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GENERAL SYNTHESIS OF CYCLOPROPENONES AND THEIR ACETALS

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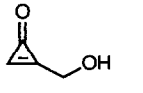
Abstract: *Metalated cyclopropenone acetals* **5** *react with a variety of electrophiles, including alkyl halides, carbonyl compounds, vinyl iodides, vinyl triflates, and aryl iodides, to give substituted cyclopropenone acetals in high yield. Hydrolysis of the acetal under acidic conditions gives the corresponding cyclopropenone. The reaction sequence has realized an efficient synthesis of an antibiotic penitricin (1).*

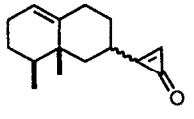
Cyclopropenone is the first member of the (4n + 3) annulenone series,[1] and enjoys the ground-state stabilization effect by the contribution of a dipolar form, that is related to the (4n + 2)π [n = 0] Hückel aromaticity. In fact, most cyclopropenones are quite stable compounds in spite of their high strain energy that amounts nearly to 70 kcal/mol.[2] Such stability has frequently been compared with the less strained but much less stable saturated analogue, cyclopropanone. Thus, there have been extensive studies on the physicochemical and theoretical studies of these molecules.[3,4]

On the other hand, fewer systematic efforts have been expended for the synthetic chemistry of cyclopropenones, and none of the existing synthetic methods may be considered acceptably flexible and versatile by the modern standard of organic synthesis. The preparation of alkyl-substituted derivatives is imposed of particularly severe limitations of efficiency, reliability, and flexibility, and the overall yield of the preparation seldom exceeds 10% and averages about a few percent.[4] In addition, the existing methods are generally not amenable to the synthesis of cyclopropenones bearing functional groups.

Surprisingly enough, Nature produces these molecules, of which three compounds, **1**,[5] **2**,[6] and **3**,[6] have been isolated and characterized. Among them, an antibiotic, penitricin (**1**), isolated from a culture filtrate of fungal strain *Penicillium aculeatum* NR 5165[5a] is the first and the only reported cyclopropenone which shows significant biological activities. The lack of efficient synthesis[5c] however precluded the detailed studies of the biological function of these molecules, and their applications.



penitricin (**1**)



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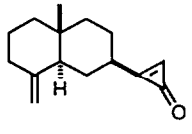
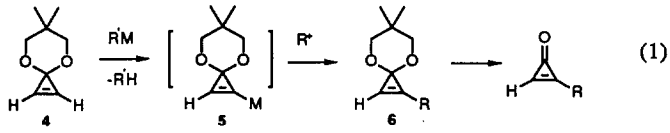


3

Conventional synthesis of cyclopropenones relies on one of the four strategies:[4a,d] (a) dichlorocarbene addition to an acetylene,[7] (b) addition of phenylchlorocarbene to a ketene acetal,[8] (c) basic cyclization of a 1,3-dibromoketone,[9] and (d) Friedel-Crafts arylation[10a] and alkylation[10b,c] of trichlorocyclopropenylium ion. All these routes have some intrinsic problems that preclude broad applications.

It is with this background that we have developed a general synthesis of cyclopropenones based on the chemistry of metalated cyclopropenone acetals **5**.[11] The synthesis outlined in eq 1 exploits the unusual acidity of the vinylic proton attached to a cyclopropene ring,[12] and is effective to introduce a variety of groups, including alkyl, aryl, and vinyl groups, to the latent cyclopropenone unit **4**. The metalated cyclopropene **5** serves here as a unique synthon of the elusive "cyclopropenone enolate". A variety of standard protective groups are tolerable on the R group, and disubstituted compounds become readily available simply by repetition of the sequence on **6**. The substituted acetal **6** can readily be hydrolyzed to the corresponding cyclopropenone.[13] A great merit of the synthesis is that one can manipulate the R group under basic conditions at the stage of the base-stable acetal, and under acidic conditions at the stage of acid-stable cyclopropenone. In addition, the reactions can be easily carried out on a 50-g scale typically in 70-90% overall yield. Thus, this synthetic sequence has opened a new avenue to the chemistry of cyclopropenones. We describe below the full details of this new synthetic method.



(1)

Results and Discussion

The preparation of the cyclopropenone acetal **4** was reported first in 1972 by Butler and co-workers,[14] and the dimethyl acetal (3,3-dimethoxycyclopropene, **7**)[14a] was used for a large-scale synthesis of cyclopropenone.[13] The trimethylene acetal **8**[14c] has been used as a source of a vinylcarbene that undergoes [3 + 2] and [1 + 2] cycloadditions to olefins.[15] We found that the acetal **4**[14a] derived from neopentyl glycol is the most synthetically useful because of its stability and availability (vide infra). In addition, neopentyl glycol derivatives possesses advantage over **8** in terms of its cost and simplicity of their NMR spectra.

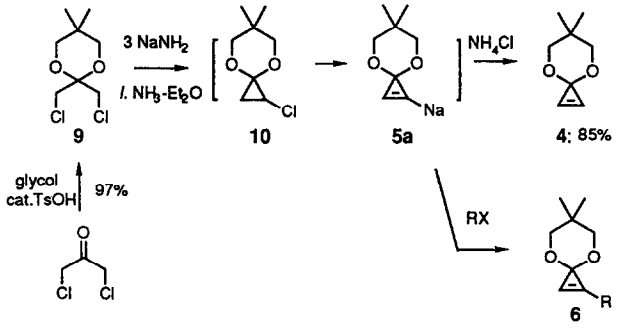
Butler's original preparation[14a] started with 2,3-dichloro-1-propene which was first converted to the dimethyl acetal of 1-bromo-3-chloroacetone by treatment with N-bromosuccinimide with methanol. Appropriate acetal exchange and cyclization with KNH_2 in liquid NH_3-Et_2O gives **4** or **8** in about 40% overall yield.

