Vinylcyclopropanation of Olefins with Vinyldiazomethane

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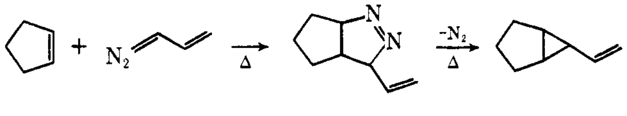
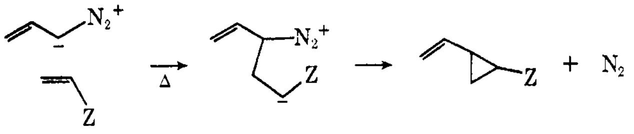
Vinylcyclopropanation of olefins by copper-catalyzed reaction with vinyldiazomethane is a short and convenient synthesis of vinylcyclopropanes. Though all copper salts examined cause decomposition of vinyldiazomethane with evolution of nitrogen, only a very few catalyze cyclopropanation. With *cis*- and *trans*-2-butenes, the catalyzed vinylcyclopropanation is stereospecific. Several pairs of isomeric vinylcyclopropanes were prepared and fully characterized. The more sterically congested endo isomer is favored in the reaction with cyclohexene in contrast with cyclopropanations with ethyl diazoacetate and trimethylsilyldiazomethane which both give almost exclusively the exo isomer. The more congested syn isomer is likewise preferentially formed in the reaction of vinyldiazomethane with vinylacetate.

We were confronted with the necessity of preparing a variety of vinylcyclopropanes in connection with another study. A very direct synthetic approach to these compounds is addition of vinylcarbene to the appropriate olefin. Diazo compounds are commonly used as precursors of carbenes and carbenoids.[1] Vinyldiazomethane reacts thermally with strained olefins,[2] or olefins with unsaturated electron-withdrawing substituents,[3] to give pyrazolines in moderate yields. The pyrazolines decompose with loss of nitrogen to give vinylcyclopropanes in low yields. Direct production of vinylcyclopropanes in trace amounts without intervention of pyrazolines occurs in certain cases, namely unsymmetrical polarized olefins with unsaturated electronegative substituents. Vinylcarbene is not considered an intermediate in such reactions. Rather, a stepwise dipolar mechanism is postulated involving ionic addition to the olefin to give a zwitterionic intermediate which cyclizes by nucleophilic displacement of nitrogen.[3] In general, thermal reaction of vinyldiazomethane with olefins is not a preparatively useful synthesis of vinylcyclopropanes. Photolysis of diazo compounds generally induces loss of nitrogen and provides the corresponding carbenes.[1] However, vinyldiazomethane undergoes a photochemical cyclization to form pyrazolenine.[4] Copper salts are often used to catalyze cyclopropanation of olefins with diazo compounds.[1,5] Therefore we examined the copper-catalyzed reaction of vinyldiazomethane with olefins. We now report the successful application of this approach to the synthesis of a variety of vinylcyclopropanes.[6]





$Z = CO_2CH_3, CN$

Results and Discussion

The efficacies of various catalysts were determined for the vinylcyclopropanation of cyclohexene with vinyldiazomethane under standard conditions (see Experimental Section). The results are summarized in Table I. The factors responsible for the observed differences in yield are not clear. All of the copper salts examined promoted the decomposition of vinyldiazomethane as evidenced by the evolution of nitrogen and disappearance of the red color of the diazo compound. Cupric trifluoromethanesulfonate and cupric hexafluoroacetylacetonate promote vinylcyclopropanation in the highest yield. Cupric trifluoroacetate also effectively catalyzes this reaction, although in lower yield. Other copper salts were ineffective even though they effectively catalyze cyclopropanations with other diazo compounds. Copper chloride is often used effectively for catalyzing the reaction of diazomethane with olefins.[7] Tri-*n*-butylphosphinecopper(I) iodide is an excellent catalyst for cyclopropanations with diazo esters.[8] The bis(di-*n*-butyl sulfide)copper(I) iodide complex catalyzes cyclopropanations with diazo ketones.[9]

Table I
Yield of Vinylcyclopropanes in the Reaction of Vinyldiazomethane with Cyclohexene with Various Copper Salts as Catalyst

