Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.21; H, 5.73; N, 4.68. Found: C, 67.89; H, 5.78; N, 4.60.

Oxidation of 2,5-Dimethoxytoluene (8a). The oxidation of **8a** (1.52 g, 10 mmol) with CAN (16.5 g, 30 mmol) was carried out in the usual manner. Sublimation of the crude product at 180 °C (30 mm) provided 0.1 g (0.8 mmol, 8%) of 2-methyl-1,4-benzoquinone (**8b**), mp 65–66.5 °C (lit.[5] mp 64–65 °C). The pressure was reduced to 0.05 mm and 1.02 g (8.5 mmol, 85%) of the dimeric quinone **8c** (mp 180–184 °C) was collected. Recrystallization from isopropyl alcohol–toluene gave pure **8c**, mp 189–190 °C (lit.[6] mp 189–190 °C).

Oxidation of 1,2,4-Trimethoxybenzene (9a). The reaction mixture of **9a** (0.82 g, 5 mmol) with CAN (8.3 g, 15 mmol) was worked up by addition to ice water (100 ml) followed by filtration to collect the crude orange product **9c** (0.2 g, 1.45 mmol, 29%), mp 225–227 °C dec (lit.[17] mp 205–240 °C dec).

1,4-Naphthoquinone (10b). Oxidation of 1,4-dimethoxynaphthalene[18] (**10a**, 1 g, 5.3 mmol) with CAN (8.8 g, 16 mmol) in the usual manner followed by sublimation (135 °C, 0.1 mm) of the crude product provided 0.79 g (4.98 mmol, 94%), mp 122.5–123.5 °C (lit.[19] mp 124–125 °C).

Oxidation of 3,5-Di-*tert*-butyl-1,2-dimethoxybenzene (11a). The crude product obtained from the reaction of **11a**[20] (3 g, 12 mmol) and CAN (26 g, 48 mmol) was chromatographed on a 30 × 250 mm silica gel column. Three 50-ml fractions using 30:70 ether–hexane as the eluent were collected. A fourth fraction (50 ml) using ether as the eluent was obtained. Evaporation of the solvent from fraction 2 gave a dark red residue that was recrystallized from hexane to give 0.1 g of *o*-quinone **11b**: mp 112–113 °C (lit.[21] mp 113–114 °C); uv ($CHCl_3$) λ_{max} 254 nm (sh, ϵ 2960), 402 (1690). Fraction 4 was evaporated and sublimed (120 °C, 0.1 mm) to give 0.76 g of yellow solid. Recrystallization from hexane provided pure quinone **11c** as long yellow needles: mp 81–82 °C (lit.[22] mp 84–85 °C); chemical ionization mass spectrum *m/e* 195 (MH^+, base peak); uv ($CHCl_3$) λ_{max} 268 nm (ϵ 16 400).

$H_2{}^{18}O$ Studies. CAN (155 mg, 0.283 mmol) and $H_2{}^{18}O$ (0.1 g, 5.5 mmol, 95% ^{18}O) were added to a small, oven-dried vial. 1,4-Dimethoxy-2,3,5,6-tetramethylbenzene[23] (**12a**, 16.8 mg, 0.087 mmol) in 0.3 ml of dry acetonitrile was added, the vial was capped, and the mixture was shaken occasionally over a 15-min period. The upper (organic) layer was separated, the solvent was evaporated under reduced pressure, and the residue was sublimed (130 °C, 0.5 mm) to give 5 mg of yellow solid. Chemical ionization mass spectral analysis indicated 90% bis-^{18}O-**12b** MH^+ *m/e* (rel intensity) 169 (100), 167 (8.7), 165 (2.0). As a control, a solution of duroquinone[24] (**12b**, 7.7 mg, 0.047 mmol) and 2,5-dimethyl-1,4-dimethoxybenzene (**2a**, 14.2 mg, 0.085 mmol) in 0.4 ml of acetonitrile was treated with CAN (178 mg, 0.325 mmol) in $H_2{}^{18}O$ (0.1 g, 5.5 mmol, 95% ^{18}O). The quinones were isolated by sublimation and analyzed by chemical ionization mass spectrometry: MH^+ *m/e* (rel intensity) 169 (19), 167 (54), 165 (100).

Acknowledgments. The authors are grateful to Professor Robert Weinkam for the mass spectral data. This research was supported by Public Health Service Research Grant MH 21219 and a NIH postdoctoral research fellowship to P.J.