We found it unnecessary to start the synthesis with the bromochloroacetone acetal, but found instead that one can start with commercially available 1,3-dichloroacetone. This change dramatically improved the overall yield. We also found that commercially available $NaNH_2$ can be used instead of KNH_2, for which the original procedure calls for the use of metallic potassium. Thus, 1,3-dichloroacetone was acetalized with neopentyl glycol (97%), and then treated with 3.5 equivalents of $NaNH_2$ in liquid NH_3 to afford, after distillation, the acetal **4** in 85% yield (Scheme I).

The preparation of **4** from the dichloride **9** required three equivalents of $NaNH_2$, the use of smaller amounts of base resulted in the formation of the chlorocyclopropane **10**. Evidently, the third equivalent of

the base was consumed by the rapid formation of the sodium salt **5a**. Realizing this fact, we found a practical synthesis of alkyl-substituted cyclopropenone acetals (Scheme I). Thus, slow controlled addition of a primary alkyl iodide or bromide to the cyclization mixture containing **5a** at -78 °C followed by warming to -35 °C gave the desired mono-substituted acetal in 71-77% yield. The slow addition of the alkylating agent was necessary to avoid the formation of 2,3-dialkylated product, which could be minimized to ca. 5% under the optimized conditions.

Scheme I

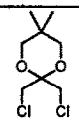
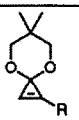
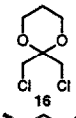
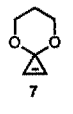
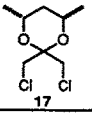
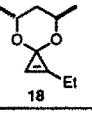


The application of the present procedure is summarized in Table I. The reaction permits the synthesis of a variety of cyclopropenone acetals derived from neopentyl glycol (entries 1-6), trimethylene glycol (entry 7), and chiral 2,4-pentanediol (entry 8). While primary alkyl bromides and iodides served well as electrophiles, secondary iodides and bromides gave poor yields of the alkylated products (entry 6). An experiment using 6-iodoundecane gave 5-undecene as a major product due to elimination of HI, together with the desired product (7%). Despite successful *alkylation* of the sodium salt **5a**, D_2O or aldehyde trapping of **5a** failed completely probably owing to the reaction of these electrophiles with liq. NH_3 before the reaction with **5a**.

Several observations were made during optimization of the conditions. (1) The sodium salt in liq. NH_3 is much more reactive toward alkyl halides, yet more stable than the corresponding lithium salt (vide infra). However, the inability of the sodium salt to add to aldehydes under the present conditions makes the lithium route[11a] (vide infra) an attractive alternative. (2) Use of the acetals derived from neopentyl glycol is beneficial over that of trimethylene acetals because of higher yield of cyclization (-50 °C, 30 min; 85% vs. 69%), and the higher stability of the sodium salt **5a** and the products **6**. Dimethyl acetals are least manageable in that the corresponding 1,3-dichloroacetone acetal cyclizes only slowly below -40°C, and the sodium salt decomposes above -30°C. In addition, the dimethyl acetal of cyclopropenone is noticeably less stable at room temperature than the corresponding 2,2-dimethyltrimethylene acetal.[16]

The preceding method, based on the in situ preparation of the sodiocyclopropene, is particularly suitable for large scale preparation of alkyl-substituted cyclopropenone acetals. However, the variety of the electrophiles is limited to primary alkyl halides. We describe below two other synthetic routes that rely on the reactions of the lithium (**5b**) and zinc (**5c**) salts of the cyclopropenone acetals. In addition to alkyl halides, these methods allow the use of carbonyl compounds, aryl and vinyl halides and triflates as electrophiles.

Table I. Alkylative Cyclization of Acetals of 1,3-Dichloroacetone.

entry	acetal	electrophile (equiv)	cyclopropenone acetal	isolated yield
	 9			
1		NH_4Cl	4: R = H	85%
2		MeI (1.5)	11: R = methyl	72%
3		EtBr (1.05)	12: R = ethyl	71%
4		*n*-BuI (1.2)	13: R = *n*-butyl	77%
5		*i*-AmBr (2)[a]	14: R = *i*-amyl	75%
6		*i*-PrBr (1.2)	15: R = *i*-propyl	24%
7	 16	NH_4Cl	 7	69%
8	 17	EtI (1.2)	 18	75%

[a]The bromide contains about 12% of 2-methylbutyl bromide, which did not take part in the reaction.

Optimization of the conditions for the generation of the lithiated cyclopropenone acetal **5b** was examined first, by treating the cyclopropenone acetal **4** with one equivalent of BuLi, and then with MeI (eq 1). Lithiation at -70 °C for 1 h in THF, followed by methylation (1.05 equiv MeI, -70 °C, 1 h) gave **11** in 66% yield as determined by gas chromatography. In contrast to **5a** in liquid NH_3, **5b** was thermally unstable. Thus, when the reaction mixture was warmed to -10~-20 °C before methylation (-70 °C), the yield of **11** dropped to 4% (with only 11% of **4** recovered). However, lithiation and methylation in the presence of hexamethylphosphoric triamide (HMPA) gave **11** in 94% yield (with 6% recovery of **4**), indicating that HMPA stabilizes **5b**.

Reaction of **5b** with BuI also proceeded cleanly with two equivalents of HMPA (Table II, entry 2). With one equivalent of HMPA, however, consumption of the cyclopropene stopped before completion of the reaction (entry 1). *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) or *N,N'*-dimethylpropyleneurea (DMPU) stabilize the lithium salt, but do not assist the alkylation reaction (entries 4 and 5).

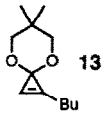
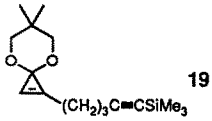
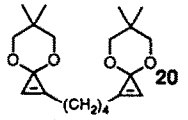
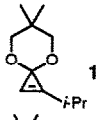
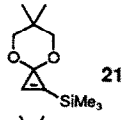
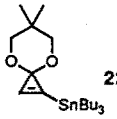
Other results with various organic halides are summarized in Table III. Butyl bromide reacted smoothly with **5b** (entry 1). The acetylene function in entry 2 is a type of functional group that is not

Table II. Butylation of the Lithiocyclopropene **5b**.

entry	additive (equiv)	BuI (equiv)	trapping conditions	% yield[a]	recovery[a]
1	HMPA (1)	2	-70 °C, 13 h	56	20
2	HMPA (2)	2	-70 °C, 13 h	93	6
3	HMPA (2.5)	2.5	-70 °C, 12 h	87[b]	-[c]
4	TMEDA (1.05)	1.2	-70~-30 °C, 6.5 h	trace	56
5	DMPU (1.05)	1.5	-70~-30 °C, 6.5 h	11	58

[a]Determined by ^{1}NMR using an internal standard. [b]Isolated yield. [c]Not determined.

