ethyl 3-chloropropanoic ester has been previously reported.[5] **Synthesis of cyclopropanone hemiketal magnesium iodide 3** from 1-ethoxycyclopropanol (**1**) has been previously reported.[8]

Synthesis of Cyclopropanol 5. (a) From the Magnesium Salt 3. To an oven-dried, nitrogen-flushed, 1-L, three-necked flask fitted with a mechanical stirrer, a pressure-equalizing dropping funnel, and a reflux condenser topped with a connecting tube leading to a mercury bubbler were added magnesium (1.46 g, 60 mmol) and diethyl ether (120 mL). To this stirred suspension was added dropwise methyl iodide (10.2 g, 60 mmol) in ether (120 mL). After all the magnesium was dissolved, the flask was cooled in an ice bath. To this was added dropwise 1-ethoxycyclopropanol (**1**) (6.12 g, 60 mmol) in ether (120 mL). A gas, presumably methane, evolved, while a white suspension was formed. To the stirred suspension was added dropwise a solution of 1.14 g (30 mmol) of lithium aluminium hydride in diethyl ether (50 mL). After the addition was over, the reaction mixture was brought to room temperature (30 min) and then maintained (oil bath) under reflux for 2 h. The mixture was then cooled to room temperature and hydrolyzed by addition of wet sodium sulfate. The ether layer was separated, washed with water (5 mL), dried over sodium sulfate, and concentrated. Fractional distillation of the residue yielded 2.6 g (75%) of cyclopropanol: bp 52 °C (90 mm) [lit.[9] bp 101 °C]; NMR (CCl_4) δ 0.50 (m, 4 H), 3.35 (m, 1 H), 4.0 (s, 1 H); mass spectrum, *m/e* (relative intensity) 58 (M^+, 20.6), 57 (100), 29 (46.9).

(b) From the Hemiketal 1. To a solution of 6.12 g (60 mmol) of cyclopropanone hemiketal **1** in diethyl ether (300 mL) cooled at 0 °C by immersion of the flask in an ice bath was added dropwise a solution of 1.14 g (30 mmol) of lithium aluminium hydride in diethyl ether (50 mL). Then the reaction mixture was refluxed for 2 h and worked up in the same way as for part a. Fractional distillation gave 1.56 g (45%) of cyclopropanol, besides 1-ethoxycyclopropanol (**1**).

Synthesis of 1-(Phenylethynyl)cyclopropanol (7, Ar = Ph).[5] Into 0.1 mol of the suspension of cyclopropanone hemiketal magnesium iodide **3** (see synthesis of **5**) in diethyl ether (400 mL) maintained at 0 °C was injected under nitrogen by means of a double-ended needle 1.1 mol of phenylacetylenemagnesium bromide[32] in tetrahydrofuran (120 mL). After the addition was over, the reaction mixture was brought to room temperature and then maintained under reflux overnight. It was cooled to 0 °C and saturated ammonium chloride solution added. After the usual workup and removal of solvents, fractional distillation gave 14.2 g (90%) of pure 1-(phenylethynyl)cyclopropanol (**7**, Ar = Ph).[5]

Synthesis of Acetaldehyde Ethyl 3-(1-Hydroxycyclopropyl)propyl Acetal (10). A solution of the acetaldehyde ethyl 3-lithiopropyl acetal (**9**) was prepared as described earlier by using 57 g (0.27 mol) of acetaldehyde ethyl 3-bromopropyl acetal, 4.2 g (0.6 mol) of lithium wire, and 232 mL of diethyl ether.[12] In a 1-L flask fitted with a septum inlet and mechanical stirrer was prepared 0.2 mol of cyclopropanone hemiketal magnesium iodide **3** in diethyl ether (500 mL; see the synthesis of **5**). The solution of the lithium reagent **9** was injected under argon by means of a double-ended needle into the suspension of **3** held at 0 °C in an ice bath. The mixture was stirred for 1 h at 0 °C after the addition was complete, brought to room temperature, and stirred overnight. Then, the mixture was poured into 500 mL of cooled saturated ammonium chloride solution. After the usual workup, distillation gave 28 g (55%) of colorless adduct **10**: bp 42 °C (0.045 mm); IR (CCl_4) 3490 (ν_{OH}), 3090 cm^{-1} (ν_{CH}); NMR (CCl_4) δ 0.40 (m, 2 H), 0.80 (m, 2 H), 1.20 (m, 6 H), 1.40–2.20 (m, 4 H), 3.20–4.10 (m, 4 H), 4.72 (q, 1 H); mass spectrum, *m/e* (relative intensity) 187 (M^+, 1.6), 143 (13.2), 115 (4.3), 99.2 (6.8), 85.1 (34.9), 73 (100), 71 (24.9), 57 (69.4), 45 (56.2).

