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CYCLOPENTENONES FROM 1,2-DISILOXYCYCLOBUTENE VIA SILYLATED 1-VINYLCYLOPROPANOLS. APPLICATION TO THE SYNTHESIS OF DIHYDROJASMONE AND *CIS*-JASMONE

J. SALAÜN* and Y. ALMIRANTIS
Laboratoire des Carbocycles, ERA 316, Bâtiment 420, Université de Paris-Sud, 91405 Orsay Cedex, France

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Abstract—An effective synthesis of 2,3-disubstituted 2-cyclopentenones involves $C_4 \rightarrow C_3$ ring contraction of the readily available 1,2-disiloxycyclobutene followed by thermal $C_3 \rightarrow C_4$ ring enlargement of trimethylsiloxyvinylcyclopropanes. To illustrate the convenience of this new approach the total syntheses of 2-methyl-3-p-tolyl-2-cyclopentenone, dihydrojasmone, and *cis*-jasmone are reported.

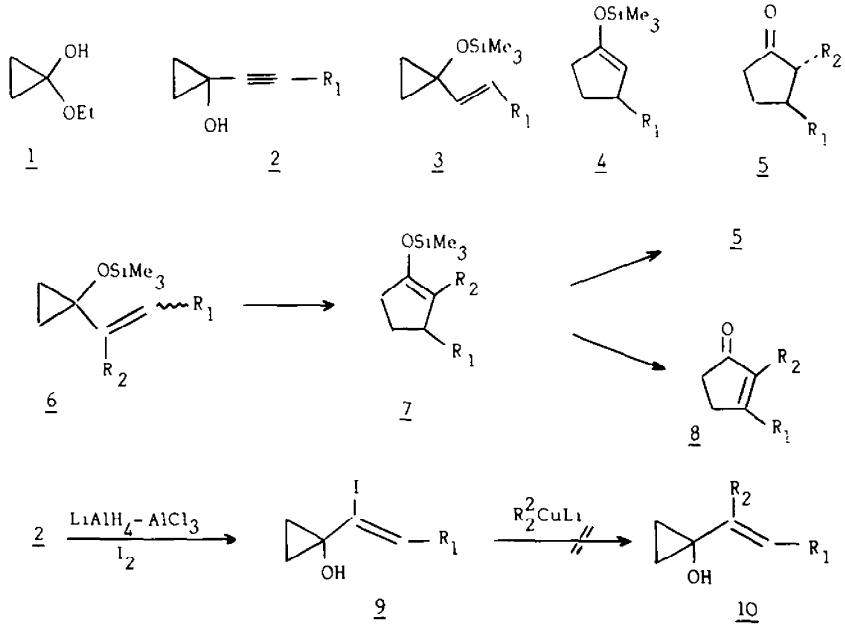
The synthesis of cyclopentanoid compounds is still a subject of extensive study because of the growing number of naturally occuring substances of biological importance which contain the five-membered ring moiety.[1] Recently, we have reported a simple and convenient method to obtain 2,3-substituted cyclopentanones, which encompass an important class of biologically active substances, from cyclopropanone ethyl hemiketal **1** and based on the thermal ring enlargement of silylated 1-vinylcyclopropanols.[2]

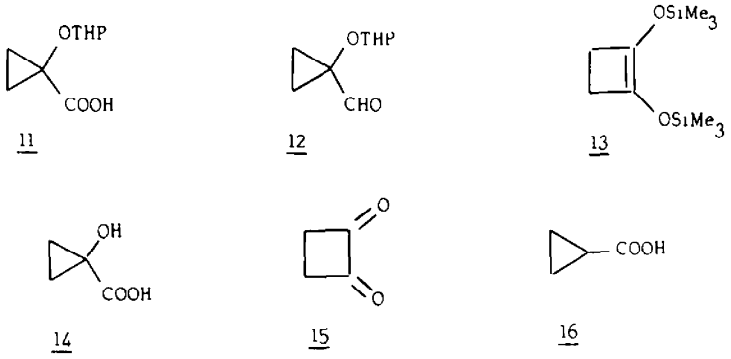
Thus, addition of acetylenic organometallic reagents $R_1C \equiv CM$ to the magnesium salt of the cyclopropanone hemiketal **1**[3] provides in good yields the cyclopropanols **2**, which after lithium aluminium hydride reduction and O-silylation lead exclusively to the *trans* 1-trimethylsiloxy-1-vinylcyclopropanes **3**. Then, on heating either in sealed tubes at 300° for 30 min or by flash thermolysis at 600° for 10 ms **3** underwent quantitative ring enlargement into the 3-substituted cyclopentanone silyl ethers **4**, which can be alkylated regiospecifically to give the expected 2,3-disubstituted cyclopentanones **5**. A total synthesis of the methyl ester of (±)-11-deoxyprostaglandin E_2 was reported to illustrate the convenience of the cyclopropanone hemiketal **1** as synthon.[2]

Therefore, it could be envisaged that the ring enlargement of disubstituted siloxyvinylcyclopropanes such as **6** would provide enol ethers **7** and upon acid or basic hydrolysis directly the 2,3-disubstituted cyclopentanones **5**, so avoiding the quite delicate final alkylation step **4**→**5**.[4] Furthermore, **7** could undergo either further regiospecific alkylation to give trisubstituted cyclopentanones, or dehydrosilylation into the cyclopentenones **8**.

Although propargylic alcohols generally undergo reduction with $LiAlH_4$–$AlCl_3$ (60:1) and subsequent iodination and alkylation with iodine and lithium dialkyl copper respectively, following a well known procedure,[5] our initial attempts to alkylate **2**, via the iodovinylcyclopropanol **9** were unsuccessful under a variety of conditions.[6]

We report in this paper a convenient preparation of the substituted vinylcyclopropanols **10** from two new synthons: the tetrahydropyranyl ethers of the 1-hydroxycyclopropanecarboxylic acid **11** and of the 1-hydroxy-





cyclopropanecarboxaldehyde **12**, that we have readily obtained from the disiloxycyclobutene **13**.

Then, we have investigated the construction of five-membered rings from the synthons **11** and **12**, via the thermal ring enlargement of 1-siloxy 1-vinylcyclopropanes **6**. We report our preliminary results in order to compare this methodology with some recent synthetic approaches aimed toward the construction of the challenging jasmonoïd system.[1,7,8]

Preparation of 1-*tetrahydropyranyloxycyclopropanecarboxylic acid* **11**

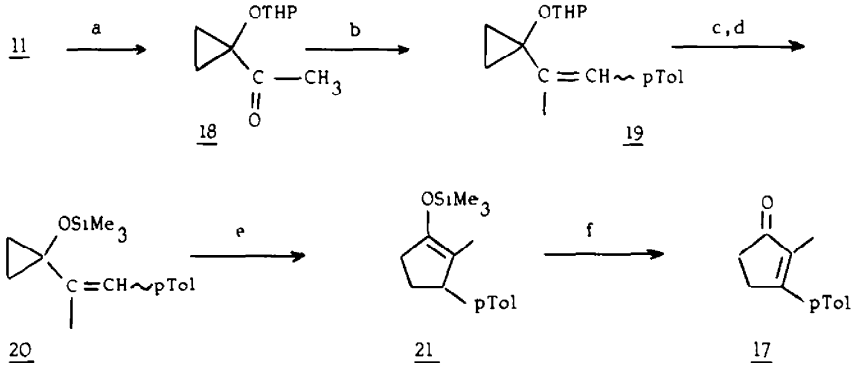
In spite of its high potientality, two functions gathered on a three-membered ring, and of its ready accessibility the 1-hydroxycyclopropanecarboxylic acid **14** has never been used as a synthon, as far as we know.