Table III. Alkylation of the Lithium Salt **5b** in the Presence of HMPA.

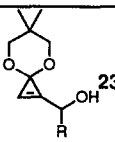
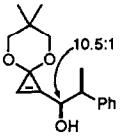
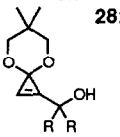
entry	RX (equiv)	trapping conditions[b]	cyclopropenone acetal	% yield[a]
1	$CH_3(CH_2)_3Br$ (1.5)	-70 → 0 °C, 4.5 h	 **13**	91
2	$Me_3SiC{\equiv}C(CH_2)_3I$ (1.1)	-70 → -40 °C, 5 h	 **19**	76
3	$I(CH_2)_4I$ (0.4)	-70 → -40 °C, 6.5 h	 **20**	82
4	$(CH_3)_2CHI$ (2)	-70 → -30 °C, 6 h	 **15**	24
5	Me_3SiCl (0.95)	-70 → r.t., 2 h	 **21**	75
6	Bu_3SnCl (0.91)	-70 °C, 2 h	 **22**	73

[a]Yield of purified, isolated products. [b]r.t. = room temperature.

compatible with the conventional synthesis via carbenes.[7] Biscyclopropenone acetal **20** was synthesized by the reaction of two equivalents of the cyclopropenyllithium **5b** with a 1,4-diiodobutane (entry 3). Secondary alkyl iodide (*i*-PrI, entry 4) gave a poor yield of the alkylation product owing to elimination of HI (vide supra). The reaction with Me_3SiCl in HMPA/THF gave trimethylsilylcyclopropene **21** together with a considerable amount of 2,3-bis(trimethylsilyl)cyclopropenone acetal, which was formed apparently by Li/H exchange involving **21**. This side reaction was eliminated by slow reverse addition of the lithium salt to a cooled THF solution of Me_3SiCl. None of such care was necessary for the reaction with Bu_3SnCl (entry 6).

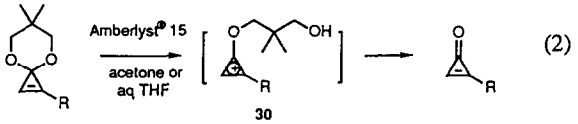
For the synthesis of penitricin (**1**), we needed to hydroxymethylate the lithium salt. Reaction of **5b** with solid paraformaldehyde was not successful at -70 to 0 °C. However, treatment of **5b** at -40 °C with gaseous formaldehyde generated by thermolysis of paraformaldehyde (at 160-170 °C),[17] followed by quenching with water gave the penitricin acetal **23** in 51% isolated yield (Table IV, entry 1). Polyether side products due to attachment of several hydroxymethyl groups could be removed by careful recrystalization. Unlike the sodium salt in liquid NH_3, the lithium derivative **5b** underwent nucleophilic addition to carbonyl compounds smoothly at -70 °C (within 1-60 min). In these reactions, TMEDA could successfully replace HMPA. It is interesting to note that addition of **5b** to 2-phenylpropionaldehyde showed unusually high diastereoselectivity[18] (10.5:1, entry 5).

Table IV. Addition of the Lithium salt **5b** to Carbonyl Compounds.

entry	carbonyl compound	6 (equiv)	product	%yield[a]
1	HCHO (10)	(1)	 **23**: R = H	51
2	CH_3CH_2CHO (1)	(1.2)	**24**: R = CH_3CH_2	84
3	$CH_3(CH_2)_6CHO$ (1)	(1.2)	**25**: R = $CH_3(CH_2)_6$	85
4	PhCHO (1.1)	(1)	**26**: R = Ph	93
5	$Ph(CH_3)CHCHO$ (1)	(1.2)	 10.5:1 **27**	82
6	$CH_3CH_2COCH_2CH_3$ (1)	(1.1)	 **28**: R = CH_3CH_2	94
7	cyclohexanone (1)	(1.1)	**29**: R = $(CH_2)_5$	92

[a]Yield of pure isolated products.

The cyclopropenone acetals were readily converted to the corresponding cyclopropenones by hydrolysis via cyclopropenylium ion intermediates (**30**) (eq 2). Thus, a solution of an acetal in acetone or aqueousTHF was treated at ambient temperature with Amberlyst® 15 (20-200 mg per 1 mmol of acetal). Filtration and separation of the neopentyl glycol by chromatography gave a variety of monosubstituted cyclopropenones (see Table V). The overall yield of penitricin from 1,3-dichloroacetone by the present route was 30%. The yield of the previous synthesis[5c] was about 1%.

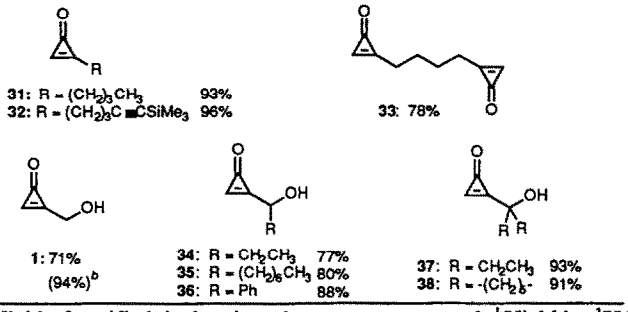


(2)

The silylated and stannylated acetals (**21** and **22**) were unstable under the conditions of hydrolysis. Treatment of the silyl compound **21** with Amberlyst® 15 gave the desired 2-trimethylsilylcyclopropenone only in 24% yield, and instead gave cyclopropenone in 40% yield. Reaction of the stannyl compound **22** under the same conditions gave a complex mixture.