Registry No.—**1a**, 150-78-7; **1b**, 106-51-4; **2a**, 2674-32-0; **2b**, 137-18-8; **3a**, 5600-82-8; **3b**, 40870-52-8; **4a**, 29907-72-0; **4b**, 59953-56-9; **5a**, 30784-23-7; **5b**, 59953-57-0; **6a**, 59953-58-1; **6b**, 59953-59-2; **7a**, 59953-60-5; **7b**, 59953-61-6; **8a**, 24599-58-4; **8b**, 553-97-9; **8c**, 4388-07-2; **9a**, 135-77-3; **9c**, 43042-33-7; **10a**, 10075-62-4; **10b**, 130-15-4; **11a**, 22385-74-6; **11b**, 3383-21-9; **11c**, 2300-74-5; **12a**, 13199-54-7; **12b**, 527-17-3; CAN, 16774-21-3; 1-(2,5-dimethoxy-4-methylphenyl)-2-aminopropane, 15588-95-1; *tert*-butoxycarbonyl azide, 1070-19-5; 1-(2,4,5-trimethoxyphenyl)-2-aminopropane hydrochloride, 15995-72-9; benzoyl chloride, 98-88-4.

References and Notes

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A Regiospecific Synthesis of Functionalized Vinylcyclopropanes via Cyclopropyl Cuprates

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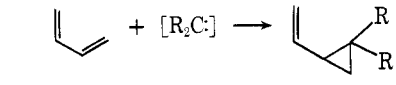
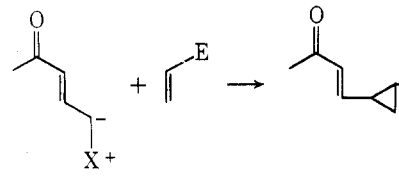
The synthetic utility of the vinylcyclopropane unit in the construction of cyclopentenes has been hampered by the lack of mild, efficient, and regiospecific routes to this class of compounds. One of the earliest approaches to vinylcyclopropanes involved the addition of carbenes to dienes[1] (route A).

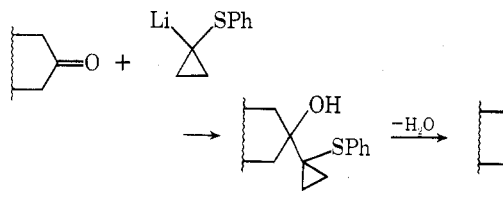


(A)

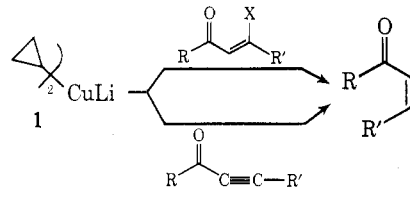


(B)

This route usually suffers from lack of regiospecificity and generality. More recently, the addition of allyl ylides to Michael acceptors has provided a mild and efficient route to functionalized vinylcyclopropanes[2] (B); the recent work of Trost and co-workers[3] also offers a number of solutions to the synthesis of vinylcyclopropanes from cyclopropyllithium reagents (C). In this note, we wish to report the facile construction of functionalized vinylcyclopropanes utilizing the conjugate addition reactions of cyclopropyl cuprates to α,β-unsaturated carbonyl compounds (D).

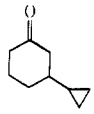
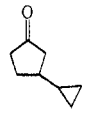
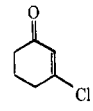
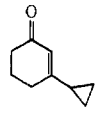
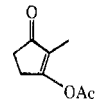
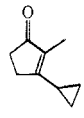
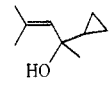
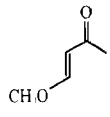
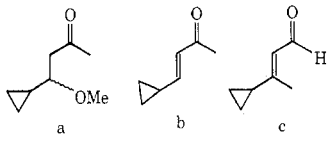
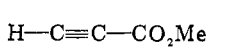
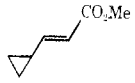
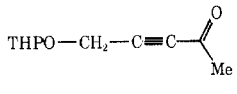
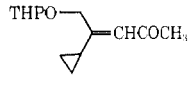


(C)



(D)