Following the reported procedure, the hydroxyacid **14** was obtained from acid-induced ring contraction of the 1,2-cyclobutanedione **15**[a], product of bromination of the 1,2-disiloxycyclobutene **13**,[10] which is formed in good yields, in the acyloin condensation of succinic esters performed in the presence of trimethylsilylchloride.[9]

As cyclopropanols undergo, under the influence of either acid or base, ring opening into ethyl ketone derivatives,[11] it appears necessary to protect first, the hydroxyl function of **14**. We have found that, on simple addition of one equivalent of 3,4-dihydro-2H-pyran to the hydroxycarboxylic acid **14** in methylenechloride, the tetrahydropyranyl ether **11** was obtained exclusively, within 30 min. On the other hand, it is known that carboxylic acids can form tetrahydropyranyl ethers too;[12] so, in these conditions, i.e. in the lack of acid catalyst, we have studied comparatively the behaviour of the cyclopropanecarboxylic acid **16**. In fact, it adds to dihydropyran much more slowly than **14** and as shown in the NMR spectra, 50% of the free acid **16** was still present in the mixture after 60 h. This result explains the specificity of the reaction **14**→**11**.

Synthesis of the 2-*methyl*-3-*p*-*tolyl*-2-*cyclopentenone* **17** *from* **11**

The preparation of the title compound **17**, was reported previously by Trost to illustrate a new method of cyclopentenone annelation based on the regioselective base induced ring opening of oxaspiropentanes.[13] We report here, an alternate direct pathway to **17** from the acid **11**. As shown in Scheme 1, the methylketone **18** prepared by addition of two equivalents of methyllithium to the acid **11**[14] was treated with p-methylbenzylidenetriphenylphosphorane[15] to give a mixture of *cis* and *trans* vinylcyclopropanes **19**. The conversion of **19** into **20** involved the deprotection of THP group by action of ethanol in presence of PPTS[16] and O-silylation by action of trimethylsilychloride and triethylamine in presence of DMSO.[17] Then, flash thermolysis at 600° of the isomeric mixture **20** produced ring enlargement into the 2,3-disubstituted cyclopentanone silyl enol ether **21**, in quantitative yield. Finally, upon treatment with Palladium acetate in presence of p-benzoquinone[18] the enol ether **21** underwent dehydrosilylation to yield the 2-

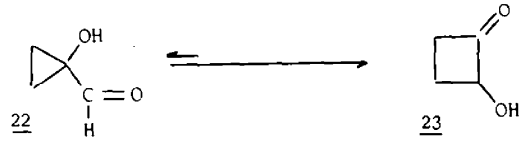


Scheme 1. Synthesis of 2-methyl-3-p.tolyl-2-cyclopentenone **17** (a) $2CH_3Li$, Ether, 36°, 88%. (b) p-TolCH=$P(C_6H_5)_3$, Ether, 36°, 76%. (c) EtOH, PPTS, 55°, 96% (d) $ClSiMe_3$, NEt_3, DMSO, 86%. (e) Flash vacuum thermolysis at 600°, 100%. (f) 0.5 molar equiv. of $Pd(OAc)_2$, 0.5 molar equiv. p-benzoquinone in CH_3CN, 91%.

cyclopentenone **17** together with a few percent of the corresponding saturated cyclopentanone. The overall yield of **17** from **11** by this route is 50.5% (Scheme 1).

Preparation of 1-*tetrahydropyranyloxycyclopropanecarboxaldehyde* 12

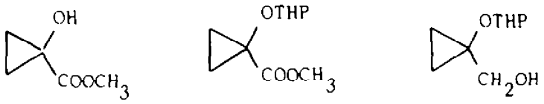
Like 1-acylcyclopropanols in general, the 1-hydroxycyclopropanecarboxaldehyde **22** cannot be isolated, it undergoes readily ring expansion into the corresponding 2-hydroxycyclobutanone **23**.[19]



22 **23**

In order to overcome this inconvenience, we have prepared the tetrahydropyranyl ether **12** from the 1,2-cyclobutanedione **15** (*vide supra*), which undergoes ring contraction into methyl 1-hydroxycyclopropanecarboxylic ester **24** by action of methoxide ion in methanol.[20,21]

The ester **25** was obtained by addition of **24** to 3,4-dihydro-2H-pyran in methylene chloride in presence of PPTS,[16] and the cyclopropylcarbinol **26** by simple lithiumaluminium hydride reduction of **25**.



24 **25** **26**

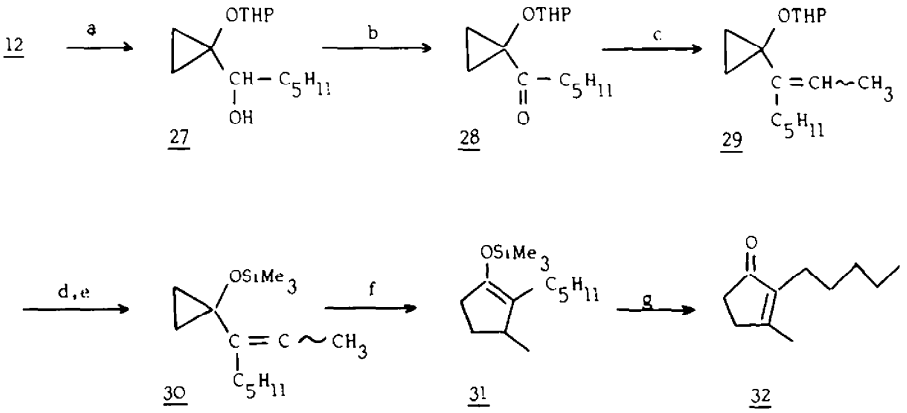
Finally, oxidation of carbinol **26** either with pyridinium dichromate[22] (45 h at 20°) or more effectively with dimethylsulphoxide activated by oxalyl chloride[23] (15 min at −60°) produced the expected cyclopropanecarboxaldehyde **12** in 50 and 98% yield, respectively. We had previously reported the synthesis of the β-methoxyethoxymethyl ether of **22**,[2] which involved a less sensitive protecting group, by means of pyridinium chlorochromate oxidation.[24] It must be underlined that, this preparation of **12** appears more convenient that the procedure recently published for the preparation of another ether derivative of the hydroxyaldehyde **22**[25] from cyclopropanone cyanohydrin.[26]