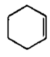
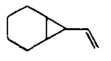
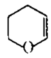
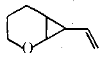
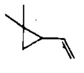
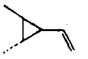
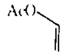
Catalyst	Yield, %
Cupric hexafluoroacetylacetonate	20
Cupric trifluoromethanesulfonate	40
Cupric trifluoroacetate	12
Tri-*n*-butylphosphinecopper(I) iodide	2
Bis(di-*n*-butyl sulfide)copper(I) iodide	2
Cuprous chloride	<2
Cupric carbonate	<1
Cupric sulfate (anhydrous)	<1

Optimum Catalyst to Diazo Ratio. The reaction between vinyldiazomethane and cyclohexene was conducted in the presence of varying amounts of cupric hexafluoroacetylacetonate (see Figure 1). The yield of vinylcyclopropane increases sharply as the relative amount of catalyst is increased until a ratio of about 20:1 of vinyldiazomethane to catalyst is reached. After leveling off, the yield decreases slightly as the relative amount of catalyst exceeds 10 mol %. Moreover, the use of larger amounts of catalyst is accompanied by the production of greater quantities of side products which are difficult to separate.

The observed deleterious effect of excessive quantities of catalyst is readily explained. Copper(II) salts are reduced by diazo compounds and yield copper(I) salts, which are the actual cyclopropanation catalysts.[5] Appreciably soluble copper(II) salts (copper hexafluoroacetylacetonate is appreciably soluble in olefin-containing solutions[10]) are reduced completely and an equivalent amount of diazo compound is destroyed. The observed decrease of yield at very low catalyst to diazo ratios may be due to destruction of the copper(I) catalyst by a similar though less rapid reduction by relatively large excesses of diazo compound. Also at lower catalyst to total vinyldiazomethane ratios, the concentration of diazo compound in the reaction mixture may

Table II

Preparative Scale Reaction of Vinyldiazomethane with Various Olefins

Olefin	Registry no.	Vinylcyclopropane	Registry no.	Yield, %	Catalyst
	110-83-8		53951-19-2 53951-20-5	20 20	Cupric hexafluoroacetylacetonate Cupric trifluoromethanesulfonate
	110-87-2		53951-21-6	24	Cupric trifluoroacetate
	1708-29-8		53951-22-7	13	Cupric hexafluoroacetylacetonate
	115-11-7		7736-30-3	20 38	Cupric hexafluoroacetylacetonate Cupric trifluoromethanesulfonate
	590-18-1		53951-23-8 54019-66-8	22 29	Cupric trifluoromethanesulfonate Cupric hexafluoroacetylacetonate
	624-64-6		54019-67-9	16	Cupric hexafluoroacetylacetonate
	108-05-4		53965-73-4 53965-72-3	9	Cupric hexafluoroacetylacetonate

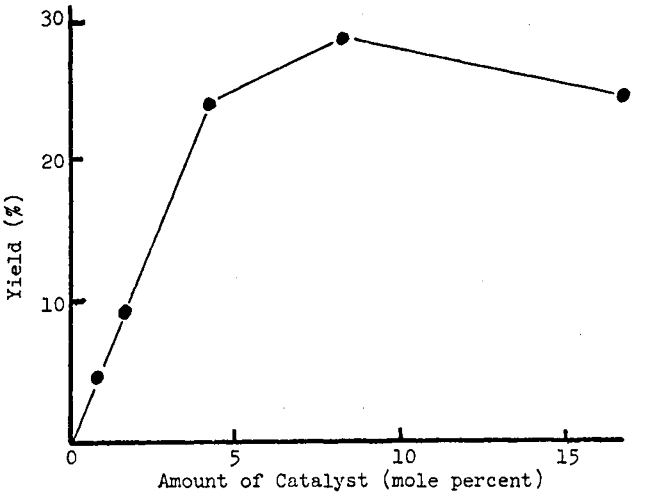
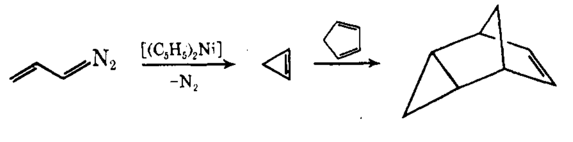