Table I

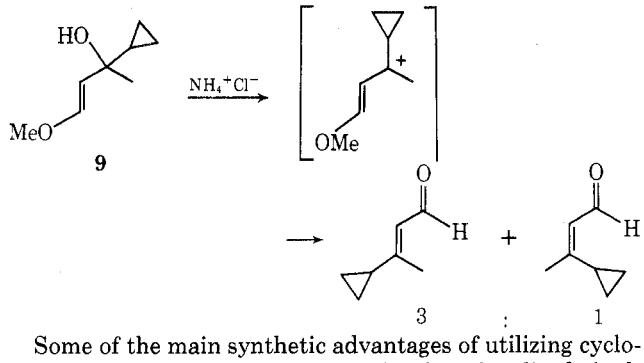
	Substrate	Products	Method	Reaction conditions	Yield, %
1			A B	−78 °C (0.5 h) −50 °C (0.25 h)	60 83
2			A	−78 °C (0.5 h)	85
3			A B	−78 °C (3 h) −78 to −20 °C (3 h)	0 80
4			A B	1.5 equiv (−78 °C, 3 h) 1.1 equiv (−78 °C, 3 h)	52 75
5			B	−40 °C (3 h)	57
6		 a b c	B B	−78 °C (3 h) −78 to −20 °C (3 h)	20 0 58 a b c 25, 21, 41
7			A B	−78 °C (0.5 h) −78 °C (0.3 h)	>95 >95
8		 (THP ≡ tetrahydropyranyl)	A	−78 °C (0.5 h)	>95

While the recent literature contains numerous references to various cyclopropyllithium derivatives,[4] very few examples of cyclopropylcopper reagents have been reported.[5] In an effort to study the stability and reactivity of cyclopropyl cuprates, we investigated the reactions of the parent cyclopropyl cuprate 1 with a variety of α,β-unsaturated carbonyl compounds. The regiospecificity observed in conjugate additions to β-haloenones and acetylenic carbonyl compounds offers a significant advantage over the dehydrative approaches exemplified in scheme C.

The cyclopropylcopper reagent 1 was generated from the corresponding cyclopropyllithium species, which in turn was prepared by the metalation of cyclopropyl bromide under two sets of conditions. Method A involves the use of *sec*-butyllithium in tetrahydrofuran at −78 °C. Method B utilizes *tert*-butyllithium in ether for the metalation of cyclopropyl bromide. With both procedures, the cuprate is generated by adding the cold cyclopropyllithium solution to a slurry of a performed cuprous bromide–dimethyl sulfide complex (0.5 equiv) at low temperatures. The cuprate **1** is generated very rapidly in THF (10 min) at −78 °C, but it has significantly less thermal stability than when generated in Et_2O. In the latter solvent, the cuprate is insoluble at −78 °C, but soluble and stable at −40 °C for hours.

In general, the cuprates were treated with the unsaturated carbonyl compounds at −78 °C for several hours. The workup procedure consisted of filtration of the reaction mixture through Celite, washing the reaction mixture with an ammonium chloride solution, and drying the organic extract. Upon evaporation of the organic solvent, high yields of the conjugate addition products were isolated in essentially a pure state. The results of the reactions of **1** with various enones and acetylenic esters are summarized in Table I.

The results found in Table I suggest that cuprate 1 can be expected to do conjugate additions to most α,β-unsaturated carbonyl compounds. The two exceptions noted in our study include the β-disubstituted enone, mesityl oxide (entry 5), and the β-alkoxy substituted enone (entry 6). In both of these cases, 1,2 addition of the cyclopropyl group predominates over 1,4 addition. Under the workup conditions, the initial 1,2 adduct **9** from 4-methoxybut-3-en-2-one undergoes the well-known acid-catalyzed rearrangement of the alkoxyallyl alcohol system without involvement of the cyclopropyl group.



Some of the main synthetic advantages of utilizing cyclopropylcopper reagents in constructing functionalized vinylcyclopropane systems include (a) regiospecificity in directing the formation of the vinyl–cyclopropane bond, (b) mildness of the reaction conditions, and (c) functional group selectivity of the cyclopropylcopper reagents over analogous lithio and magnesium species.