A variety of vinyl- and arylcyclopropenones and their acetals have also become available by the palladium catalyzed reaction of the zinc salt **5c**. Addition of a 1 M THF solution (containing two equivalents of HMPA) of $ZnCl_2$ to the lithium salt **5b** gives the zinc salt **5c**, which is stable even at 50 °C in THF. The $Pd(PPh_3)_4$-catalyzed[19] coupling reaction of **5c** with vinyl iodides, vinyl triflates and aryl iodides proceeded smoothly in THF at room temperature to afford vinyl and aryl derivatives in high yield (Scheme II, Table VI). Hydrolysis of some of these acetals was found to be capricious, since the use of the sulfonic acid resin

Table V. Cyclopropenones by Hydrolysis of the Corresponding Acetals.[a]



[a]Yield of purified, isolated products except as noted. [b]Yield by ^{1}H NMR.

tended to cleave the three-membered ring. This problem was nicely solved by the use of Amberlyst® 15 treated with 2,6-di-*tert*-butylpyridine prior to use[20] (Amberlyst/DTBP) instead of Amberlyst® 15 itself. This mild polymeric acid may serve as a useful and readily removable equivalent of soluble pyridinium p-toluenesulfonate.[21]

Scheme II (For details, see Table VI).

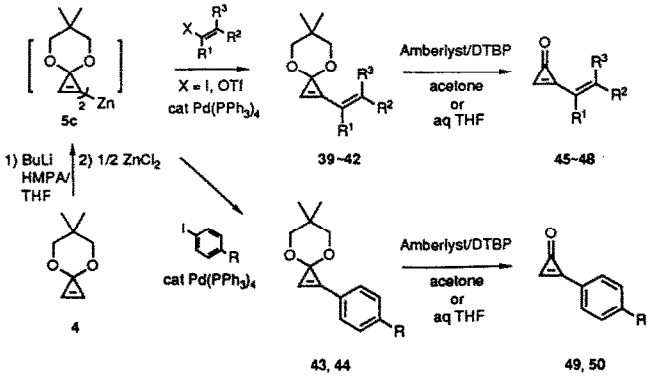
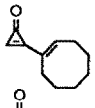
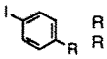
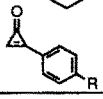
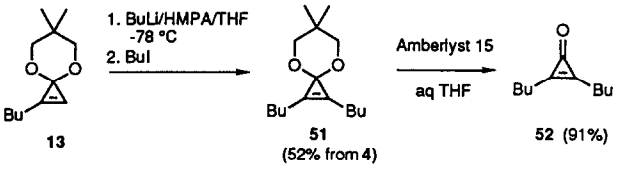


Table VI. Preparation of Vinyl- and Arylcyclopropenones.

electrophile	substd acetals, % yield[a]	cyclopropenone		% yield[b]
	39: 94		45	84 (94)[c]
	40: 87		46	99
	41: 95		47	92
	42: 83		48	80
 R = H R = OMe	43: 73 44: 79		49 50	93 92

[a]Isolated yield based on the electrophile. [b]Isolated yield. [c]Yield based on conversion.

Disubstituted cyclopropenones were synthesized by repetition of the metalation/alkylation sequence. For instance, lithiation of the butylcyclopropenone acetal **13** followed by trapping with BuI afforded the dibutylcyclopropenone acetal **51**. The acetal was hydrolyzed to the corresponding cyclopropenone in high yield.



13 **51** (52% from 4) **52** (91%)

The impact of the development of the present synthesis of cyclopropenone acetals has already been quite significant. It has provided access to a precursor of synthetically useful trimethylenemethanes[22] and vinylcarbenes,[23] that undergo [3 + 2] cycloadditions, and permitted the exploration of cyclopropenones as a key unit of biologically active molecules.[23] In addition, carbometalation at the strained olefinic portion of the molecule has opened a new avenue for asymmetric carbometalation reaction.[24] The method provides for the first time a general synthesis of cyclopropenones, and will help chemists to explore the full potential of the cyclopropenone chemistry in the future.

Experimental

General. ^{1}H NMR (200 and 270 MHz) and ^{13}C NMR (50 and 67.5 MHz) spectra were measured for a $CDCl_3$ solution of a sample on a JEOL FX-200 and a GSX-270 instruments. ^{1}H NMR spectra are reported in parts per million from internal tetramethylsilane, and ^{13}C NMR spectra from $CDCl_3$ (77.0 ppm). IR spectra were recorded on a Hitachi 260-10 instrument or a JASCO IR-800; absorptions are reported in cm^{-1}.

Material. Ethereal solvents were distilled from sodium benzophenone ketyl immediately before use. Hexamethylphosphoric triamide (HMPA) was distilled from calcium hydride under nitrogen and stored over molecular sieves. Tetramethylethylenediamine (TMEDA) was distilled from calcium hydride and stored under nitrogen. Amberlyst 15/DTBP was prepared by mixing Amberlyst 15® (1 g) and 2,6-di-*tert*-butylpyridine (DTBP, 1 mL) in hexane (5 mL), followed by filtration, and drying in vacuo (1 mmHg) at room temperature for 1 h.

Preparation of 1,3-Dichloroacetone Acetal 9. A mixture of 1,3-dichloroacetone (152 g, 1.2 mol), neopentyl glycol (138 g, 1.32 mol), *p*-toluenesulfonic acid (4.6 g, 0.024 mol), and benzene (100 mL) was refluxed for 19 h with azeotropic removal of water. The resulting solution was partitioned between hexane (500 mL) and sat. $NaHCO_3$ (200 mL). The organic phase was washed with water (100 mL) and with sat. NaCl (100 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Distillation (bp 99-100 °C, 3.5 mmHg) yielded 249 g (97%) of **9** as a colorless oil: IR (neat) 2950, 2860, 1105, 1025, 770; ^{1}H NMR ($CDCl_3$, 270 MHz) 1.00 (s, 6 H), 3.57 (s, 4 H), 3.80 (s, 4 H). Anal. ($C_8H_{14}O_2Cl_2$): C, H.