Synthesis of 3-Cyclopropylidene-1-propanol (12). A solution of 3.76 g (20 mmol) of cyclopropanol **10** in tetrahydrofuran (40 mL) was placed in a 100-mL reaction flask which was flushed with argon and fitted with a side arm with a rubber serum cap. At 0 °C was added dropwise 20 mmol of *n*-butyllithium (13.3 mL of a 1.5 N solution in hexane). The reaction mixture was stirred for 2 h and then cooled to 40 °C (dry ice–acetonitrile bath). Next, a solution of 5 g (26 mmol) of *p*-toluenesulfonyl chloride in 10 mL of tetrahydrofuran was added and the mixture stirred for 30 min at −40 °C. The mixture was allowed to warm to room temperature and stirred overnight. Then, the mixture was cooled to 0 °C, placed in a separatory funnel, and washed rapidly with cold 5% sodium bicarbonate solution. The organic layer was decanted and dried over magnesium sulfate, and the solvent was removed to yield 6.4 g (93%) of a pale yellow oil.

(26) W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).
(27) W. S. Wadsworth, *Org. React.*, **25**, 125 (1977), and references cited therein.
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(29) E. J. Corey and M. Chaykowsky, *J. Am. Chem. Soc.*, **87**, 1354 (1965).
(30) A. W. Johnson in "Organic Chemistry", Vol. 7, A. T. Blomquist, Ed., Academic Press, New York and London, 1966, Chapter 7, p 270.
(31) W. Kirmse in "Organic Chemistry", Vol. 1, A. T. Blomquist and H. Wasserman, Eds., Academic Press, New York and London, 1971, Chapter 3, p 85.
(32) H. Taniguchi, M. Mathai, and S. Miller, *Org. Synth.*, **50**, 97 (1970).

A solution of 6.4 g (18.5 mmol) of the crude tosylate in dimethyl sulfoxide (10 mL) was added dropwise to a solution of 3.36 g (30 mmol) of potassium *tert*-butoxide in dimethyl sulfoxide (20 mL). During the addition the temperature of the mixture rose to 40–45 °C. When the addition was over, the mixture was stirred for an additional 3 h at room temperature. The mixture was poured into 50 mL of crushed ice and water and extracted three times with 75 mL of diethyl ether. The extracts were washed with water and dried over magnesium sulfate, and the solvent was removed by distillation. Fractional distillation of the residue gave 2.30 g (73%) of the methylenecyclopropane **11**: bp 67 °C (13 mm); IR (CCl_4) 1730 cm^{-1} ($\nu_{C=C}$); NMR (CCl_4) δ 0.80–2.30 (m, 12 H), 3.20–3.80 (m, 4 H), 4.65 (q, 1 H), 5.30 (m, 1 H).