Experimental Section

All liquid reagents were distilled and stored under nitrogen or argon

and were transferred via glass syringes. Solvents were distilled from $LiAlH_4$. All reactions were run under argon in meticulously cleaned glassware which was flame dried under argon prior to use. Cuprous bromide–dimethyl sulfide complex was prepared according to House's procedure.[6] Ir spectra were recorded on a Perkin-Elmer 457 or 727B. NMR spectra were recorded in CCl_4, with Me_4Si as internal standard, on a Varian T-60. Yields were determined by NMR with $CHCl_3$ as an internal reference and are absolute values based on added substrate. Spectral and analytical samples were prepared by VPC (5% SE-30 on 60/80 Chromosorb P) unless otherwise stated. Analyses were carried out by Spang Microanalytical Laboratories, Ann Arbor, Mich.

Lithium Dicyclopropylcuprate. Method A. To a solution of cyclopropyl bromide (0.3 ml, 0.44 g, 3.63 mmol) in 15 ml of THF at −78 °C was added *sec*-BuLi (3.63 mmol) in pentane. After 2 h, the cyclopropyllithium solution was transferred with pressure via a double-tipped needle to a slurry of $CuBr{\cdot}Me_2S$ (0.39 g, 1.89 mmol) in THF at −78 °C. After 15 min, the solution was pale yellow with no suspended solid and ready for use. Prolonged periods at −78 °C led to darkening of the solution presumably owing to decomposition of the cuprate.

Method B. To a solution of cyclopropyl bromide (0.3 ml, 0.44 g, 3.63 mmol) in 20 ml of Et_2O at −78 °C was added *t*-BuLi (3.75 mmol) in pentane. After 2 h, the cyclopropyllithium solution was transferred with pressure via a double-tipped needle to a slurry of $CuBr{\cdot}Me_2S$ (0.39 g, 1.89 mmol) in 35 ml of Et_2O at −78 °C. The reaction mixture was stirred at −78 °C for 30 min, and then at −50 °C for 30 min to ensure complete formation of the reagent. The lithium dicyclopropylcuprate appeared as a white slurry in a clear solution.

General Procedure for Cuprate Additions. The substrates listed in Table I were added to the cuprate at −78 °C and quenched at that temperature with excess NH_4Cl solution unless otherwise stated. In some cases, after addition, the reaction was warmed to a specified temperature before quenching.

3-Cyclopropylcyclohexanone (Entry 1). To a solution of lithium dicyclopropylcuprate (1.81 mmol), prepared by method B, was added cyclohexenone (0.173 g, 1.8 mmol). After 15 min, the reaction mixture was quenched with NH_4Cl solution and allowed to warm to room temperature. The reaction mixture was filtered through Celite, washed with NH_4Cl solution (10 ml), and dried over anhydrous Na_2SO_4. Evaporation yielded 240 mg of a yellow liquid which was shown to be composed of starting material (15%) and **1** (83%) by NMR and VPC analyses: NMR δ 0.0–2.80 (m, 14 H); ir 3080, 1710 cm^{-1}; MS *m/e* 138 (M^+), 110, 67 (b), 55, 41.

Anal. Calcd for $C_9H_{14}O$: C, 78.33; H, 10.23. Found: C, 78.30; H, 10.29.

3-Cyclopropylcyclopentanone (2). To lithium dicyclopropylcuprate (1.81 mmol), prepared by method A, was added cyclopentenone (0.148 g, 1.8 mmol). The reaction mixture was stirred at −78 °C for 30 min, quenched with an ammonium chloride solution, and worked up in the usual manner. A colorless oil (161 mg), which was composed of 15% starting material and 85% of **2**, was isolated: NMR ($CHCl_3$ as internal standard) δ −0.20 to 1.00 (m, 5 H), 1.25–2.45 (m, 7 H); ir 3075, 1743, 1405, 1151, cm^{-1}; MS *m/e* 124 (M^+), 96, 67 (b), 28.

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.44; H, 9.66.

3-Cyclopropylcyclohex-2-enone[5e] (3). To lithium dicyclopropylcuprate (1.81 mmol), prepared by method B, was added 3-chlorocyclohex-2-enone (0.23 g, 1.8 mmol). The pale yellow reaction mixture was allowed to warm slowly over a 3-h period to −20 °C, during which time it turned orange-brown. It was then quenched and worked up in the usual manner. Evaporation of solvent resulted in a pale yellow liquid (241 mg) which represented starting material (14%) and **3** (80%) as indicated by its NMR spectrum and VPC (10% OV225 on 100/120 Chromosorb W) analysis: NMR δ 0.50–1.10 (m, 4 H), 1.28–2.42 (m, 7 H), 5.61 (s, 1 H); ir 3080, 1665, 1620 cm^{-1}; MS *m/e* 136 (b, M^+), 121, 108, 80, 79, 67, 39, 28.