Trimethylene Acetal 16. Acetal **16** was similarly prepared from 1,3-dichloroacetone and 1,3-propanediol (69%): IR (neat) 2980, 2880, 1440, 1250, 1115, 1035, 770; ^{1}H NMR ($CDCl_3$, 270 MHz) 1.80 (m, 2 H), 3.80 (s, 4 H), 3.98 (dd, J = 5.8, 5.8 Hz, 4 H). Anal. ($C_6H_{10}O_2Cl_2$): C, H.

Chiral Acetal 17. Acetal **17** was synthesized by acetal exchange (89%) from the corresponding dimethyl acetal, which was prepared from 1,3-dichloroacetone and methyl orthoformate (Amberlyst 15®, CH_2Cl_2; 96%): IR (neat) 2970, 1220, 1140, 1025, 950, 760; ^{1}H NMR ($CDCl_3$, 270 MHz) 1.25 (d, J = 5.9 Hz, 6 H), 1.67 (t, J = 7.3 Hz, 2 H), 3.67 (d, J = 11.7 Hz, 2 H), 3.70 (d, J = 11.7 Hz, 2 H), 4.05 (m, 2 H).

General Procedure for the "One-Pot" Cyclization/Alkylation. 2-Ethylcyclopropenone Acetal 12. To a suspension of $NaNH_2$ (minimum assay 90%; 36.3 g, maximum 0.93 mol) in dry ammonia (400 mL) cooled at -70 °C was added a solution of the acetal **9** (63.9 g, 0.30 mol) in 150 mL of Et_2O in 30 min. Cooling bath was removed and the mixture was stirred for 1 h. An aliquot was removed and analyzed by GC (OV-1) for the content of chlorocyclopropane **10**. An appropriate amount of additional $NaNH_2$ was added and the mixture was stirred for 30 min. The flask was cooled to -70 °C, and ethyl bromide (23.5 mL, 0.315 mol) in 80 mL of Et_2O was added slowly during 1 h. After stirring for 10 min, the cooling bath was removed and the solution was stirred for 30 min, and solid NH_4Cl (20 g) was added. The bath was removed and ammonia was allowed to evaporate, during which ether (400 mL) was added slowly. The ethereal solution was filtered by suction, and the filtrate was concentrated. The residue was distilled to yield **12** as a colorless oil (35.8 g, 71 %; bp 50-52 °C, 1 mmHg): IR (neat) 2950, 1730 (w), 1280, 1070, 1020; ^1H NMR (270 MHz, $CDCl_3$) 1.01 (s, 3 H), 1.05 (s, 3 H), 1.22 (t, J = 7.3 Hz, 3 H), 2.55 (qd, J = 7.3, 1.2 Hz, 2 H), 3.61 (d, J = 10.3 Hz, 2 H), 3.63 (d, J = 10.3 Hz, 2 H), 7.32 (t, J = 1.2 Hz, 1 H).

The cyclization reaction was also carried out on a 0.6-mol scale, and quenched by addition of solid NH_4Cl to a solution of **5a**. Workup as above gave the cyclopropenone acetal **4** as a colorless oil in 85 % distilled yield.

General Procedure for the Reaction of Lithiocyclopropene 5b with Carbonyl Compounds. 2-(1-Hydroxyoctyl)cyclopropenone Acetal 25. To a solution of the cyclopropenone acetal **4** (0.93 mL, 6.6 mmol) and TMEDA (2.72 mL, 18 mmol) in THF (10 mL) at -70 °C was added 3.8 ml of BuLi (a 1.74 M solution in hexane, 6.6 mmol) over 5 min. After stirring for 0.5 h, octanal (0.94 mL, 6.0 mmol) was added dropwise, and the mixture was stirred for 1 h. The reaction was terminated by addition of a pH 7.4 phosphate buffer (1/15 M) in THF (1:5 by volume, 3.5 mL). After usual aqueous workup, crude product was purified on silica gel column to obtain the cyclopropenone acetal **25** (1.34 g, 85%): IR (neat) 3430, 2940, 2870, 1725, 1475, 1280, 1080; ^1H NMR ($CDCl_3$, 200 MHz) 0.88 (t, J = 7.2 Hz, 3 H), 1.03 (s, 3 H), 1.04 (s, 3 H), 1.26-1.32 (m, 8 H), 1.44-1.48 (m, 2 H), 1.70-1.76 (m, 2 H), 2.17 (br s, 1 H), 3.63 (s, 4 H), 4.71 (br s, 1 H), 7.47 (d, J = 1.2 Hz, 1 H).

General Procedure for the Hydrolysis of Cyclopropenone Acetals. 2-(1-Hydroxyoctyl)cyclopropenone (35). To a solution of the acetal **25** (1.07 g, 4 mmol) in THF (6 mL) was added Amberlyst® 15 (100 mg), and the suspension was stirred for 2 h at room temperature. The mixture was filtered and concentrated to afford a crude oily product. Purification on silica gel gave the cyclopropenone **35** as a white solid (0.58 g, 81%): mp 69 °C; IR (neat) 3400, 2930, 2860, 1590, 1465, 1080; ^1H NMR ($CDCl_3$, 60 MHz) 0.87 (m, 3 H), 1.2-2.0 (m, 12 H), 3.70 (d, J = 5 Hz, 1 H), 4.75 (m, 1 H), 8.44 (s, 1 H). Anal. ($C_{11}H_{18}O_2$): C, H.