Synthesis of dihydrojasmone from **12**

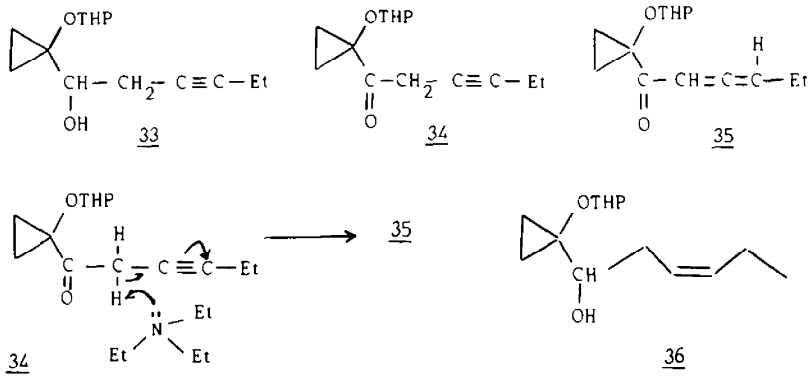
Jasmonoïds are among the best known and most often synthesized members of the cyclopentanoïd class, not only because they continue to be important raw materials in the perfume industry but also because these relatively simple compounds incorporate the 2,3-dialkylated cyclopentanone and cyclopentenone units, structural features of a large number of biologically active natural products. Our approach to the synthesis of dihydrojasmone from the cyclopropanecarboxaldehyde **12** is illustrated in Scheme 2. Addition of n-amylmagnesium bromide to the aldehyde **12** in ether resulted in the formation of the cyclopropylcarbinol **27**. Oxidation at −60° in methylene chloride with dimethylsulphoxide activated by oxalyl chloride[23] led to the ketone **28**, which was treated with ethylidenetriphenylphosphorane to produce a *cis* and *trans* mixture of the disubstituted vinylcyclopropanes **29**. Deprotection of the THP group by means of ethanol in presence of PPTS[16] and O-silylation by $ClSiMe_3$, NEt_3 and DMSO[17] gave the 1-siloxy 1-vinylcyclopropanes **30**. Then, flash thermolysis at 600° of the isomeric mixture of olefins **30** produced exclusively the expected cyclopentanone silyl enol ether **31**, which undergoes dehydrosilylation on treatment with palladium acetate and p-benzoquinone[18] to yield the dihydrojasmone **32**. The overall yield of **32** from **12** by this route is 61% (Scheme 2).

Synthesis of cis-jasmone from **12**

The attempted syntheses of cis-jasmone following the procedures analogous to those used in Scheme 2 did not give the expected results. Thus, while addition of 2-pentynylmagnesium bromide to aldehyde **12** results mainly in the formation of allenic derivatives, ($\nu_{C=C=C}$ at 1962 cm^{-1}),[28] the propargylic alcohol **33** was obtained stepwise upon treatment with propargylmagnesium bromide in ether[29] and with lithium amide and ethylbromide in liquid ammonia, successively.



Scheme 2. Synthesis of dihydrojasmone (a) $C_5H_{11}MgBr$, Et_2O, 95%. (b) DMSO, $(COCl)_2$, −60°, NEt_3, 88.5%. (c) $CH_3CH{=}P(C_6H_5)_3$, THF, 15 h, 82%. (d) EtOH, PPTS, 55°, 6h, 100%. (e) $ClSiMe_3$, NEt_3, DMSO, 96%. (f) Flash vacuum thermolysis at 600°, 100%. (g) 0.5 molar equiv. of $Pd(OAc)_2$, 0.5 molar equiv. of p-benzoquinone, CH_3CN, 92%.



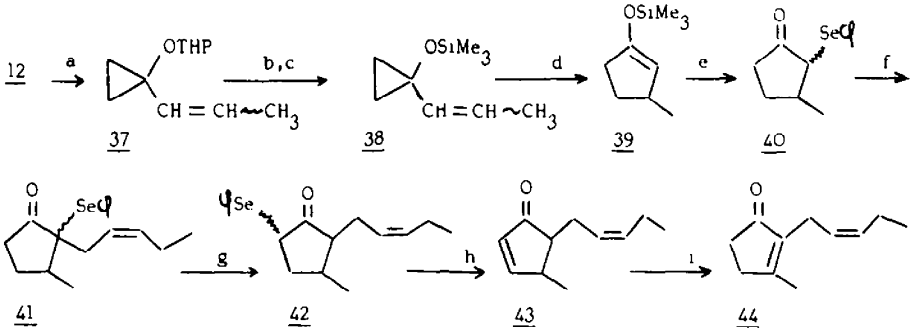
Unfortunately, oxidation of **33** with oxalyl chloride activated DMSO,[23] in the conditions successfully used with alcohol **27** (*vide supra*), followed by work up with triethylamine gave the conjugated allenic ketone **35** ($\nu_{C=C=C}$ 1955 and $\nu_{C=O}$ 1680 cm^{-1}) as major compound, beside the expected acetylenic ketone **34** ($\nu_{C\equiv C}$ 2230 and $\nu_{C=O}$ 1720 cm^{-1}).

It was possible however to limit the isomerisation **34**→**35** by using a more hindered base, e.g. diisopropylethylamine, but not in a convenient way. On the other hand, oxidation of **33** with pyridinium dichromate in presence of pyridinium trifluoroacetate[22] gave allenic ketone **35**, also. As oxidation of olefinic alcohols are usually efficient,[23] the previous catalytic hydrogenation ($Pd/BaSO_4$ 5%, quinoline, ethyl acetate) of the triple bond of **33** would allow to overcome this difficulty; but, due probably to steric hindrance, attempts to reduce **33** into the *cis* olefin **36** yielded poor results (only 15% of 36 was formed after hydrogenation at atmospheric pressure for one week).

Then, we approached the problem of the synthesis of *cis*-Jasmone from the aldehyde **12** in the fashion shown in Scheme 3. First, **12** was treated with ethylidenetriphenylphosphorane to produce the *cis* and *trans* olefin 37. Deprotection of the THP group (EtOH, PPTS[16]) and O-silylation ($ClSiMe_3$, NEt_3, DMSO[17]) led to the 1-siloxy 1-vinylcyclopropane **38** in 92% overall yield. Flash thermolysis (600°, 10 ms) transforms **38** into the 3-methyl 1-trimethylsiloxycyclopentene **39**, quantitatively. Addition of phenylselenenyl bromide[30] to the enol silyl ether **39** following a reported procedure[31] gave the 3-methyl-2-phenylselenocyclopentanone **40**. Then, treatment of crude **40** with lithium diisopropylamide in THF containing 2 molar equivalents of HMPA[32] followed by alkylation with *cis* 2-pentenyl bromide resulted in the formation of cyclopentenone **41** in 89% overall yield. As it was known that, oxidative elimination[30] of α-selenocyclanones such as **41** leads usually to mixture of endo and exocyclic enones,[32] we have used from this point, the procedure recently reported by Liotta *et al.* to transform a precursor of dehydrojasmone, closely related to **41**.[71] Thus, the transformation of **41** into **44** which involved successively, isomerization into α-selenocyclopentanone **42** upon treatment with lithium diisopropylamide in THF–HMPA at −78°, oxidative elimination into cyclopentenone **43** by a two phase system containing methylene-chloride and 30% hydrogen peroxide and finally, isomerization of **43** to **44** by sodium methoxide in methanol allowed us to achieve the total synthesis of *cis*-Jasmone **44** from the aldehyde **12** in 45.5% overall yield (Scheme 3).