3-Cyclopropyl-2-methylcyclopent-2-enone (4). To lithium dicyclopropylcuprate (1.81 mmol), prepared by method B, was added 3-acetoxy-2-methylcyclopent-2-enone (0.28 g, 1.80 mmol). Stirring was continued at −78 °C for 3 h before the orange-brown solution was quenched. Workup in the usual way produced a colorless liquid (190 mg) which was a single compound as indicated by its NMR spectrum and VPC (10% OV225 on Chromosorb W, 5% CW on 60/80 Chromosorb P, 6 ft × 0.25 in.) and was identified as **4** (75%): NMR δ 0.75–1.18 (m, 4 H), 1.73 (broad s, 3 H), 1.80–2.30 (m, 5 H); ir 3088, 1690, 1632 cm^{-1}; MS *m/e* 136 (M^+), 121, 93, 79, 67, 28 (b).

Anal. Calcd for $C_9H_{12}O$: C, 79.48; H, 8.89. Found: C, 79.36; H, 8.90.

2-Cyclopropyl-4-methylpent-3-en-3-ol[7] (5). To lithium dicyclopropylcuprate (1.81 mmol), prepared by method A, was added 4-methylpent-3-en-2-one (0.165 g, 1.80 mmol). The reaction mixture was allowed to warm from −78 to −40 °C where it was quenched after 3 h and worked up in the usual manner. Evaporation of solvent produced a yellow liquid (259 mg) which was composed of 4-methylpent-3-en-2-one (47%) and **5** (57%) by NMR and VPC (10% OV225 on 100/120 Chromosorb W, 6 ft × 0.25 in.): NMR δ 0.2–1.20 (m, 5 H), 1.25 (s, 3H), 1.42–1.90 (broad m, 1 H), 1.65 (d, 3 H, J = 1.6 Hz), 1.81 (d, 3 H, J = 1.6 Hz), 5.12 (m, 1 H); ir 3610, 3080, 1665 (weak), 1445, 1375 cm^{-1}; MS *m/e* 140 (M^+), 122, 107, 94, 91, 79, 43, 28 (b).

Reaction of 4-Methoxybut-3-en-2-one with Lithium Dicyclopropylcuprate (6). To lithium dicyclopropylcuprate (1.81 mmol), prepared by method B, was added 4-methoxybut-3-en-2-one (0.181 g, 1.81 mmol). The yellow solution was stirred at −78 °C for 3 h, then quenched and worked up in the usual manner. A yellow liquid (180 mg) was produced which was composed of two products as well as 20% of unreacted starting material. The products were separated by VPC (10% FFAP, Chromosorb W 60/80, 6 ft × 0.25 in.) and shown to be the following.

3-Cyclopropylbut-2-enal (58%) was a mixture of *E* and *Z* isomers in the ratio 3:1: NMR δ 0.61–1.02 (m, 4 H), 1.25–1.75 (m, 2.7 H, including 1.59, d, J = 1.5 Hz), 1.90 (d, 2.3 H, J = 1.2 Hz), 5.73 (broad d, 1 H, J = 7.4 Hz), 9.10 (d, 0.67 H, J = 7.4 Hz), 10.08 (d, 0.33 H, J = 7.4 Hz); ir 3085, 2835, 2748, 1670, 1618, 895 cm^{-1}; MS *m/e* 110 (M^+), 109, 95, 82, 67, 58, 43, 28 (b).

4-Cyclopropyl-4-methoxybutan-2-one (20%): NMR δ 0.00–1.00 (m, 5 H), 2.07 (s, 3 H), 2.40–3.17 (m, 3 H), 3.30 (s, 3 H); ir 3080, 1718, 1350, 1100 cm^{-1}; MS *m/e* 142 (M^+), 141 (both weak), 127, 114, 111, 110, 95, 91, 85, 83, 67, 58, 46, 44, 28 (b). The same initial procedure followed by warming to −20 °C over a period of 2 h before quenching resulted in an additional product: 3-cyclopropylbut-2-enal (41%), 4-cyclopropyl-4-methoxybutan-2-one (25%).