To a solution of 0.437 g (2.56 mmol) of ketal **11** in absolute ethanol (5 mL) was added 82 mg (0.3 mmol) of pyridinium *p*-toluenesulfonate.[13] The mixture was stirred at 55 °C for 3 h, and then the ethanol was removed by distillation. The residue was dissolved in 20 mL of diethyl ether, the mixture was washed with saturated sodium chloride solution and dried over sodium sulfate, and most of the ether was removed by careful distillation through a 30-cm packed column. The residue was purified by preparative gas chromatography on a column of 20% Carbowax 20-M at 135 °C to give the cyclopropylidenepropanol **12**: IR (CCl_4) 3640 and 3450 (ν_{OH}), 3060 (ν_{CH}), 1730 cm^{-1} ($\nu_{C=C}$); NMR (CCl_4) δ 1.05 (m, 4 H), 2.20 (s, 1 H), 2.40 (t, 2 H), 3.60 (t, 3 H), 5.75 (m, 1 H); mass spectrum, *m/e* (relative intensity) 98 (M^+, 1.9), 67 (100), 53 (55.6), 31 (30).

Synthesis of 1-(2-Propynyl)cyclopropanol (14). A suspension of 0.35 mol of cyclopropanone hemiketal magnesium iodide **3** in diethyl ether (1600 mL) was prepared in a 2-L flask fitted with a rubber serum cap (see synthesis of **5**). In a 250-mL flask fitted with magnetic stirrer, a pressure-equalizing dropping funnel, a reflux condenser, and a rubber serum cap were placed 6.30 g (0.23 mol) of powdered aluminium and 1 g of mercuric chloride in diethyl ether (40 mL). The mixture was stirred at 30 °C for 30 min, and then 41.65 g (0.35 mol) of propargylic bromide was added dropwise in order to maintain a gentle reflux. When the addition was over (about 4 h), the mixture was refluxed for 2 h. The solution of propargylaluminium bromide was cooled to 0 °C and injected under nitrogen by means of a double-ended needle into the suspension of **3**. The stirred mixture was allowed to warm to room temperature and refluxed for 2 h. Then, the cooled mixture was poured into 800 mL of cooled saturated ammonium chloride solution. After the usual workup, distillation gave 16.8 g (50%) of 1-(2-propynyl)cyclopropanol (**14**): bp 47–48 °C (10 mm); IR (neat) 3350 (ν_{OH}), 2120 cm^{-1} ($\nu_{C\equiv C}$); NMR δ (CCl_4) 0.55–0.9 (m, 4 H), 1.95 (t, 1 H), 2.57 (d, 2 H), 3.93 (s, 1 H); mass spectrum, *m/e* (relative intensity) 96 (M^+, 7.9), 81 (20.7), 78 (3), 67 (29.3), 57 (26.6), 56 (100), 55 (25), 39 (55).

Synthesis of 1-[3-(Trimethylsilyl)-2-propynyl]cyclopropanol (15). To a solution of 9.6 g (0.1 mol) of cyclopropanol **14** in tetrahydrofuran (150 mL) held at −78 °C (dry ice–methanol bath) was added dropwise under argon 0.22 mol of *n*-butyllithium (147 mL of a 1.5 N solution in hexane). The mixture was stirred for 2 h at −78 °C, and then a solution of 24 g (0.22 mol) of trimethylsilyl chloride in tetrahydrofuran (120 mL) was added dropwise. The mixture was stirred at −78 °C for 2 h and allowed to warm to room temperature overnight. The mixture was poured into 200 g of crushed ice, the mixture decanted, and the aqueous phase extracted with diethyl ether (4 × 150 mL). The combined extracts were washed with half-saturated brine (50 mL), dried over sodium sulfate, and concentrated to yield 23.9 g (100%) of crude trimethylsilyl 1-[3-(trimethylsilyl)-2-propynyl]cyclopropyl ether: IR (neat) 2180 cm^{-1} ($\nu_{C\equiv C}$); NMR δ (CCl_4) 0.12 (s, 18 H), 0.67 (s, 4 H), 2.6 (s, 2 H); mass spectrum, *m/e* (relative intensity) 225 (3.9), 167 (58.7), 73 (100).