CONCLUSION

The efficiency of this sequence in five-membered ring construction is pointed out in the above study. The following considerations must be taken into account to demonstrate the general utility of this methodology which involves a $C_4 \rightarrow C_3$ ring contraction followed by a $C_4 \rightarrow C_5$ ring enlargement. First of all, the acyloin condensation which provides the initial four-membered ring, e.g. 1,2-disiloxycyclobutene **13**, has been used effectively



Scheme 3. Synthesis of cis-jasmone (a) $CH_3CH=P(C_6H_5)_3$, THF, reflux, 18 h, 84%. (b) EtOH, 55°, 100%. (c) $ClSiMe_3$, NEt_3, DMSO, 92%. (d) Flash vacuum thermolysis at 600°, 100%. (e) C_6H_5SeBr, Et_2O, −78. (f) LDA, THF, HMPA, cis 2-pentenyl bromide, −78°C, 2 hr, RT, 15 hr, 89%. (g) LDA, THF, HMPA, −78°C. (h) H_2O_2 30%, CH_2Cl_2. (i) $NaOCH_3$, CH_3OH, RT, 83%.

for the preparation of substituted or polycyclic cyclobutane derivatives,[33] allowing therefore to aim this strategy towards (among others) the synthesis of fused polycyclopentanoïds (polyquinanes) which possess significant antibiotic and antitumor properties.[34] On the other hand, when the thermolysis conditions required for the vinylcyclopropane–cyclopentene ring enlargement ($C_3 \rightarrow C_5$) become impractical with complex polyfunctional molecules, metal promoted alternatives are provided by some recent developments in metallocarbene chemistry (e.g. for instance use of $(C_2H_4)_2Rh$ (acac) in toluene).[35] It must be underlined that, an oxycyclopropane- cyclopentenol rearrangement undergone at room temperature has been reported, recently.[36] Applications of this methodology to cyclopentanoïds prostanoïds, triquinanes, spirosesquiterpenes) are under investigation and will be reported in due course.

EXPERIMENTAL

1,2-Disiloxycyclobutene **13** has been prepared from n-butyl succinate following the reported procedure.[10]

1,2-Cyclobutanedione **15** has been prepared by bromination of **13** according to the reported procedure.[9]

1-Hydroxycyclopropanecarboxylic acid **14** was obtained quantitatively upon treatment of **15** with N-hydrochloric acid following the reported procedure.[9]

1-Tetrahydropyranyloxycyclopropanecarboxylic acid **11**

To a solution of 9 g (0.107 mol) of 3,4-dihydro-2H-pyran in 200 ml of methylene chloride was added 10.2 g (0.1 mol) of the solid cyclopropanol **14**. After stirring for 30 min, the acid **14** was solubilized, completely. The solution was stirred at room temperature for an additional 2 h. Removal of solvent on a rotary evaporator left 18.6 g (100%) of 1-tetrahydropyranyloxycyclopropanecarboxylic acid **11**; IR (CCl_4): 1700 cm^{-1} (ν_{COOH}); NMR (CCl_4): δ 1.0–2.1 (m, 10H), 3.15–4.0 (m, 2H), 4.85 (s, 1H) and 10.30 (s, 1H).

Comparatively, a solution of 0.91 g (10.5 mmol) of cyclopropanecarboxylic acid and of 0.92 g (11 mmol) of 3,4-dihydro-2H-pyran in 20 ml of methylene chloride was stirred at room temperature for 60 h. A singlet at δ 12.1 ppm in the NMR spectra of the crude product showed the presence of 50% of the free acid.

Methyl (1-tetrahydropyranyloxycyclopropyl) ketone **18**

To a solution of 5.98 g (32 mmol) of acid **10** in 50 ml of anhydrous ether was added 40 ml of 1.75 N solution (70 mmol) of methyllithium in ether. The mixture was refluxed for 16 h. The mixture was cooled to 0° (ice-water bath) and 75 ml of water were added dropwise. The organic phase was washed with saturated ammonium chloride solution and water, and the aqueous layer was neutralized with aqueous ammonium chloride and extracted with ether. The combined extracts were dried over $MgSO_4$ and evaporated to give 5.7 g (88%) of methyl (1-tetrahydropyranyloxycyclopropyl) ketone **18**; IR (CCl_4): 1710 cm^{-1} ($\nu_{C=O}$); NMR (CCl_4): δ 0.50–2.1 (m, 10H), 2.25 (s, 3H), 3.10–4.0 (m, 2H), 4.60 (m, 1H).

Cis and trans 1-(1-methyl 2-p-tolylvinyl)-1-tetrahydropyranyloxycyclopropanes **19**

To 4.85 g (12 mmol) of p-methylbenzyltriphenylphosphonium chloride[15] in 25 ml of anhydrous tetrahydrofuran were added 9.6 ml (12 mmol) of n-butyllithium in hexane 1.25 N. The yellow-orange suspension was stirred at room temperature for 2 h. Then, 2.2 g (12 mmol) of ketone **18** were added and the resulting mixture refluxed for 16 h, until the color was completely discharged. After usual work up and removal of solvents, filtration of triphenylphosphineoxide, the residue was chromatographed on silica. Elution with pentane-diethyl ether (90–10) gave first 1.25 g (38%) of *trans* **19**; IR (CCl_4): 1615 and 1645 cm^{-1} ($\nu_{C=C}$); NMR (CCl_4): δ 0.40–1.90 (m, 10H), 1.97 (s, 3H), 2.30 (s, 3H), 3.20–4.0 (m, 2H), 4.88 (m, 1H), 6.30 (s, 1H) and 6.90–7.45 (q, 4H). Then, 1.25 g (38%) of *cis* **19**; IR (CCl_4): 1615 and 1645 cm^{-1} ($\nu_{C=C}$); NMR (CCl_4): δ 0.70 – 1.80 (m, 10H), 1.90 (s, 3H), 2.30 (s, 3H), 3.15–4.0 (m, 2H), 4.70 (m, 1H), 6.40 (s, 1H) and 7.0 (s, 4H).

Trans 1-(1-methyl 2-p-tolylvinyl) cyclopropanol

A solution of 1 g (3.68 mmol) of the trans tetrahydropyranyl ether **19** in 10 ml of ethanol containing 110 mg (0.4 mmol) of PPTS[16] was stirred at 55° for 4 h, to complete the reaction as shown by TLC of an aliquot. The solvent was removed on a rotary evaporator and the residue treated with 50 ml of ether. The solution was washed twice with half saturated brine, dried over Na_2SO_4 and concentrated to give 664 mg (96%) of practically pure *trans* 1-(1-methyl 2-p.tolylvinyl) cyclopropanol; IR (CCl_4): 3610 and 3450 (ν_{OH}), 1645 and 1610 cm^{-1} ($\nu_{C=C}$); NMR (CCl_4): δ 0.35–0.60 (m, 2H), 0.65–1.0 (m, 8H), 1.98 (s, 3H), 2.30 (s, 3H), 3.10–4.0 (m, 2H), 6.22 (s, 1H) and 6.80–7.40 (q, 4H); MS: *m/e* (rel. intensity) 188 (M^+, 27), 173 (M-15, 100), 159 (83), 131 (74) and 91 (41).