4-Cyclopropylbut-3-en-2-one (21%): NMR δ 0.35–1.15 (m, 4 H), 1.15–1.70 (m, 1 H), 2.07 (s, 3 H), 5.98 (s, 1 H), 6.08 (d, 2 H, J = 2.8 Hz); ir 3075, 1670, 1618 cm^{-1}; MS *m/e* 110 (M^+), 95, 67, 51, 43 (b), 41 (identical in all respects with material obtained by condensation of triphenylphosphoranylidene-2-propanone with cyclopropylaldehyde).

Methyl *trans*-3-Cyclopropylpropenoate (7). To lithium dicyclopropylcuprate (1.81 mmol), prepared by method A, was added methyl propynoate (0.15 g, 1.80 mmol). The reaction mixture was quenched after 30 min at −78 °C and worked up as usual. A colorless liquid (180 mg) was isolated which was one component by NMR and TLC and identified as **7** (>95%): NMR δ 0.5–1.10 (m, 4 H), 1.2–1.8 (m, 1 H), 3.61 (s, 3 H), 5.7 (d, 1 H, J = 15 Hz), 6.25 (d of d, 1 H, J = 15, 8.6 Hz); ir 3080, 1720, 1652, 1265, 1145 cm^{-1}; MS *m/e* 126 (M^+), 111, 98, 95, 67 (b).

Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.69, H, 8.01.

5-(Tetrahydropyran-2-oxy)-4-cyclopropylpent-3-en-2-one (8). To lithium dicyclopropylcuprate (1.81 mmol), prepared by method A, was added 5-(tetrahydropyran-2-oxy)pent-3-yn-2-one (0.328 g, 1.80 mmol). The colorless solution immediately became bright red. After the reaction mixture was stirred at −78 °C for 30 min, it was quenched and worked up in the usual manner yielding a yellow oil (570 mg). The major component, identified as **8**, was isolated in 95% yield by preparative TLC on silica with petroleum ether (bp 30–60 °C)–Et_2O in the ratio 3:1 (the *Z*:*E* ratio was 3:1): NMR δ 0.50–0.95 (m, 4 H), 1.25–1.97 (m, 7 H), 2.12 (s, 3 H), 3.10–4.07 (m, 4 H), 4.55 (s, 1 H), 6.26 (s, 1 H); ir 3080, 1682, 1598, 1352 cm^{-1}; MS *m/e* 224 (M^+), 196, 140, 123, 112, 96, 85 (b), 67, 57, 47.

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.57; H, 9.02.

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Registry No.—**1**, 59939-07-0; **2**, 59939-08-1; **3**, 34194-40-6; **4**, 59939-09-2; **5**, 13679-03-3; **6a**, 59939-10-5; **6b**, 54139-51-4; **6c**, 872-77-5; **7**, 59939-11-6; **8**, 59939-12-7; lithium dicyclopropylcuprate, 41430-32-4; cyclohexenone, 930-68-7; cyclopentenone, 930-30-3; 3-chlorocyclohex-2-enone, 5682-75-7; 3-acetoxy-2-methylcyclopent-2-enone, 3883-57-6; 4-methylpent-3-en-2-one, 141-79-7; 4-methoxybut-3-en-2-one, 4652-27-1; methyl propynoate, 922-67-8; 5-(tetrahydropyran-2-oxy)pent-3-yn-2-one, 52804-46-3.

References and Notes

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A Convenient Photochemical Synthesis of a Precursor to the Spirovetivanes[1]

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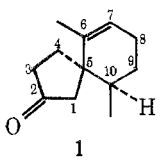
Recently, we reported the synthesis of the spiro enone **1**,[2] and its conversion into (±)-α-vetispirene (**2**)—a member of the spirovetivane family of sesquiterpenes.[3] In the better of the two routes to **1** employed previously,[2] the methoxy dienone **3** was converted into the spiro[4.5]decenone derivative **4** by photochemical rearrangement in glacial acetic acid. The



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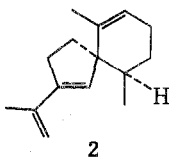

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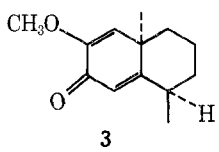

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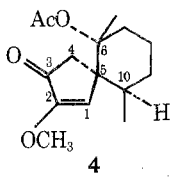