A solution of 20.1 g (83.7 mmol) of the trimethylsilyl ether in methanol (60 mL) was stirred at room temperature overnight. Removal of the methanol on a rotary evaporator gave 13.83 g (98.3%) of practically pure 1-[3-(trimethylsilyl)-2-propynyl]-cyclopropanol (**15**): IR (neat) 3380 and 3330 (ν_{OH}), 2180 cm^{-1} ($\nu_{C\equiv C}$); NMR δ (CCl_4) 0.15 (s, 9 H), 0.50–0.85 (m, 4 H), 2.58 (s, 2 H), 3.3 (s, 1 H); mass spectrum, *m/e* (relative intensity) 168 (M^+, 5.3), 153 (22), 95 (5.3), 75 (47), 73 (100).

Synthesis of 3-Cyclopropylidene-1-propyne (16). A solution of 13 g (77.3 mmol) of the cyclopropanol **15** and 16.23 g (85 mmol) of tosyl chloride in pyridine (100 mL) was held at 0 °C for 7 days. Then, the mixture was worked up as usual to yield 21 g (85%) of 1-(tosyloxy)-1-[3-(trimethylsilyl)-2-propynyl]cyclopropane: IR (CCl_4) 2180 cm^{-1} ($\nu_{C\equiv C}$); NMR δ (CCl_4) 0.08 (s, 9 H), 0.86–1.23 (m, 4 H), 2.45 (s, 3 H), 3 (s, 2 H), 7.1–8 (q, 4 H). A solution of 20.5 g (63.6 mmol) of the tosylate in dimethyl sulfoxide (120 mL) was added dropwise to a mixture of 18.5 g (0.16 mol) of potassium *tert*-butoxide in dimethyl sulfoxide (180 mL) in order to maintain the temperature below 40 °C. When the addition was over, the mixture was stirred at room temperature for 2 h and then poured on 60 g of crushed ice. It was extracted with decalin (4 × 100 mL). The combined extracts were washed to neutrality and dried over sodium sulfate. Distillation of the solution at ordinary pressure gave 3.55 g (50%) of a mixture [bp 70 °C (760 mm)] containing the 3-cyclopropylidene-1-propyne (**16**): yield 90%; IR (neat) 2118 cm^{-1} ($\nu_{C\equiv C}$); NMR δ (CCl_4) 1.0–1.5 (m, 4 H), 2.78 (br s, 1 H), 5.85 (m, 1 H); mass spectrum, *m/e* (relative intensity) 78 (M^+, 100), 77 (99.4), 63 (32.8), 52 (83), 51 (79), 50 (77). It also contained 3-cyclopropylidene-1-(trimethylsilyl)-1-propyne: yield 10%; IR (neat) 2118 cm^{-1} ($\nu_{C\equiv C}$); NMR δ (CCl_4) 0.08 (s, 9 H), 1.0–1.5 (m, 4 H), 5.85 (m, 1 H); mass spectrum, *m/e* (relative intensity) 149 (M^+, 2), 78 (100), 77 (91.7), 75 (65), 52 (64.7), 51 (58.7), 50 (59) (from GC + MS).

Reaction of 3 with Ethyl α-Bromoacetate and Activated Zinc. A suspension of 13.7 g (0.2 mol) of activated zinc in diethyl ether (120 mL) was prepared as reported.[16] At 0 °C 33.4 g (0.2 mol) of ethyl bromoacetate was added, and the mixture was injected under nitrogen by means of a double-ended needle into a suspension of 0.2 mol of the magnesium salt **3** (see synthesis of **5**) in diethyl ether (500 mL). The mixture was allowed to warm to room temperature and stirred overnight. Then, it was cooled to 0 °C and saturated ammonium chloride solution added. After the usual workup and removal of solvent, fractional distillation gave, besides a polymeric residue, 8.3 g of cyclopropanone hemiketal 1 ethyl propanoate [bp 82–83 °C (28 mm)], and 2.9 g of ethyl 3-iodopropanoate [**18**; bp 43 °C (0.02 mm)] readily identified from its spectra: IR (neat) 1730 cm^{-1} ($\nu_{C=O}$); NMR δ (CCl_4) 1.29 (t, 3 H), 2.90 (m, 2 H), 3.35 (m, 2 H), 4.15 (q, 2 H); mass spectrum, *m/e* (relative intensity) 228 (M^+, 32.8), 155 (55.3), 127 (13.8), 101 (100), 73 (71.5), 29 (52.8).