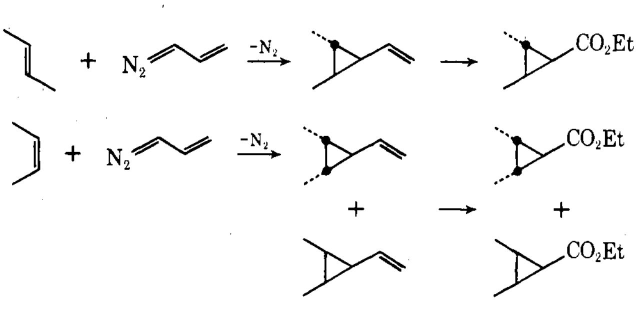
Figure 1. Vinylcyclopropane yield as a function of mole percent of catalyst in the reaction of cyclohexene with vinyldiazomethane.

build up owing to the low rate of catalytic reaction, and side reactions involving two molecules of diazo compound may become important.

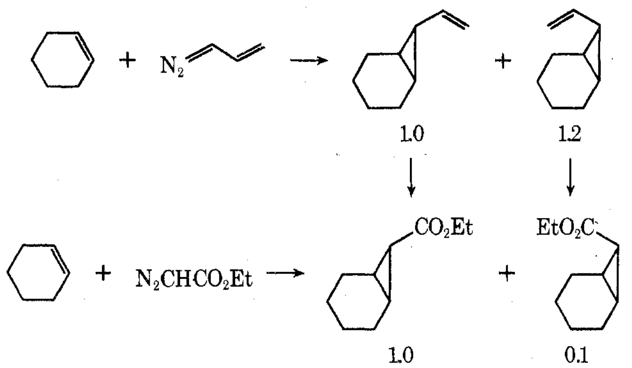
Preparative Vinylcyclopropanation. Many side reactions are expected to interfere with the vinylcyclopropanation of olefins with vinyldiazomethane. The products themselves are olefins and therefore are susceptible to undesirable further additions of carbenes. Vinyldiazomethane is unstable and rearranges to pyrazolenines (3*H*-pyrazoles).[4] However, we developed procedures which consistently gave solutions of vinyldiazomethane in pentane or cyclohexene in greater than 82% yield (see Experimental Section). The solutions decomposed slowly at 0°. After standing for 7 hr the yield decreased to 76% and after 48 hr it decreased to 63%. Finally, vinylcarbenes exhibit a general tendency to react intramolecularly to give cyclopropenes.[1] For example, vinyldiazomethane is converted to cyclopropene with loss of nitrogen under catalysis by nickelocene. In cyclopentadiene as solvent, *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene is formed.[11] In spite of these many potential interfering side reactions, *isolated* yields of vinylcyclopropanes as high as 38% are obtained from copper salt catalyzed reaction of vinyldiazomethane with olefins. Thus, this synthetic approach may be the method of choice for the preparation of a variety of vinylcyclopropanes from readily available olefins, since it is very short and convenient, and the necessary reagents are readily available and inexpensive (see Table II).



Stereospecific Vinylcyclopropanation of 2-Butenes. Copper hexafluoroacetylacetonate catalyzes the reaction of vinyldiazomethane with *trans*-2-butene to give a single vinylcyclopropane product which exhibits two nonequivalent methyl doublets in its proton magnetic resonance spectrum. Similar reaction of *cis*-2-butene gives two isomeric vinylcyclopropyl products which each exhibit only one methyl doublet in their ^{1}H NMR spectra. The isomeric 1,2-dimethyl-3-vinylcyclopropanes were further identified as the expected products of stereospecific additions of vinylcarbene to the isomeric olefins by conversion to the respective ethyl 2,3-dimethylcyclopropanecarboxylates, which are identical with authentic samples.[5,12]



Stereochemical Course of Cyclohexene Vinylcyclopropanation. Both cupric hexafluoroacetylacetonate and trifluoromethanesulfonate catalyze the vinylcyclopropanation of cyclohexene with vinyldiazomethane to give two isomeric products in a ratio of 1.2:1.0. These isomers were characterized as *endo*- and *exo*-7-vinylbicyclo[4.1.0]heptane, respectively, by conversion to the known corresponding *endo*- and *exo*-7-carbomethoxybicyclo[4.1.0]heptanes.[13] This endo/exo ratio remains constant during the course of the addition of vinyldiazomethane to the reaction mixture. The ratio was found to be 1.22 ± 0.02 during addition of 10–100% of the total diazo compound. The observed preferential formation of an endo isomer is unusual. *Copper-catalyzed cyclopropanation of cyclohexene* with ethyl



diazoacetate or with trimethylsilyldiazomethane favors production of the exo isomer by 0.10 and 0.11–1.00, respectively.[8a,14] Since the vinyl goup is less bulky than a carboethoxy or trimethylsilyl group, preferential formation of the more congested endo isomer of the vinyl derivative and the less congested exo isomer of the carboethoxy or trimethylsilyl may be simply the result of steric control.