Cis 1-(1-methyl 2-p-tolylvinyl)cyclopropanol

Treatment of the *cis* tetrahydropyranyl ether **19** in the same conditions gave the *cis* 1-(1-methyl 2-p.tolylvinyl) cyclopropanol; IR (CCl_4): 3602 and 3450 (ν_{OH}), 1645 and 1610 cm^{-1} ($\nu_{C=C}$); NMR (CCl_4): 0.80 (s, 4H), 1.75 (s, 3H), 2.25 (s, 3H), 6.45 (m, 1H) and 6.98 (s, 4H); M.S.: *m/e* (rel. intensity) 188 (M^+, 34), 173 (M-15, 16), 159 (100), 131 (76) and 91 (36).

Trans 1-(1-methyl 2-p-tolylvinyl)-1-trimethylsiloxycyclopropane **20**

To a solution of 480 mg (2.55 mmol) of *trans* 1-(1-methyl 2-p. tolylvinyl)cyclopropanol, of 385 mg (3.81 mmol) dry triethylamine and 24 mg (0.3 mmol) of dimethylsulphoxide[17] in 10 ml of anhydrous ether was added with stirring 275 mg (2.55 mmol) of trimethylsilyl chloride. The reaction was completed after 4 h, as shown by TLC of an aliquot. Then, the mixture was poured into 10 ml of ice water. The organic phase was washed with water, dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica; elution with pentanediethylether (95-5) gave 560 mg (86%) of *trans* 1-(1-methyl 2-p. tolylvinyl)-1-trimethylsiloxycyclopropane **20**; IR (CCl_4): 1660 and 1615 cm^{-1} ($\nu_{C=C}$); NMR (CCl_4): δ 0.20 (s, 9H), 0.50 (m, 2H), 0.90 (m, 2h), 2.15 (s, 3H), 2.40 (s, 3H), 6.30 (m, 1H) and 7.10–7.50 (q, 4H); MS: *m/e* (rel. intensity) 260 (M^+, 9), 2.45 (m-15, 67), 169 (20) and 73 (100).

Cis 1-(1-methyl 2-p-tolylvinyl)-1-trimethylsiloxycyclopropane **20**

The *cis* 1-(1-methyl 2-p-tolylvinyl)-1-cyclopropanol was silylated analogously to the *trans* isomer to yield the *cis* siloxycyclopropane **20**; IR (CCl_4): 1680 and 1610 cm^{-1} ($\nu_{C=C}$); NMR (CCl_4): δ 0.20 (s, 9H), 0.90 (s, 4H), 1.95 (s, 3H), 2.37 (s, 3H), 6.45 (m, 1H) and 7.05 (s, 4H); MS: *m/e* (rel. intensity) 260 (M^+, 12), 245 (M-15, 100), 169 (18) and 73 (68).

2-Methyl-3-p-tolyl-1-trimethylsiloxycyclopentene **21**

400 mg (1.54 mmol) of either *cis* or *trans* siloxyvinylcyclopropane **20** were evaporated under vacuum and heated at 600° for 10 ms.[2] The product of thermolysis was condensed in a liquid nitrogen cooled trap; thus, the expected cyclopentanone enol silyl ether **21** was obtained quite pure and in virtually quantitative yield. IR (CCl_4): 1690 cm^{-1} ($\nu_{C=C}$); NMR (CCl_4): δ 0.10 (s, 9H), 1.0–1.40 (m, 4H), 2.15 (s, 6H), 3.30 (m, 1H) and 6.80 (s, 4H); MS: *m/e* (rel. intensity) 260 (20), 245 (M-15, 58), 169 (12) and 73 (100).

2-Methyl 3-p-tolyl-2-cyclopentenone **17**

To a solution of 173 mg (0.77 mmol) of $Pd(OAc)_2$ and 83 mg (0.77 mmol) of p-benzoquinone in 6 ml of acetonitrile (distilled over P_2O_5) was added 400 mg (1.54 mmol) of silyl enol ether **21**, under nitrogen at room temperature and the mixture was stirred for 6 hr. TLC of an aliquot indicated total dehydrosilylation. First, chromatography on silica gel eluting with benzene to remove palladium derivatives and then chromatography on silica gel eluting with pentane-ether gave 2-methyl 3-p.tolyl 2-cyclopentenone **17**; IR (CCl_4): 1705 ($\nu_{C=O}$), 1630 cm^{-1} ($\nu_{C=C}$); NMR (CCl_4): δ 1.85 (m, 3H), 2.15–2.50 (m, 2H), 2.35 (s, 3H), 2.60–2.90

(m, 2H) and 6.98–7.35 (q, 4H); MS: *m/e* (rel. intensity) 186 (M^+, 51), 171 (M-15, 100), 143 (33), 128 (48), 91 (15).

Methyl 1-hydroxycyclopropanecarboxylate **24**

A mixture of 20 g (238 mmol) of 1,2-cyclobutanedione **15** in 200 ml of methanol containing 2.5 g of sodium methylate was stirred at room temperature, for 2.5 hr. Then, the mixture was neutralized by addition of a 10% solution of sulfuric acid and the solvent removed on a rotary evaporator. The residue was extracted by 3 × 200 ml of methylene chloride. The organic layer was washed with water, dried over $MgSO_4$ and concentrated to give 20.55 g (76%) of practically pure methyl 1-hydroxycyclopropanecarboxylate **24**; IR (neat): 3430 (ν_{OH}) and 1730 cm^{-1} ($\nu_{C=O}$); NMR ($CCDl_4$): δ1–1.3 (m, 4H), 3.7 (s, 3H) and 4.04 (s, OH).

Methyl 1-tetrahydropyranyloxycyclopropylcarboxylate **25**

A solution of 19.2 g (168 mmol) of cyclopropanol **24**, of 14.3 g (168 mmol) of 3,4-dihydro-2H-pyran in 300 ml of methylene chloride containing 4.02 g (16.8 mmol) of PPTS[16] was stirred at room temperature for 3 h. Then, the solvent was removed on a rotary evaporator, and the residue treated with 300 ml of ether. The organic phase was washed with half saturated brine, dried over Na_2SO_4 and concentrated to give 32.8 g (100%) of practically pure methyl 1-tetrahydropyranyloxycyclopropanecarboxylate **25**; IR (neat): 1750 cm^{-1}; NMR ($CDCl_3$): δ 1.–1.4 (t, 2H), 1.4–2.5 (m, 8H), 3.1–4.4 (m, 2H), 3.6 (s, 3H) and 4.95 (t, H).

1-*Tetrahydropyranyloxycyclopropylcarbinol* **26**

To a suspension of 3.42 g (90 mmol) of lithiumaluminium hydride in 250 ml of ether was added dropwise a solution of 30 g (150 mmol) of the ester **25** in 250 ml of ether. When the addition was over, the mixture was refluxed for 30 min. Then, the mixture was cooled to room temperature and hydrolyzed by addition of wet sodium sulfate. The ether layer was separated, dried over Na_2SO_4 and concentrated on a rotary evaporator to yield 25.3 g (98%) of 1-tetrahydropyranyloxycyclopropylcarbinol **26**; IR (neat): 3440 (ν_{OH}) and 2960 cm^{-1} (ν_{C-H}); NMR ($CDCl_3$): δ 0.40–1. (m, 4H), 1.–2.1 (m, 6H), 2.8–4. (m, 4H), 4.05 (t, H) and 4.6 (t, H).