Synthesis of Cyclopropanone Cyanohydrin (19). To a suspension of 70 mmol of the magnesium salt **3** (see synthesis of **5**) in diethyl ether (250 mL) held at 0 °C was added a solution of 2.31 g (70 mmol) of lithium cyanide[33] in tetrahydrofuran (120 mL). The mixture was allowed to warm to room temperature and refluxed for 40 h. Then, it was cooled to 0 °C and saturated ammonium chloride solution added. After the usual workup most of the solvents were removed by distillation through a 30-cm packed column. Fractional distillation of the residue gave 4.35 g (75%) of cyclopropanone cyanohydrin (**19**): bp 48 °C (0.35 mm);[19] IR ($CDCl_3$) 3575 and 3360 (ν_{OH}), 2240 cm^{-1} ($\nu_{C\equiv N}$); NMR δ ($CDCl_3$) 1.20 (s, 4 H), 4.10 (br s, 1 H); mass spectrum, *m/e* (relative intensity) 83 (M^+, 11.9), 82 (86), 55 (63.8), 54 (100).

Reaction of Cyclopropanone Hemiketal 1 with Lithium Cyanide. To a solution of 0.66 g (20 mmol) of lithium cyanide in tetrahydrofuran (50 mL) held at 0 °C was added dropwise a solution of 1.02 g (10 mmol) of cyclopropanone hemiketal 1 in tetrahydrofuran (20 mL). The mixture was allowed to warm to room temperature and was refluxed for 2 h. After usual workup, the solvent was removed by distillation. The IR and NMR spectra of the residue showed the presence of ethyl propanoate, exclusively.

Synthesis of 1-(Aminomethyl)cyclopropanol (21) Derivatives. A solution of 0.83 g (10 mmol) of cyanohydrin **19** in methylene chloride (70 mL) was treated with 1.26 g (15 mmol) of 3,4-dihydropyran and 0.3 g of pyridinium *p*-toluenesulfonate.[13] The mixture was stirred at room temperature for 4 h, washed with half-saturated brine, and dried over sodium sulfate. The solvent was removed by distillation. The crude tetrahydropyranyl ether was diluted with ether (50 mL) and treated with 0.91 g (24 mmol) of lithium aluminium hydride. The mixture was refluxed for 1 h. It was cooled to room temperature and hydrolyzed by addition of wet sodium sulfate. The ether layer was separated, washed

(33) I. B. Johns and H. R. Dipietro, *J. Org. Chem.*, **29**, 1970 (1964).

with half-saturated brine, dried over sodium sulfate, and concentrated by distillation of solvent to give 1.70 g of the crude aminotetrahydropyranyl ether of **21**: IR (neat) 3360 cm^{-1} (ν_{NH}); NMR δ (CCl_4) 0.40–0.90 (m, 4 H), 1.40 (s, 2 H), 1.60 (m, 6 H), 3.20–4.20 (m, 4 H), 4.75 (t, 1 H).