Structural Characterization of Isomeric 1-Acetoxy-2-vinylcyclopropanes. The reaction of vinyldiazomethane with vinyl acetate is catalyzed by copper hexafluoroacetylacetonate. Two isomeric 1-acetoxy-2-vinylcyclopropanes are obtained in a ratio of 1.0:2.0 As in the case of the isomeric cyclohexene adducts discussed above, the major product is the more sterically congested syn isomer. This isomer, *cis*-1-acetoxy-2-vinylcyclopropane, was characterized by analysis of its ^{1}H NMR spectrum. Thus one proton on C-3 shows a coupling of 4.1 Hz with the proton α to the acetoxy group. This coupling constant is characteristic of trans-vicinal protons.[15] The other proton on C-3 shows a coupling of 9.3 Hz with the allylic proton. This is characteristic of cis-vicinal protons.[15] Taken together, these facts imply a cis relationship between the vinyl and acetoxy groups. Confirmation of this assignment was obtained with the aid of a shift reagent.[16] Changes in proton chemical shifts were induced by europium(III) tris-1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate. The extrapolated magnitudes of these shifts for a 1:1 mole ratio of acetoxyvinylcyclopropane to europium are indicated in Chart I. Thus, the shifts of the vinyl protons in the case of the cis isomer are two to four times greater than those in the trans isomer. All other comparisons, though less dramatic, unequivocally support the assigned structures.

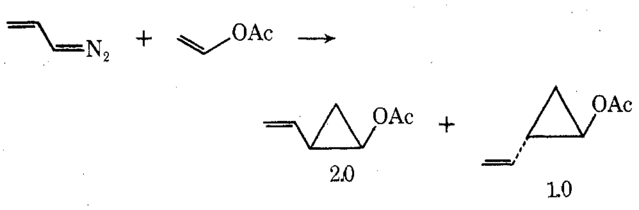
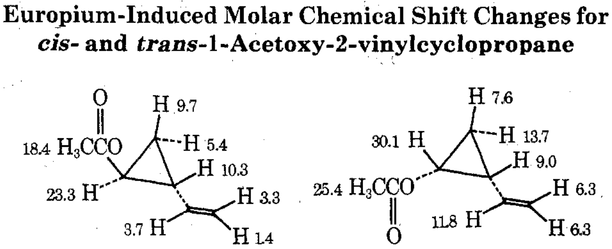
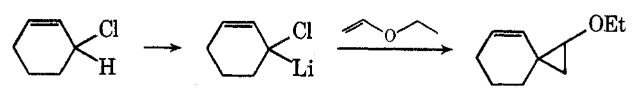


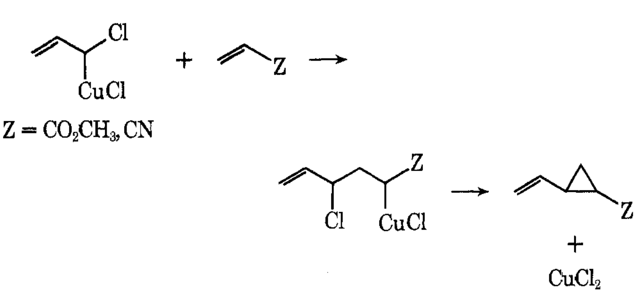
Chart I
Europium-Induced Molar Chemical Shift Changes for *cis*- and *trans*-1-Acetoxy-2-vinylcyclopropane



Comparison with Other Vinylcyclopropanation Reactions. Though allylic halides generally yield cyclopropenes upon α-lithiation, a single instance of the addition of a vinyl carbenoid to an olefin was observed recently. Thus α-lithiation of 3-chlorocyclohexene in the presence of ethyl vinyl ether produces a vinylcyclopropane.[17] It is not yet known whether this reaction proceeds with the stereospecificity characteristic of carbenoid additions as found in the copper-catalyzed reaction of vinyldiazomethane with unactivated olefins.