1-*Tetrahydropyranyloxycyclopropanecarboxaldehyde* **12**

(a) *Oxidation byt pyridinium dichromate.*[22] A mixture of 0.91 g (5.27 mmol) of cyclopropylcarbinol **26** in 8 ml of methylene chloride containing 3 g (1.6 equiv) of pyridinium dichromate was stirred at room temperature for 27 h. TLC of an aliquot showed that the reaction was not completed. Then, 2 g (1 equiv) of PDC in 5 ml of CH_2Cl_2 were added and the mixture stirred for an additional 18 h. The reaction was diluted with 100 ml of ether, filtered and evaporated to afford a mixture of 50% of the expected aldehyde **11** and 50% of the carbinol **26**.

(b) *Oxidation by dimethylsulphoxide activated by oxalyl chloride.*[23] To a stirred solution of 4 ml (44 mmol) of oxalyl chloride in 100 ml of methylenechloride cooled to −60°, was added dropwise a solution of 6.8 ml of DMSO in 15 ml of CH_2Cl_2 at −50 to −60°. The reaction mixture was stirred for 2 min and a solution of 6.88 g (40 mmol) of cyclopropylcarbinol **26** in 40 ml of CH_2Cl_2 was added within 5 min and stirring was continued for an additional 15 min. Then 28 ml (200 mmol) of triethylamine was added and the reaction mixture was stirred for 5 min at −50° and then allowed to warm to room temperature. Water (100 ml) was added and the aqueous layer was extracted twice with 100 ml of CH_2Cl_2. The combined organic layers were washed with 100 ml of saturated brine and dried over $MgSO_4$. TLC of an aliquot showed the formation of a single product. The filtered solution was concentrated on a rotary evaporator to yield 6.76 g (98%) of practically pure, without further work up, 1-tetrahydropyranyloxycyclopropanecarboxaldehyde **12**; IR (CCl_4): 3100 (ν_{C-H}) and 1725 cm^{-1} ($\nu_{C=O}$); NMR (CCl_4): δ 0.90–1.40 (q, 4H), 1.40–2.0 (m, 6H), 3.20–4.10 (m, 2H) and 4.65 (m, 1H).

1-(1-*Tetrahydropyranyloxycyclopropyl*) *hexan*-1-*ol* **27**

To a suspension of 195 mg (8 mmol) of magnesium in 10 ml of ether was added dropwise 1.21 g (8 mmol) of hexyl bromide in 10 ml of ether. After all the magnesium was dissolved, the flask was cooled at 0° in an ice-water bath and 1.18 g (6.94 mmol) of cyclopropanecarboxaldehyde **12** was added dropwise. Then, the mixture was refluxed for 4 h. After usual work-up, removal of solvent on a rotary evaporator yielded 1.6 g (95%) of the expected hexanol **27**: IR (CCl_4): 3450 (ν_{OH}) and 3100 cm^{-1} (ν_{C-H}); NMR (CCl_4): δ 0.45 – 1.95 (m, 21H), 3.–4.1 (m, 4H) and 4.80 (m, 1H).

1-(1-*Tetrahydropyranyloxycyclopropyl*) *hexanone* **28**

To a stirred solution of 2.4 mmol of oxalyl chloride in 5 ml of CH_2Cl_2 was added a solution of 0.37 ml (4.8 mmol) of DMSO[23] at −60°. The reaction mixture was stirred for 2 min then a solution of 529 mg (2.18 mmol) of hexanol **27** in 2 ml of CH_2Cl_2 was added within 5 min. and stirring was continued for an additional 15 min. After addition of triethylamine 1.53 ml at −60° the reaction mixture was worked up in the same way as for preparation of aldehyde **12**, to give 465 mg (88.5%) of hexanone **28**; IR (CCl_4): 1710 cm^{-1} ($\nu_{C=O}$); NMR (CCl_4): δ 0.65–1.90 (m, 19H), 2.50 (m, 2H), 3.20–3.80 (m, 2H) and 4.45 (m, 1H).

3-(1-*Tetrahydropyranyloxycyclopropyl*)-2-*octene* **29**

To a suspension of 1.11 g (3 mmol) of ethyltriphenylphosphonium bromide in 15 ml of anhydrous tetrahydrofuran was added 2 ml of 1.5 N solution (3 mmol) of n-butyllithium in hexane. The mixture was stirred for 2 h at room temperature and then a solution of 581 mg (2.4 mmol) of hexanone **28** in 2 ml of THF was added. The complete discharge of the yellow-orange color of the phosphorane was obtained after the mixture was refluxed for 18 h. Usual work-up, removal of solvents and filtration of triphenylphosphine oxide led to 502 mg (82%) of octene **29** (as a *cis* and *trans* mixture); NMR (CCl_4): δ 0.88 (m, (4H), 1.1–2.2 (m, 17H), 1.75 (d, 3H, J = 6.7 Hz), 3.10–3.90 (m, 2H), 4.60 (m, 1H) and 5.20–5.55 (q, 1H, J = 6.7 Hz).

1-(1-*Ethylidenehexyl*)*cyclopropanol*

A solution of 502 mg (1.99 mmol) of octene **29** in 10 ml of ethanol containing 50 mg (0.2 mmol) of PPTS[16] was refluxed. TLC of aliquots showed that the reaction was completed within 6 h. Then, after removal of ethanol on a rotary evaporator the residue was chromatographed on silica. Elution with pentane–ether (90:10) gave 334 mg (100%) of 1-(1-ethylidenehexyl) cyclopropanol; IR (CCl_4): 3610 and 3475 (ν_{OH}), 3100 cm^{-1} (ν_{C-H}); NMR (CCl_4): δ 0.4–0.65 (m, 2H), 0.7–2.4 (m, 12H), 2.75 (d, 3H, J = 6.7 Hz) and 5.1–5.45 (q, 1H, J = 6.7 Hz); MS: *m/e* (rel. intensity) 240 (M^+, 2), 153 (M-15, 5), 139 (30), 97 (16), 57 (69) and 55 (100).

1-(1-*Ethylidenehexyl*)-1-*trimethylsiloxycyclopropane* **30**

To a solution of 113 mg (0.672 mmol) of 1-(1-ethylidenehexyl) cyclopropanol in 3 ml of ether containing 101 mg (1 mmol) of NEt_3 and 5.46 mg (0.07 mmol) of DMSO[17] was added 76 mg (0.7 mmol) of $ClSiMe_3$. The mixture was stirred at room temperature, TLC of aliquots showed that the reaction was completed within 4.5 h. After usual work-up,[2] the residue was chromatographed on silica to give 155 mg (96%) of siloxycyclopropane **30**; IR (CCl_4): 3100 (ν_{C-H}); NMR (CCl_4): δ 0.25 (s, 9H), 0.8 (m, 2H), 0.9–2.4 (m, 13H), 1.95 (d, 3H, J = 6.7 Hz) and 5.20–5.60 (q, 1H, J = 6.7 Hz); MS: *m/e* (rel. intensity) 225 (M-15, 8.5), 169 (7.2), 75 (22) and 73 (100). 2-Pentyl-3-methyl-1-trimethylsiloxycyclopentene **31** was obtained from thermolysis at 600° for 10 ms of siloxycyclopropane **30**; IR (CCl_4): 1680 cm^{-1} ($\nu_{C=C}$); NMR (CCl_4): δ 0.1 (s, 9H), 0.70–2.5 (m, 19H); MS: *m/e* (rel. intensity) 240 (M^+, 5), 225 (M-15, 17), 211 (21), 169 (11), 155 (11) and 73 (100).