Synthesis of the Benzamide Derived from the Aminocyclopropanol 21. To a solution of 2 g (11.7 mmol) of **20** in diethyl ether (25 mL) was added a solution of 1.62 g (11.7 mmol) of potassium carbonate in 25 mL of water. To the mixture was added dropwise a solution of 1.68 g of benzoyl chloride in benzene (100 mL). It was stirred overnight. The aqueous phase was decanted and extracted with diethyl ether. The joined organic phases were washed with half-saturated brine and dried over sodium sulfate. The solvents were removed on a rotary evaporator to yield 2.7 g of a crude amide: IR (neat) 3340 (ν_{NH}), 1645 and 1535 cm^{-1} ($\nu_{C=O}$). The amide was dissolved in ethanol (40 mL), and 252 mg of pyridinium *p*-toluenesulfonate[13] was added. The mixture was stirred at 55 °C (bath temperature) for 3 h. Then, the ethanol was removed on a rotary evaporator and the residue dissolved in ether (20 mL). The solution was washed with half-saturated brine, dried over sodium sulfate, and concentrated on a rotary evaporator to yield a partially crystallized residue. Recrystallization of the solid from chloroform–hexane gave 0.92 g of benzamide derivative as white prisms: mp 103.8 °C; IR ($CDCl_3$) 3680, 3580, 3340 (ν_{OH} and ν_{nH}), 1640 and 1560 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) δ 0.55 (m, 2 H), 0.70 (m, 2 H), 3.42–3.52 (d, 2 H), 4.20 (m, 1 H), 7.20–7.90 (m, 5 H); mass spectrum, *m/e* (relative intensity) 191 (M^+, 2.2), 135 (26), 134 (19.3), 105 (100), 77 (44).

Anal. Calcd for $C_{11}H_{13}O_2N$: C, 69.09; H, 6.85; O, 16.73; N, 7.32. Found: C, 69.27; H, 6.89; N, 7.29.

Reaction of 3 with Trimethylsilyl Cyanide. To a white suspension of 26 mmol of the cyclopropanone hemiketal magnesium iodide **3** in 150 mL of diethyl ether (see synthesis of **5**) held at 0 °C (ice bath) was added 5.15 g (52 mmol) of trimethylsilyl cyanide[21] and 10 mg of anhydrous zinc iodide. The mixture was allowed to warm to room temperature and was then refluxed for 48 h. The light yellow mixture was cooled and poured into an iced ammonium chloride solution. After the usual workup, fractional distillation gave, besides 0.3 g of hemiketal **1**, 3.4 g (75%) of 1-ethoxy-1-(trimethylsiloxy)cyclopropane (**23**):[34] bp 45 °C (14 mm); NMR δ (CCl_4) 0.10 (s, 9 H), 0.72 (m, 4 H), 1.08 (t, 3 H), 3.55 (q, 2 H); mass spectrum, *m/e* (relative intensity) 174 (M^+, 0.3), 117 (14), 101 (11.8), 75 (39.3), 73 (100), 56 (19.9), 45 (24.1).

Likewise, addition of trimethylsilyl cyanide to cyclopropanone hemiketal **1**, under the same conditions, gave **23**.

Synthesis of Benzylidenecyclopropanes 32. (a) Benzylidenecyclopropane (32, X = H). To 7.8 g (20 mmol) of benzyltriphenylphosphonium chloride[35] in diethyl ether (50 mL) was added dropwise 20 mmol of *n*-butyllithium (12.7 mL of a 1.58 N solution in hexane). The yellow-orange suspension was stirred for 30 min and then injected under argon by means of a double-ended needle into a white suspension of 25 mmol of cyclopropanone hemiketal magnesium iodide **3** in diethyl ether (see synthesis of **5**). When the addition was over, the mixture was allowed to warm to room temperature. After 1 h thin-layer chromatography of the mixture showed the lack of olefin. The mixture was then refluxed. Although most of olefin **32** seemed to be formed after 15 h (TLC), the complete discharge of the yellow-orange color of the phosphorane was obtained after the mixture was refluxed for 22 h. After the usual workup and removal of solvents, filtration of triphenylphosphine oxide and fractional distillation of the residue gave 1.6 g (61.5%) of benzylidenecyclopropane (**30**): bp 33 °C (0.04 mm) [lit.[23] bp 35–38 °C (10.1 mm)]; spectral data indentical with those reported for the olefin prepared from benzaldehyde and cyclopropylidenephosphorane.[23]