Recently vinylcyclopropanes were obtained by the reaction of 1,3-dichloropropene or allylidene chloride with copper(0) in the presence of α,β-unsaturated esters or nitriles.[18] It may be that these cyclopropanations involve Michael addition of copper(II) carbenoids followed by 1,3-elimination from the resulting β-chloroorganocopper(II) chloride intermediates. An activating group such as ester or nitrile appears necessary for these vinylcyclopropanations.



In contrast with copper-catalyzed vinylcyclopropanation of unactivated olefins with vinyl diazomethane, no examples of vinylcyclopropanation of unactivated olefins with the allylidene chloride–copper(0) reagent are known.

Experimental Section

General. Preparative gas–liquid phase chromatography was performed with a Varian Model 202B instrument. Proton magnetic resonance spectra were recorded with a Varian A-60A or HA-100 FT spectrometer with tetramethylsilane as an internal standard and CCl$_4$ as solvent. ^{1}H NMR spectral data are at 60 MHz unless otherwise indicated. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

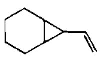
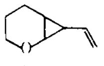
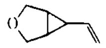
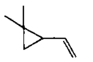
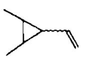
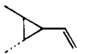
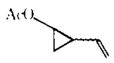
Materials. Olefinic reactants (gases) were Matheson reagent or Phillips pure reagent grade. Liquid olefinic reactants were reagent grade or purified by distillation prior to use. Pentane used as reaction solvent was purified by stirring over concentrated H$_2$SO$_4$ for a minimum of 24 hr, washed with saturated aqueous NaHCO$_3$ and then with water, dried (MgSO$_4$), and distilled. Ethyl allylnitrosocarbamate,[19] diazoethane,[20] cupric trifluoromethanesulfonate,[21] ethyl diazoacetate,[22] isomeric ethyl 2,3-dimethylcyclopropanecarboxylates,[12] and isomeric 7-carboethoxybicyclo[4.1.0]heptanes[13] were prepared by known procedures.

Vinyldiazomethane.[23] A methanolic solution of sodium methoxide (0.13 mol) was prepared under dry nitrogen by dissolving sodium metal in methanol (50 ml) in a 500-ml single neck round-bottom flask equipped with a West condenser. Pentane (200 ml) was added. The flask was shielded from light by wrapping with aluminum foil. The reaction mixture was cooled with an ice–water bath. A solution of ethyl allylnitrosocarbamate (7.9 g, 50 mmol) in pentane (100 ml) was added over 1 hr with a pressure-equalizing addition funnel which replaced the West condenser. The mixture was stirred for an additional 1.5 hr at 0° after completion of the addition. The resulting red solution was washed twice with cold aqueous 5% NaOH solution (100 ml). The dark red solution of vinyldiazomethane was dried over anhydrous KOH and stored at 0° shielded from light. *Caution!* Vinyldiazomethane is potentially explosive.

The yield of vinyldiazomethane (82–85%) was determined by measuring the volume of evolved nitrogen from reaction of an aliquot of diazo compound solution with an excess of *p*-nitrobenzoic acid in tetrahydrofuran.

General Vinylcyclopropanation Procedure. Preparative

Table III
Reaction Conditions for Preparative Scale (50 mmol) Vinylcyclopropanations and Conditions for Product Isolation and Isomer Separation

Vinylcyclopropane	(g) Catalyst[a]	Olefin, ml	Bp, °C (mm)	GLC column for isomer separation	Relative GLC retention times and assignment
	(0.7) $Cu(hfacac)_2$ (0.7) $Cu(OTf)_2$	300 300	60–68 (22)	SE-30[b] (125°)	1.00:1.21 exo endo
	(0.4) $Cu(OTFA)_2$	50	80–82 (15)	FFAP[c] (80°)	1.00:1.09
	(1.3) $Cu(hfacac)_2$	70	80–95 (70)	Not separated	
	(0.75) $Cu(hfacac)_2$ (0.75) $Cu(OTf)_2$	125 125	77–81	SE-30 (60°)	
	(0.75) $Cu(OTf)_2$ (1.0) $Cu(hfacac)_2$	75 100	88–95	SE-30 (47°)	1.00:1.44
	(1.0) $Cu(hfacac)_2$	100		SE-30 (50°)	
	(0.5) $Cu(hfacac)_2$	160	76–85 (50)	FFAP (115°)	1.00:1.15 trans cis