Dihydrojasmone **32**

A solution of 120 mg (0.5 mmol) of siloxycyclopentene was treated analogously to **21** by $Pd(OAc)_2$ and p-benzoquinone in acetonitrile.[18] After work-up the residue was chromatographed on silica. Elution with benzene gave first, 14 mg (6%) of 2-hexyl-3-methylcyclo-pentanone; IR (CCl_4): 1745 cm^{-1} ($\nu_{C=O}$); NMR (CCl_4): δ 0.82 (t, 3H), 1.0–1.60 (m, 13H) and 1.90–2.60 (m, 3H); MS: *m/e* (rel. intensity) 168 (M^+, 5), 153 (M-15, 4), 98 (36), 83 (100), 55 (47) and 41 (48). Then, 76.5 mg (92%) of dihydrojasmone **32**; IR (CCl_4): 1705 ($\nu_{C=O}$) and 1650 ($\nu_{C=C}$); NMR (CCl_4): δ 0.87 (t, 3H), 1.05–1.50 (m, 8H), 2.0–2.6 (m, 4H) and 2.07 (s, 3H); MS: *m/e* (rel intensity) 166 (M^+, 6.5), 151

(M-15, 46), 137 (15), 123 (17), 109 (22), 95 (22), 55 (35) and 41 (100). The lack of any signal at 6.70 in the NMR spectra of the crude product of dehydrosilylation showed the lack of 3-methyl 2-pentylidenecyclopentanone.[7]

1-(1-*Tetrahydropyranyloxycyclopropyl*) 3-*hexyn*-1-*ol* **33**

To a suspension of 0.608 g (25 mmol) of magnesium in 5 ml of ether containing a catalytic amounts of mercury (II) chloride was added dropwise 2.98 g (25 mmol) of propargyl bromide, at temperature kept below 20° by external cooling When the addition was over, the mixture was stirred at room temperature (~20°) for an additional 3 hr. Then, the mixture was cooled to 0° (ice-water bath) and a solution of 3.40 g (20 mmol) of aldehyde **12** in 20 ml of ether was added. The reaction mixture was brought to room temperature and stirred overnight. The mixture was poured into 50 ml of cooled saturated ammonium chloride solution. After usual work-up, the residue was chromatographed to give 3.2 g (76%) of 1-(1-tetrahydropyranyloxycyclopropyl)-3-propyn-1-ol; IR (CCl_4): 3600 and 3420 (ν_{OH}), 3320 ($\nu_{\equiv C-H}$) and 2120 cm^{-1} ($\nu_{C\equiv C}$); NMR (CCl_4): δ 0.70 (m, 4H), 1.55 (m, 7H), 2.45 (m, 2H), 3.1–4.1 (m, 3H) and 4.80 (m, 1H).

To a suspension of 30 mmol of lithium amide (prepared from 210 mg of lithium) in 40 ml of liquid ammonia was added a solution of 2.4 g (11.4 mmol) of the previously-obtained propynol in 10 ml of tetrahydrofuran. The mixture was stirred for 30 min, then a solution of 2.18 g (20 mmol) of ethylbromide in 5 ml of THF was added dropwise. When the addition was over the mixture was stirred for 40 h. After removal of ammonia, the residue was poured into a slurry of ice and extracted with ether. The organic phase was dried over $MgSO_4$ and concentrated to give 2.5 g (92%) of the hexynol **33**; IR (CCl_4): 3580 and 3430 (ν_{OH}), 2230 cm^{-1} (ν_{C-C}); NMR (CCl_4): δ 0.62 (m, 4H), 1.05 (t, 3H, 1.50 (m, 6H), 1.90–2.6 (m, 4H), 3.30–4.10 (m, 2H), and 4.75 (m, 1H).

Oxidation of **33** *by oxalyl chloride-activated dimethylsulphoxide*

Treatment of **33** by DMSO–$(COCl)_2$ and work-up with NEt_3[23] at −60°, analogously to **27** gave a mixture of the conjugated allenic ketone **35** as major compound; IR (CCl_4): 1955 ($\nu_{C=C=C}$) and 1680 cm^{-1} ($\nu_{C=O}$); and a small amount (~5%) of the acetylenic ketone **34**; IR (CCl_4): 2220 (ν_{C-C}) and 1710 cm^{-1} ($\nu_{C=O}$). Treatment of **33** by DMSO–$(COCl)_2$ at −60° and work-up with diisopropylethylamine gave a mixture of **35** (~60%) and **34** (~40%).

Oxidation of **33** *by PDC and pyridinium trifluoroacetate*[22]

To a suspension of 282 mg (0.75 mmol) of pyridinium dichromate in 1.5 ml of methylene chloride containing 60 mg (0.4 equiv) of pyridinium trifluoracetate was added 119 mg (0.5 mmol) of **3**. TLC of aliquots showed that oxidation was obtained in 50% yield after stirring for 42 h. An additional 1.5 equiv PDC was added and the mixture stirred for additional 24 h. After work-up, examination of the crude product in IR showed the formation of a mixture of **33**, **34** and allenic **35**, which were not separated.

Hydrogenation of **33**

To a suspension of 94 mg of Pd over $BaSO_4$ (5%) in 10 ml of ethyl acetate containing 0.1 ml of quinoline was added 1.17 g (4.9 mmol) of **33**. The mixture was hydrogenated at atmospheric pressure for one week, to give only 15% of olefinic product as shown by comparison of the signal at δ 5.20–5.90 with the signal at δ 4.80 ppm (1H, tetrahydropyranylether).

1-(1-*Propenyl*)-1-*tetrahydropyranyloxycyclopropane* **37**

To a suspension of 11.13 g (30 mmol) of ethyltriphenylphosphonium bromide in 100 ml of anhydrous tetrahydrofuran was added dropwise 20 ml of a 1.5 solution (30 mmol) of n-butyllithium in hexane and the mixture was stirred at room temperature for 2.5 h. Then, a solution of 4.25 g (25 mmol) of aldehyde **12** in 20 ml of THF was added dropwise and the mixture refluxed with stirring for 18 h to obtain complete discharge of the yellow-orange color of the phosphorane. After usual work-up, filtration of triphenylphosphine oxide, removal of solvent gave 3.82 g (84%) of cyclopropane **37**; IR (CCl_4): 3100 (ν_{C-H}) and 1650 cm^{-1} ($\nu_{C=C}$); NMR (CCl_4): δ 0.50–1.0 (m, 4H), 1.55 (m, 6H), 1.75 (d, 3H), 3.10–4.0 (m, 2H), 4.75 (m, 1H), 5.30–5.80 (m, 2H).

1-(1-*Propenyl*)-1-*trimethylsiloxycyclopropane* **38**

A solution of 3 g (16.5 mmol) of ether **17** in 25 ml of ethanol containing 0.5 g (2 mmol) of PPTS[16] was stirred at 55°. TLC of aliquots showed complete reaction after 72 h. After removal of ethanol on rotary evaporator, 100 ml of ether was added to the residue. Usual work-up gave 1.61 g (100%) of a mixture of *cis* and *trans* 1-(1-propenyl) cyclopropanol; IR (CCl_4): 3610, 3450 (ν_{OH}), 3090 (ν_{C-H}), 1650 cm ($\nu_{C=C}$); NMR (CCl_4): δ 0.40–1.0 (m, 4H), 1.65 and 1.85 (2d, 3H), 4.5 (m, 1H) and 5.20–5.8 (m, 2H); MS: *m/e* (rel intensity) 98 (M^+, 12), 83 (M-15, 16), 69 (100), 55 (25), 41 (75). (For a synthesis of *trans* 1-(1-propenyl) cyclopropanol from cyclopropanone hemiketal see ref 2).