(b) *p*-Methylbenzylidenecyclopropane (32, X = CH_3). In the same way, the phosphorane prepared from 50 mmol of (*p*-methylbenzyl)triphenylphosphonium chloride[36] in diethyl ether (100 mL) and 50 mmol of *n*-butyllithium (32.9 mL of a 1.52 N solution in hexane) was, after stirring of the mixture for 2 h, injected under argon to a white suspension of 60 mmol of the magnesium salt **3** held at 0 °C. After the addition was over, the orange reaction mixture was brought to room temperature and then refluxed until the color of the mixture was completely discharged (~40 h). After the usual workup, distillation gave 3.7 g (51%) of *p*-methylbenzylidenecyclopropane: bp 52 °C (0.1 mm) with spectral data identical with those reported for the olefin prepared from *p*-methylbenzaldehyde and cyclopropylidenephosphorane.[37]

(c) *p*-Methoxybenzylidenecyclopropane (32, X = OCH_3). The phosphorane prepared from 50 mmol of (*p*-methoxybenzyl)triphenylphosphonium chloride[38] and 50 mmol of *n*-butyllithium (30.8 mL of a 1.62 N solution in hexane) was stirred for 2 h and then injected under argon into the white suspension of 60 mmol of the magnesium salt **3** held at 0 °C. The mixture was refluxed for 16 h to obtain the complete discharge of the color. After the workup, distillation of the residue gave 2.70 g (34%) of *p*-methoxybenzylidenecyclopropane [bp 72–74 °C (0.1 mm)] with spectral data indentical with those reported for the olefin prepared from *p*-methoxybenzaldehyde and cyclopropylidenephosphorane.[37]

(d) Additions of Benzylidenephosphorane 31 to Cyclopropanone Hemiketal 1. A solution of 1.5 g (14.7 mmol) of cyclopropanone hemiketal **1** in diethyl ether (10 mL) was added to the phosphorane **31** prepared from 10 mmol of benzyltriphenylphosphonium chloride and 10 mmol of *n*-butyllithium in diethyl ether (100 mL). Refluxing the mixture for 65 h did not induce the discharge of the yellow-orange color of the suspension. The lack of olefin **32** was carefully checked by thin-layer and gas chromatographies.

Synthesis of *p*-Nitrobenzylidenecyclopropane (32, X = NO_2). (a) From Cyclopropylidenephosphorane (28). To a suspension of 4.5 g (0.15 mol) of sodium hydride (80% suspension in mineral oil) in 1,2-dimethoxyethane (200 mL) were added 35 g (75 mmol) of (3-bromopropyl)triphenylphosphonium bromide[23] and two drops of ethanol at room temperature under N_2. The mixture was stirred at 60 °C for 6 h. Then, a solution of 11.3 g (75 mmol) of *p*-nitrobenzaldehyde in 1,2-dimethoxyethane (25 mL) was added, and the mixture was stirred at 60 °C for 4 h. The mixture was poured into crushed ice and extracted with pentane. The pentane extract was dried, concentrated, and chromatographed on silica. Elution with pentane–diethyl ether (95:5) and crystallization from carbon tetrachloride gave 5.6 g (42.8%) of *p*-nitrobenzylidenecyclopropane: mp 64.7 °C; IR (CCl_4) 1740 cm^{-1} ($\nu_{C=C}$); NMR δ (CCl_4) 1.40 (m, 4 H), 6.72 (m, 1 H), 7.55–8.25 (q, 4 H); mass spectrum, *m/e* (relative intensity) 175 (M^+, 6.4), 158 (24.2), 129 (65.8), 128 (100), 127 (28).

(b) From Cyclopropanone Hemiketal Magnesium Iodide 3. The phosphorane prepared from 21.75 g (50 mmol) of (*p*-nitrobenzyl)triphenylphosphonium chloride[38] and 50 mmol of *n*-butyllithium (30.8 mL of a 1.62 N solution in hexane) was injected under argon into a white suspension of 60 mmol of the magnesium salt **3** prepared from 6.12 g of hemiketal **1** held at 0 °C. The mixture was refluxed for 6 days, and the lack of olefin **32** (X = NO_2) was checked by TLC and GC. After the workup, distillation gave 1 g of starting hemiketal **1** only.