[a] $Cu(hfacac)_2$ = cupric hexafluoroacetylacetonate, $Cu(OTf)_2$ = cupric trifluoromethanesulfonate, $Cu(OTFA)_2$ = cupric trifluoroacetate. [b] Free fatty acid phase (Analabs) 20% on 60/80 Chromosorb P. [c] Silicone gum rubber–methyl (Analabs) 15% on 60/80 Chromosorb P.

scale reactions were conducted in a 500-ml round-bottom flask under a static atmosphere of nitrogen. The diazo compound solution (50 mmole) was added with a pressure-equalizing addition funnel. A bubbler filled with mineral oil was employed to detect the evolution of nitrogen during the reaction. In the case of gaseous olefins, a Dry Ice–acetone cold finger condenser was required. The reaction mixture was vigorously stirred magnetically while the solution of vinyldiazomethane was added dropwise over 1 hr to an excess of the olefin and sufficient catalyst to cause rapid disappearance of the red color of the vinyldiazomethane as it was added. Yields of vinylcyclopropanes are given in Table II. Reaction and isolation conditions are indicated in Table III. In the case of gaseous olefins, unreacted olefin was allowed to evaporate prior to work-up. The reaction mixture was washed with dilute aqueous ammonium hydroxide until the washes were colorless, then washed with water, and dried ($MgSO_4$). Solvents and excess olefin were removed by distillation and the products were isolated by distillation and preparative gas–liquid phase chromatography as indicated in Table III. Boiling ranges are uncorrected. In the case of vinylcyclopropanation of cyclohexene, the olefin was used in place of pentane as solvent for the vinyldiazomethane, and this solution was added dropwise to a suspension of catalyst in 5 ml of cyclohexene. *Caution!* Dihydropyran undergoes a violently exothermic polymerization in the presence of traces of cupric trifluoromethanesulfonate. This salt cannot be used for vinylcyclopropanation of highly nucleophilic vinyl ethers. The vinylcyclopropane products were characterized by their ^1H NMR spectra and by elemental analysis. Some products were further characterized by oxidative conversion to the corresponding carboethoxycyclopropanes, which were identified by ^1H NMR and GLC comparison with authentic samples. 1,1-Dimethyl-2-vinylcyclopropane was also prepared by another route starting from the corresponding carboethoxycyclopropane.

7-Vinylbicyclo[4.1.0]heptane. Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.57; H, 11.47.

Endo isomer had ^1H NMR δ 0.8–2.2 (11 H, ring protons), 4.5–5.3 (2 H, m, vinyl CH_2), 5.4–6.0 (1 H, m, vinyl CH).

Exo isomer had ^1H NMR δ 0.75–1.02 (2 H, cyclopropyl at C-1, C-6), 1.02–2.2 (9 H, ring protons), 4.5–5.0 (2 H, m, vinyl CH_2), 5.0–5.6 (1 H, m, vinyl CH).

These isomers were characterized as *endo*- and *exo*-7-vinylbicyclo[4.1.0]heptane, respectively, by ozonolysis–oxidation–ethylation and comparison of the product esters with authentic samples of *endo*- and *exo*-7-carboethoxybicyclo[4.1.0]heptane.[12] The olefin (40 mg) in glacial acetic acid (1 ml) and formic acid (0.5 ml) was stirred magnetically while an excess of ozone was bubbled through the reaction mixture. Then 30% hydrogen peroxide (1 ml) was added and the resulting mixture was boiled under reflux for 2 hr.[24] The product was extracted into ether (2 × 20 ml). The extract was washed with water and then extracted with saturated aqueous Na_2CO_3 solution. After acidification of the aqueous extract with HCl, the product was taken up into ether (20 ml). The ether solution was dried ($MgSO_4$) and then treated with an ether solution of diazoethane. Solvent was removed by rotary evaporation to yield crude ethyl ester.