A solution of 6.2 g (63.2 mmol) of 1-(1-propenyl) cyclopropanol was silylated analogously to **30** with $ClSiMe_3$, NEt_3 and DMSO[17] to yield 9.55 g (92%) of siloxycyclopropane **38**; IR (CCl_4): 3100 (ν_{C-H}), 1675 ($\nu_{C=C}$); NMR (CCl_4): δ 0.05 (s, 9H), 0.6 (m, 2H), 0.82 (m, 2H), 1.65 (d, 3H, J = 6.66 Hz), 5.05–5.68 (m, 2H); MS *m/e* (rel. intensity) 170 (M^+, 1), 155 (M–15, 61), 75 (57), 73 (100), 45 (29) and 41 (19). 3-Methyl-1-trimethylsiloxycyclopentene **39** was obtained quantitatively from thermolysis of **38**; spectroscopic data of **39** were identical with those previously reported for this enol silyl ether.[2]

Cis and trans 3-*methyl*-2 *phenylselenenyl cyclopentanone* **40**

A solution of 1.40 g (8.25 mmol) of **39** in 10 ml of anhydrous ether was cooled to −78° with dry ice–acetone bath. Then, 8.25 mmol of phenylselenenyl bromide prepared *in situ* from 1.3 g (4.13 mmol) of diphenyldiselenide and 666 mg (4.13 mmol) of bromine in 15 ml of anhydrous ether was added dropwise (~45 min). The reddish brown color of phenylselenenyl bromide was discharged immediately upon addition. When addition was over, the reaction mixture was poured into 40 ml of a 10% aqueous sodium hydrogen carbonate solution. The aqueous phase was extracted with 2 × 20 ml of ether and the combined ether extract dried with Na_2SO_4. After removal of the solvent on a rotary evaporator, the residue was chromatographed on silica; elution with pentane-ether (90: 10) gave 1.85 g (88.5%) of **40** with IR and NMR spectroscopic data identical with these recently reported for this α-seleno cyclopentanone;[7] MS: *m/e* (rel intensity) 256 (17), 255 (13), 254 (M^+, 100), 253 (8), 252 (49), 251 (18), 250 (19), 97 (36), 69 (45) and 55 (27).

Cis and trans 3-*methyl*-2-(2-*pentenyl*)-2-*phenylselenenyl cyclopentanone* **41**

To a solution of 0.29 g (2.88 mmol) of diisopropylamine in 3 ml of tetrahydrofuran containing two crystals of α, α′-bipyridyl, cooled at −78° with dry ice–acetone bath was added dropwise 1.68 ml of a 1.5 N (2.252 mmol) solution of n-butyllithium in hexane. The solution was stirred for 15 min. and then added slowly under nitrogen by means of a double-ended needle to a solution of 400 mg (1.575 mmol) of α-selenocyclopentanone **40** in 7 ml of tetrahydrofuran, until the color remained pink. When the addition was over, the solution was stirred for 15 min. and 0.6 ml of HMPA and 0.94 g (6.3 mmol) of 1-bromo-2-pentene were added. The reaction mixture was then allowed to stir for 2 hr at −78° and additional 15 hr at room temperature. Then, 2.5 ml of 10% HCl was added to quench the reaction. After removal of THF *in vacuo*, the residue was extracted with 3 × 10 ml of ether. The combined organic layers were washed with 3 × 3 ml of 10% HCl, 2 × 3 ml of saturated bicarbonate solution and with 2 × 3 ml of water. The ether solution was dried with $MgSO_4$ and concentrated on a rotary evaporator; the residue was chromatographed on silica to give 451 mg (89%) of cyclopentanone **41**; IR ($CDCl_3$): 1735 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$): δ 0.9–1.55 (d, 6H), 1.85–3.10 (m, 9H), 5.20–5.90 (m, 2H) and 7.40–7.95 (m, 5H); MS: *m/e* (rel intensity) 324 (9), 323 (9), 322 (M^+, 49), 321 (61), 320 (24), 319 (9.7), 318 (10), 165 (100), 81 (54), 79 (46), 77 (81) AND 55 (60).

Cis and trans 3-methyl-2-(2-pentenyl)-5-phenylselenenyl cyclopentanone **42**

Following the procedure of Liotta,[7] treatment of **41** with 0.5 equiv of LDA in THF/HMPA at −78°, gave quantatively, after quenching the enolate with saturated ammonium chloride solution the α′ selenocyclopentanone **42**: NMR ($CDCl_3$): δ 0.75–1.0 (t, 3H), 1.0–1.30 (d, 3H), 1.50–2.65 (m. 8H), 3.40–3.95 (m, 1H), 5.–5.60 (m, 2H) and 7.10–7.80 (m, 5H).

4-Methyl-5-(2-pentenyl) cyclopent-2-en-1-one **43**

To a solution of 250 mg (0.776 mmol) of selenocyclopentanone **42** in 2.5 ml of methylenechloride were added six 0.25 ml portions of 30% H_2O_2 at 10 min intervals. When the additions were over. the mixture was stirred an additional 5 min at room temperature and then transferred into a separatory funnel to separate the layers. The organic layer was washed sequentially with 2 ml of water, 2 ml of saturated $NaHCO_3$ and again with 2 ml of water. The solution was dried over $MgSO_4$ and concentrated on a rotary evaporator. The residue was chromatographed on silica to yield 115 mg (90%) of cyclopentenone **43**; IR ($HCCl_3$): 1700 ($\nu_{C=O}$) and 1630 cm^{-1} ($\nu_{C=C}$); NMR ($HCCl_3$): δ 0.90 (t, 3H), 1.15 (d, 3H), 1.40–3 (m, 7H), 5.20–5.80 (m, 1H), 6.10–6.30 (m, 2H) and 7.45–7.70 (dd, 6 Hz); MS: *m/e* (rel intensity) 164 (M^+, 30), 149 (M-15, 5), 135 (M-29, 25), 96 (M-C_5H_8, 100), 55 (31), 53 (30). As by-product was recovered 12 mg (10%) of 3-methyl 2-(2-pentenyl) cyclopentanone; IR (CCl_4): 1735 ($\nu_{C=O}$), 1665 cm^{-1} ($\nu_{C=C}$); NMR ($CDCl_3$): δ 0.90 (t, 3H), 1.10 (d, 3H), 1.5–2.6 (m, 10H) and 5.35 (m, 2H); MS: *m/e* (rel intensity) 166 (M^+, 12), 98 (41), 55 (41), 53 (27) and 41 (100).

Cis-jasmone **44**

Treatment of cyclopentenone **43** with sodium methoxide in methanol following the Liotta procedure[7] gave the expected cis-jasmone with spectroscopic data identical with those reported (cf ref 7 and references cited therein).

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