Synthesis of Cyclopropylidenecylohexane (34). (a) From Cyclopropylidenephosphorane (28). Cyclopropylidenecyclohexane (**34**) was prepared in 58% yield by following the procedure of Schweizer.[23]

(b) From Cyclopropanone Hemiketal Magnesium Iodide 3. This synthesis from **3** and the deep red phosphorane **33** prepared from cyclohexyltriphenylphosphine iodide[25] has failed.

Synthesis of Ethyl Cyclopropylideneacetate (38). Triethyl phosphonoacetate (11.2 g, 0.05 mol) was added dropwise at 20 °C to a slurry of 80% sodium hydride (1.5 g, 0.05 mol) in 100 mL of dry 1,2-dimethoxyethane.[26] After the addition the solution was stirred for 1 h at room temperature and then injected, under nitrogen, into a suspension of 0.05 mol of the magnesium iodide **3** (see synthesis of **5**) in diethyl ether (300 mL) kept at 0 °C. The mixture was allowed to warm to room temperature and then heated at 38 °C for 48 h and at 50 °C for 24 h with stirring, during which time a white semisolid precipitated. The mixture was cooled and filtered. The filtrate was washed with dilute acid to neutrality,

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(36) G. Drefahl and G. Plotner, *Chem. Ber.*, **93**, 990 (1960).
(37) J. Salaün and M. Hanack, *J. Org. Chem.*, **40**, 1994 (1975).
(38) R. Ketcham, D. Jambotkar, and L. Martinelli, *J. Org. Chem.*, **27**, 4666 (1962).

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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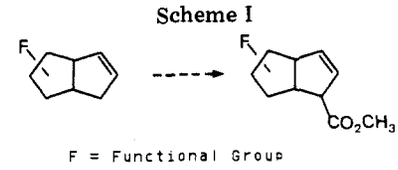
β,γ-Unsaturated esters are of interest for the synthesis of mono- and sesquiterpenes where the alkene linkage is destined for cleavage to a dialdehyde as well as for the synthesis of γ-butyrolactones. A general method for the preparation of deconjugated esters of this type from allylic alcohols is described. 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).

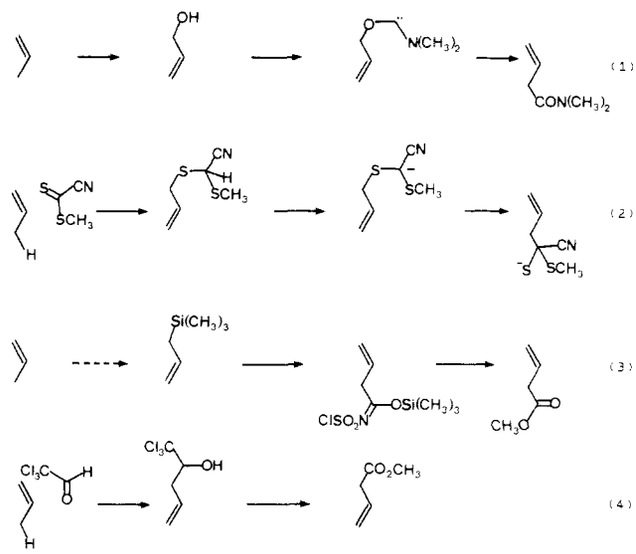
Several methods were known at that time for accomplishing this operation (eq 1–3, Scheme II), though each had inherent limitations that made their successful use in the present context appear improbable. Thus, the [2,3] sigmatropic rearrangement of the carbene intermediate in Büchi's sequence[4] works 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

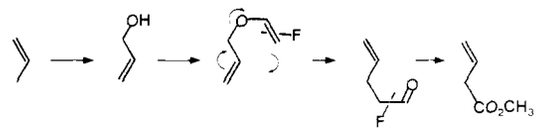


F = Functional Group

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.

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