1,1-Dimethyl-2-vinylcyclopropane. Anal. Calcd for C_7H_{12}: C, 87.42; H, 12.58. Found: C, 87.46; H, 12.50. This olefin was also prepared by an indirect route starting with ethyl 2,2-dimethylcyclopropanecarboxylate. Isobutylene (200 ml) was condensed into a 1-l. round-bottom flask equipped with a Dry Ice–acetone cooled cold finger condenser. The reaction mixture was stirred magnetically. Cupric trifluoromethanesulfonate (2 g) and ether (150 ml) were added. The addition of ether raised the boiling point of the mixture to 6°. Ethyl diazoacetate (10 g) was added slowly with a hypodermic syringe through a rubber serum cap. The resulting mixture was stirred for several hours as excess isobutylene was allowed to evaporate. The reaction mixture was then washed with dilute aqueous ammonium hydroxide until the washes were colorless, and then with water. After drying ($MgSO_4$), solvent was rotary evaporated and the residue distilled under reduced pressure to yield ethyl 2,2-dimethylcyclopropanecarboxylate (62%): bp 79–81° (40 mm); ^1H NMR δ 0.76 (1 H, dd, J = 4.0, 8.2 Hz, C-3), 1.03 (1 H, dd, J = 4.0, 5.0 Hz, C-3), 1.17 (3 H, s, methyl), 1.20 (3 H, s, methyl), 1.25 (3 H, t, J = 7 Hz, ester methyl), 1.42 (1 H, dd, J = 5.0, 8.2 Hz, C-1), 4.06 (2 H, q, J = 7 Hz, ethyl CH_2).

The ester (6 g) in ether (50 ml) was added to $LiAlH_4$ (3 g) in ether (150 ml) under dry nitrogen with mechanical stirring over 10 min. The resulting mixture was boiled under reflux for 1 hr. After cooling, water (3 ml) was cautiously added dropwise followed by aqueous 15% sodium hydroxide (3 ml) and then water (9 ml). The resulting white granular precipitate was removed by filtration and washed with ether. The filtrate and washings were concentrated by rotary evaporation and the residue was distilled under reduced pressure to give an alcohol, bp 50° (6 mm).

Chromium trioxide (60 g) was added over 5 min to a mechanically stirred solution of pyridine (49 ml) in dry methylene chloride (600 ml) in a 1-l. flask equipped with a pressure-equalizing addition funnel under an atmosphere of dry nitrogen. After stirring for an additional 15 min, the above alcohol in methylene chloride (50 ml) was added over 10 min. The resulting mixture was stirred for 15 min. The organic solution was decanted and the tarry residue was triturated thrice with 150-ml portions of ether. The combined organic solution was washed with 5% NaOH (3 × 150 ml), 5% HCl (150 ml), saturated aqueous $NaHCO_3$ (150 ml), saturated aqueous $CuSO_4$ (2 × 150 ml), and saturated aqueous NaCl (150 ml). After drying ($MgSO_4$), solvents were removed by fractional distillation and the residue distilled under reduced pressure to give 2,2-dimethylcyclopropanecarboxaldehyde (76% from the ester): bp 51–61° (45 mm); ^1H NMR δ 0.40–0.59 (2 H, m, C-3), 0.76 (3 H, s, CH_3), 0.82 (3 H, s, CH_3), 0.94–1.46 (1 H, m, C-1), 9.36 (1 H, d, -CHO).

n-Butyllithium in hexane (23.0 ml of 1.65 *N*) was added to a magnetically stirred suspension of methyltriphenylphosphonium bromide (14.4 g) in dry tetrahydrofuran (60 ml) under an atmosphere of dry nitrogen at 0°. After stirring for 30 min, the above aldehyde in tetrahydrofuran (10 ml) was added dropwise over 2 min. The resulting mixture was stirred at room temperature for 20 min. Pentane (100 ml) was added and the mixture was washed with water (4 × 100 ml), dried ($MgSO_4$), and concentrated by distillation through a 20-cm Vigreux column. The residue was distilled to give 1,1-dimethyl-2-vinylcyclopropane (24% overall from ethyl diazoacetate) which was identical (^1H NMR) with a sample prepared by direct vinylcyclopropanation of isobutylene: ^1H NMR δ 0.25–0.75 (2 H, m, C-3), 1.03 (3 H, s, methyl), 1.08 (3 H, s, methyl), 1.29 (1 H, dd, J = 5.5, 8.0 Hz, C-2), 4.75–5.15 (2 H, m, vinyl), 5.15–6.0 (1 H, m, vinyl).