General Procedure for the Synthesis of 2-Vinylcyclopropenone Acetals. Preparation of 2-(trans-1-Hexenyl)cyclopropenone Acetal 39. To a solution of the cyclopropenone acetal **4** (2.95 mL, 21 mmol) and HMPA (12.2 mL, 70 mmol) in THF (30 mL) at -70 °C was added BuLi (12.9 mL of a 1.63 M solution in hexane, 21 mmol) over 6 min. After stirring for 30 min, zinc chloride (10.5 mL of a 1 M solution in THF, 10.5 mmol) was added, and the dry ice-hexane bath was removed. $Pd(PPh_3)_4$ (0.75 g, 0.70 mmol) and *trans*-1-iodo-1-hexene (2.0 mL, 14 mmol) was added, and the mixture was stirred for 2 h. Triethylamine (0.7 mL) was added. The solution was diluted with hexane, and passed through a short column of silica gel (27 g, elution with 20% Et_2O in hexane). The filtrate was evaporated to afford an orange oil (3.5 g). Column chromatography on silica gel (elution with 5% ethyl acetate in hexane) afforded the title compound as a colorless oil (2.92 g, 94%): IR (neat) 3110, 1470, 1285, 1265, 1150, 1075, 1030, 1000; ^1H NMR ($CDCl_3$, 200 MHz) 0.91 (t, J = 6.9 Hz, 3 H), 1.02 (s, 3 H), 1.10 (s, 3 H), 1.22-1.54 (m, 4 H), 2.24 (q, J = 7.2 Hz, 2 H), 3.63 (s, 4 H), 6.12 (d, J = 16.4 Hz, 1 H), 6.38 (dt, J = 16.4, 7.2 Hz, 1 H), 7.29 (s, 1 H). Anal. ($C_{14}H_{22}O_2$): C, H.

Physical Properties of Substituted Cyclopropenone Acetals.

2-Methylcyclopropenone Acetal 11. *Rf* 0.20 (6% ethyl acetate in hexane); IR (neat) 2950, 1840 (w), 1735, 1280, 1070; ^1H NMR ($CDCl_3$, 200 MHz) 0.99 (s, 3 H), 1.07 (s, 3 H), 2.19 (s, 3 H), 3.63 (s, 4 H), 7.34 (s, 1 H). Anal. ($C_9H_{14}O_2$): C, H.

2-Butylcyclopropenone Acetal 13. *Rf* 0.25 (6% ethyl acetate in hexane); IR (neat) 2950, 2940, 2870, 2850, 1730, 1470, 1280, 1080, 1025, 995, 940, 740; ^1H NMR ($CDCl_3$, 200 MHz) 0.93 (t, J = 7.4 Hz, 3 H), 1.00 (s, 3 H), 1.06 (s, 3 H), 1.41 (m, 2 H), 1.60 (m, 2 H), 2.53 (t, J = 7.2 Hz, 2 H), 3.58 (d, J = ca. 11 Hz, 2 H), 3.61 (d, J = ca. 11 Hz, 2 H), 7.31 (br s, 1 H). Anal. ($C_{12}H_{20}O_2$): C, H.

2-iso-Amylcyclopropenone Acetal 15. *Rf* 0.25 (5% ethyl acetate in hexane); IR (neat) 2950, 1730 (w), 1470, 1280, 1075, 1025; ^{1}H NMR ($CDCl_3$, 270 MHz) 0.92 (d, J = 6.4 Hz, 6 H), 1.00 (s, 3 H), 1.52 (m, 1 H), 3.60 (d, J = 11.5 Hz, 2 H), 7.32 (s, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) 22.2, 22.4, 22.5, 23.0, 27.6, 30.4, 36.1, 77.1, 83.7, 115.2, 138.0. Anal. ($C_{13}H_{22}O_2 \cdot 0.49H_2O$): C, H.

Chiral 2-Ethylcyclopropenone Acetal 18. *Rf* 0.20 (5% ethyl acetate in hexane); IR (neat) 2970, 2930, 1720, 1135, 1020; ^{1}H NMR ($CDCl_3$, 200 MHz) 1.21 (t, J = 7.6 Hz, 3 H), 1.28 (d, J = 6.5 Hz, 2 H), 1.69 (m, 2 H), 2.51 (qd, J = 7.6, 1.5 Hz, 2 H), 4.28 (m, 2 H), 7.24 (t, J = 1.5 Hz, 1 H). Anal. ($C_{10}H_{16}O_2$): C, H.

2-[(5-Trimethylsilyl)pent-4-ynyl]cyclopropenone Acetal 19. *Rf* 0.40 (5% ethyl acetate in hexane); IR (neat) 2950, 2170, 1725, 1020, 840; ^{1}H NMR ($CDCl_3$, 200 MHz) 0.14 (s, 9 H), 1.00 (s, 3 H), 1.08 (s, 3 H), 1.85 (m, 2 H), 2.34 (t, J = 7.2 Hz, 2 H), 2.66 (t, J = 7.4 Hz, 2 H), 3.62 (br s, 4H), 7.40 (br s, 1H). Anal. ($C_{16}H_{26}O_2Si$): C, H.

Biscyclopropenone Acetal 20. *Rf* 0.20 (15% ethyl acetate in hexane); IR ($CHCl_3$) 2960, 2850, 1830, 1735, 1470, 1280, 1075, 1025, 995; ^{1}H NMR (CCl_4, 60 MHz) 0.97 (s, 6 H), 1.06 (s, 6 H), 1.46 (m, 4 H), 2.17 (m, 4 H), 3.55 (br s, 8 H), 7.37 (m, 2 H). Anal. ($C_{20}H_{30}O_4$): C, H.

2-(Trimethylsilyl)cyclopropenone Acetal 21. *Rf* 0.30 (5% ethyl acetate in hexane); IR (neat) 2950, 1640, 1470, 1295, 1250, 1080, 1030, 845; ^{1}H NMR (CCl_4, 60 MHz) 0.27 (s, 9 H), 0.91 (s, 3 H), 1.02 (s, 3 H), 3.34 (s, 4 H), 8.06 (s, 1 H). Anal. ($C_{11}H_{20}O_2$): C, H.

2-(Tributylstannyl)cyclopropenone Acetal 22. *Rf* 0.55 (10% ethyl acetate in hexane); IR (neat) 2950, 2920, 1615, 1460, 1245, 1075, 1025; ^{1}H NMR ($CDCl_3$, 200 MHz) 0.90-1.60 (m, 33 H), 3.59 (s, 4 H), 8.34 (s, 1 H). Anal. ($C_{20}H_{38}O_2Sn$): C, H.