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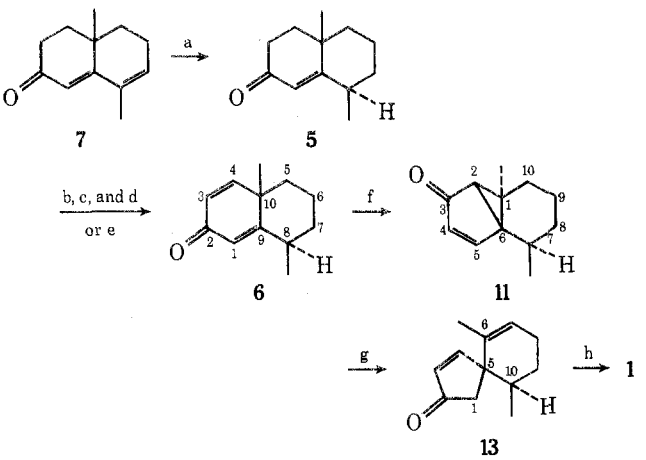
cis relationship between the 1-methylene group and the 10-methyl group was established by removal of the 3-carbonyl group and hydrolysis of the enol ether function. These conditions also converted the 6-acetoxyl group into a hydroxyl group and the 6,7 double bond was introduced by dehydration. Although this approach was completely stereospecific, the synthesis of **3** and its conversion into **1** required a rather large number of steps. Since **1** appeared to be a useful intermediate for the synthesis of other spirovetivanes, the development of a shorter route to this compound was of interest.

We felt that a simple approach to **1** would involve as a key step the photoisomerization of the *cis*-dimethyl cross-conjugated dienone **6** into the tricyclodecenone derivative **11** which has a cis relationship between C-2 of the cyclopropane ring and the secondary methyl group. Selective electrophilic cleavage of the external (1,2) bond of the cyclopropane ring of **11** would then yield a spiro[4.5]decane derivative readily

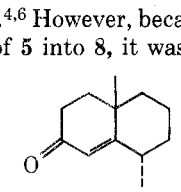
Scheme I



a, Pd/C, cyclohexene, C_2H_5OH; b, LDA, THF, −70 °C; c, PhSeCl, −70 °C; d, H_2O_2, e, DDQ, dioxane, reflux; f, *hν* (2537 Å), dioxane, 25 °C; g, H_2SO_4, HOAc–Ac_2O; h, Pd/C, 95% C_2H_5OH NaOH.

convertible into **1**. These transformations have been accomplished as shown in Scheme I.

Selective reduction of the 7,8 double bond of the known transannular dienone **7**[4] was carried out by transfer hydrogenation using palladium on carbon and cyclohexene in refluxing ethanol.[5] This procedure led to the formation of the thermodynamically unstable *cis*-8,10-dimethyl octalone **5** in 90% yield. The reaction was highly selective and under carefully controlled conditions GLC analysis of the product indicated that it contained less than 5% of the more stable trans isomer **8**.[4,6] However, because of the extreme ease of isomerization of **5** into **8**, it was necessary to carefully avoid the



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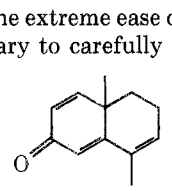

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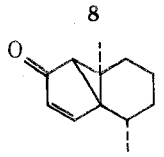

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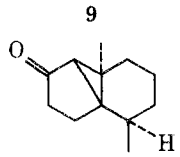

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presence of acidic or basic impurities. Best results were obtained when the starting material and all reagents were carefully purified just prior to use and when the reduction was carried out on a relatively small scale, i.e., 5–10 g. The cross-conjugated dienone **6** could be obtained by conventional oxidation of **5** with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in benzene or dioxane.[7] However, the desired product was contaminated with a significant amount of the trienone **9**, even when only 1 equiv of the oxidizing agent was employed. The formation of **9** would be expected to occur via the trienol resulting from proton transfer from C-8. Enolization of **5** would be expected to occur rather readily because it would lead to relief of a severe 1,3-diaxial methyl–methyl interaction. In order to avoid the formation of the trienone, the selenoxide elimination procedure of Reich and co-workers[8] was employed for the conversion of **5** into **6**. Treatment of the enone with lithium diisopropylamide (LDA) in THF at −70 °C gave the homoannular lithium enolate resulting from kinetic deprotonation at C-3.[9] This enolate was trapped with phenylselenenyl chloride at −70 °C and the crude phenylseleno ketone was oxidized with hydrogen peroxide in ethyl acetate–THF to give **6** in approximately 55% yield.

Kropp has reported the conversion of the trans dimethyl