7-Vinyl-2-oxabicyclo[4.1.0]heptane. Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.41; H, 9.72. The product probably is a mixture of isomers, but these were not separated: ^1H NMR δ 0.75–2.2 (6 H, C-4, C-5, C-6, C-7), 2.9–3.8 (3 H, C-1, C-3), 4.6–5.4 (2 H, m, vinyl CH_2), 5.4–6.4 (1 H, m, vinyl CH).

6-Vinyl-3-oxabicyclo[3.1.0]hexane. Anal. Calcd for $C_7H_{10}O$: C, 76.33; H, 9.15. Found: C, 76.19; H, 9.20. The product probably is a mixture of isomers, but these were not separated: ^1H NMR δ 1.2–1.9 (3 H, cyclopropyl), 3.83 (4 H, s, C-2, C-4), 4.9–5.3 (2 H, m, vinyl CH_2), 5.4–6.0 (1 H, m, vinyl CH).

1-Acetoxy-2-vinylcyclopropane. Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.44; H, 7.87.

Cis isomer had ^1H NMR (100 MHz) δ 0.64–0.88 (1 H, dt, J = 6.6, 6.6, 4.1 Hz, C-3 trans to C-1 proton), 0.97–1.22 (1 H, dt, J = 9.3, 6.5, 6.5 Hz, C-3 cis to C-2 proton), 1.48–1.84 (1 H, m, C-2), 1.99 (3 H, s, acetate CH_3), 4.06–4.29 (1 H, dt, J = 4.1, 6.5, 6.5 Hz, C-1), 4.88–5.25 (2 H, m, vinyl CH_2), 5.30–5.68 (1 H, m, vinyl CH).

Trans isomer had ^1H NMR (100 MHz) δ0.71–1.10 (2 H, m, C-3), 1.40–1.76 (1 H, m, C-2), 1.95 (3 H, s, acetate CH_3), 3.83–4.02 (1 H, m, C-1), 4.84–5.14 (2 H, m, vinyl CH_2), 5.30–5.78 (1 H, m, vinyl CH).

Various quantities of europium(III) tris-1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate (0–0.2 equiv) were added to the above solutions. The induced chemical shift changes extrapolated to a 1:1 mole ratio are indicated in Chart I.

***cis*- and *trans*-3-Vinyl-*cis*-1,2-dimethylcyclopropane.** Anal. Calcd for C_7H_{12}: C, 87.42; H, 12.58. Found: C, 87.13; H, 12.42. Two isomers were obtained in a ratio of 0.27:1.00, respectively, for the products of relative GLC retention times of 1.00 and 1.44 on an SE-30 column.

Minor isomer had ^1H NMR δ 0.5–1.1 (3 H, cyclopropyl), 1.06 (6 H, d, J = 3.8 Hz, C-1, C-2), 4.5–5.1 (2 H, m, vinyl CH_2), 5.1–5.7 (1, H, m, vinyl CH).

Major isomer had ^1H NMR δ 0.9–1.7 (3 H, cyclopropyl), 1.01 (6 H, d, J = 1.4 Hz, CH_3 at C-1, C-2), 4.8–5.8 (3 H, m, vinyl).

3-Vinyl-*trans*-1,2-dimethylcyclopropane. Anal. Calcd for C_7H_{12}: C, 87.42; H 12.58. Found: C, 87.40; H, 12.55. ^1H NMR δ 0.2–0.7 (3 H, m, cyclopropyl) 0.97–1.12 (6 H, two doublets, J = 5.4 Hz, CH_3 at C-1, C-2), 4.71–5.15 (2 H, m, vinyl CH_2), 5.18–5.81 (1 H, m, vinyl CH).

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Registry No.—Vinyldiazomethane, 2032-04-4; cupric hexafluoroacetylacetonate, 14781-45-4; cupric trifluoromethanesulfonate, 34946-82-2; cupric trifluoroacetate, 16712-25-7; ethyl diazoacetate, 623-73-4; ethyl 2,2-dimethylcyclopropanecarboxylate, 16783-11-2; 2,2-dimethylcyclopropanecarboxaldehyde, 26119-44-8; europium(III) tris-1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate, 17631-68-4.

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