Penitricin Acetal 23. *Rf* 0.20 (35% ethyl acetate in hexane); ^{1}H NMR ($CDCl_3$, 200 MHz) 1.02 (s, 3 H), 1.07 (s, 3 H), 2.09 (m, 1 H), 3.60-3.70 (m, 4 H), 4.72 (dd, J = 6.1, 1.7 Hz, 2 H), 7.54 (t, J = 1.7 Hz, 1 H). Anal. ($C_9H_{14}O_3$): C, H.

2-(1-Hydroxypropyl)cyclopropenone Acetal 24. *Rf* 0.25 (35% ethyl acetate in hexane); IR (neat) 3420, 2950, 1725 (w), 1470, 1270, 1080, 1020; ^{1}H NMR ($CDCl_3$, 200 MHz) 1.03 (s, 3 H), 1.04 (t, J = 7.4 Hz, 3 H), 1.06 (s, 3 H), 1.79 (m, 2 H), 2.21 (m, 1 H), 3.64 (s, 4 H). 4.67 (dt, J = 6.1, 5.7 Hz, 1 H), 7.51 (d, J = 1.0 Hz, 1 H). Anal. ($C_{11}H_{18}O_3$): C, H.

2-(α-Hydroxybenzyl)cyclopropenone Acetal 26. *Rf* 0.25 (30% ethyl acetate in hexane); mp 70-71 °C; IR ($CHCl_3$) 3420, 2960, 2960, 1720, 1460, 1280, 1035; ^{1}H NMR ($CDCl_3$, 200 MHz) 0.89 (s, 3 H), 1.08 (s, 3 H), 2.45 (d, J = 5.4 Hz, 1 H), 3.32 (d, J = 10.7 Hz, 1 H), 2.45 (dd, J = 11.0, 1.3 Hz, 1 H), 3.61 (m, 2 H), 5.82 (dd, J = 5.3, 1.3 Hz, 1 H), 7.40-7.50 (m, 5 H), 7.55 (d, J = 1.3 Hz, 1 H). Anal. ($C_{15}H_{18}O_3$): C, H.

2-(1-Hydroxy-2-phenylpropyl)cyclopropenone Acetal 27. *Rf* 0.25 (25% ethyl acetate in hexane); IR ($CHCl_3$) 3410, 2910, 1720, 1280, 1025, 705, 640; ^{1}H NMR ($CDCl_3$, 200 MHz) major diastereomer: 1.01 (s, 6 H), 1.39 (d, J = 7.2 Hz, 3 H), 2.07 (d, J = 5.9 Hz, 1 H), 3.15 (m, 1 H), 3.56 (s, 4 H), 4.83 (m, 1 H), 7.25-7.45 (m, 6 H, phenyl and cyclopropenyl); The following ^{1}H signals due to the minor diastereomer were observed: 1.44 (d, J = 7.2 Hz), 4.75 (dd, J = 7.8, 1.1 Hz). Anal. ($C_{17}H_{22}O_3$): C, H.

2-(1-Hydroxy-1-ethylpropyl)cyclopropenone Acetal 28. *Rf* 0.30 (30% ethyl acetate in hexane); IR (neat) 3450, 2960, 1720, 1280, 1090, 1030; ^{1}H NMR ($CDCl_3$, 200 MHz) 0.96 (t, J = 7.4 Hz, 6 H), 0.99 (s, 3 H), 1.06 (s, 3 H), 1.72-1.78 (m, 2 H), 1.94 (s, 1 H), 3.61 (s, 4 H), 7.49 (s, 1 H). Anal. ($C_{13}H_{22}O_3$): C, H.

2-(1-Hydroxycyclohexyl)cyclopropenone Acetal 29. *Rf* 0.25 (25% ethyl acetate in hexane); ^{1}H NMR ($CDCl_3$, 200 MHz) 1.00 (s, 3 H), 1.09 (s, 3 H), 1.40-1.90 (m, 11 H), 3.66 (s, 4 H), 7.51 (s, 1 H). Anal. ($C_{14}H_{22}O_3$): C, H.

2-(cis-1-Hexenyl)cyclopropenone Acetal 40. *Rf* 0.25 (6% ethyl acetate in hexane); IR (neat) 3100, 3010, 1710, 1470; ^{1}H NMR ($CDCl_3$, 200 MHz) 0.77 (s, 3 H), 0.97 (t, J = 6.9 Hz, 3 H), 1.23 (s, 3 H), 1.45 (m, 2 H), 2.46 (m, 2 H), 3.57-3.71 (m, 4 H), 5.95-6.14 (m, 2 H), 7.58 (s, 1 H). Anal. ($C_{14}H_{22}O_2$): C, H.

2-(1-Cyclooctenyl)cyclopropenone Acetal 41. *Rf* 0.25 (4% ethyl acetate in hexane); IR (neat) 3110, 3030, 1720, 1630, 1470, 1280, 1080, 1030, 1000; ^{1}H NMR ($CDCl_3$, 200 MHz) 1.00 (s, 3 H), 1.13 (s, 3 H), 1.43-1.66 (m, 8 H), 2.20-2.35 (m, 2 H), 2.45 (br t, J = 6.7 Hz, 2 H), 3.66 (s, 4 H), 6.35 (t, J = 8.4 Hz, 1 H), 7.31 (s, 1 H). Anal. ($C_{16}H_{24}O_2$): C, H.

2-(1-Cyclohexenyl)cyclopropenone Acetal 42. *Rf* 0.25 (5% ethyl acetate in hexane); IR (neat) 3100, 3030, 1710, 1690, 1480; ^{1}H NMR ($CDCl_3$, 200 MHz) 1.00 (s, 3 H), 1.08 (s, 3 H), 1.60- 1.74 (m, 4 H), 2.17-2.31 (m, 4 H), 3.63 (s, 4 H), 6.37 (br s, 1 H), 7.31 (s, 1 H). Anal. ($C_{14}H_{20}O_2$): C, H.

2-Phenylcyclopropenone Acetal 43. *Rf* 0.25 (4% ethyl acetate in hexane); IR (CCl_4) 3100, 2250, 1960, 1900, 1810, 1720, 1470, 1260; ^{1}H NMR ($CDCl_3$, 200 MHz) 1.08 (s, 3 H), 1.16 (s, 3 H), 3.87 (s, 4 H), 7.45 (m, 3 H), 7.65 (m, 2 H), 7.70 (s, 1 H). Anal. ($C_{14}H_{16}O_2$): C, H.

2-(4-Methoxyphenyl)cyclopropenone Acetal 44. *Rf* 0.30 (4% ethyl acetate in hexane); IR (CCl_4) 1820, 1610, 1510, 1475, 1280, 1260, 1170, 1080; ^{1}H NMR ($CDCl_3$, 200 MHz) 1.08 (s, 3 H), 1.15 (s, 3 H), 3.75 (s, 4 H), 3.84 (s, 3 H), 6.90-7.05 (m, 2 H), 7.52 (s, 1 H), 7.53-7.65 (m, 2 H). Anal. ($C_{15}H_{18}O_3$): C, H.

2,3-Dibutylcyclopropenone Acetal 51. *Rf* 0.30 (5% ethyl acetate in hexane); IR (neat) 2950, 2925, 2860, 1815, 1465, 1280, 1185, 1075, 990, 930; ^{1}H NMR ($CDCl_3$, 200 MHz) 0.94 (t, J = 7.2 Hz, 6 H), 1.03 (s, 6 H), 1.40 (m, 4 H), 1.59 (m, 4 H), 2.47 (t, J = 7.4 Hz, 4 H), 3.63 (s, 4 H). Anal. ($C_{16}H_{28}O_2$): C, H.

Physical Properties of Substituted Cyclopropenones.

2-Butylcyclopropenone (31). *Rf* 0.30 (2% acetone in CH_2Cl_2); IR (neat) 3050, 2960, 2875, 1835, 1590, 860; ^{1}H NMR (CCl_4, 60 MHz) 0.8-2.0 (m, 7 H), 2.67 (m, 2 H), 8.48 (br s, 1 H). Anal. ($C_7H_{10}O$): C, H.

2-[(5-Trimethylsilyl)pent-4-ynyl]cyclopropenone (32). *Rf* 0.60 (5% acetone in CH_2Cl_2); IR (neat) 2950, 2170, 1825, 1590, 840, 760; ^{1}H NMR ($CDCl_3$, 200 MHz) 0.15 (s, 9 H), 1.95 (m, 2 H), 2.40 (t, J = 6.1 Hz, 2 H), 2.83 (t, J = 7.4 Hz, 2 H), 8.28 (s, 1 H). Anal. ($C_{11}H_{16}OSi$): C, H.

Biscyclopropenone 33. Mp 102-103 °C; IR ($CHCl_3$) 3000, 2950, 1825, 1595; ^{1}H NMR ($CDCl_3$, 200 MHz) 1.20 (m, 4 H), 2.79 (m, 4 H), 8.55 (s, 2 H). Anal. ($C_{10}H_{10}O_2$): C, H.

Penitricin (1). The spectral properties fully coincided with the reported values; *Rf* 0.15 (ethyl acetate) IR (neat) 3350, 1940, 1835, 1585, 1065, 640; ^{1}H NMR ($CDCl_3$, 200 MHz) 3.41 (br s, 1 H), 4.79 (br s, 2 H), 8.56 (t, J = 1.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 67.5 MHz) 58.8, 146.7, 156.3, 169.5. Anal. ($C_4H_4O_2$): C, H.

2-(1-Hydroxypropyl)cyclopropenone (34). Full characterization was established after conversion to the corresponding trimethylsilyl ether (BSA/THF, r.t.; 72%): *Rf* 0.65 (10% acetone in hexane); IR (neat) 2960, 1835, 1590, 1255, 1015, 845; ^{1}H NMR ($CDCl_3$, 200 MHz) 0.17 (s, 9 H), 1.02 (t, J = 7.4 Hz, 3 H), 1.80 (m, 2 H), 4.71 (br t, J = ca. 7 Hz, 1 H), 8.46 (br s, 1 H). Anal. ($C_9H_{16}O_2Si$): C, H.

2-(α-Hydroxybenzyl)cyclopropenone (36). *Rf* 0.25 (ethyl acetate); IR (neat) 3340, 1840-1820, 1580; ^{1}H NMR ($CDCl_3$, 270 MHz) 3.91 (br s, 1 H), 5.86 (s, 1 H), 7.30-7.50 (m, 5 H), 8.48 (s, 1 H). Anal. ($C_{10}H_8O_2$): C, H.

2-(1-Hydroxy-1-ethylpropyl)cyclopropenone (37). *Rf* 0.35 (ethyl acetate); IR (neat) 3390, 2970, 1830, 1580, 1460; ^{1}H NMR ($CDCl_3$, 270 MHz) 0.99 (t, J = 7.4 Hz, 6 H), 1.82-1.86 (m, 4 H), 2.57 (s, 1 H), 8.51 (s, 1 H). Anal. ($C_8H_{12}O_2$): C, H.

2-(1-Hydroxycyclohexyl)cyclopropenone (38). *Rf* 0.20 (Et_2O); mp 82-82.5 °C; IR ($CHCl_3$) 3390, 2490, 2860, 1825, 1585, 1455, 1090; ^{1}H NMR ($CDCl_3$, 200 MHz) 0.90-2.10 (m, 10 H), 4.06 (br s, 1 H), 8.49 (s, 1 H). Anal. ($C_9H_{12}O_2$) C, H.

2-(trans-1-Hexenyl)cyclopropenone (45). *Rf* 0.30 (5% acetone in CH_2Cl_2); IR (neat) 3050, 1830, 1640, 1570; ^{1}H NMR ($CDCl_3$, 200 MHz) 0.93 (t, J = 7.4 Hz, 3 H), 1.25-1.60 (m, 4 H), 2.25-2.40 (m, 2 H),

6.21 (ddt, J = 15.6, 1.3, 1.3 Hz, 1 H), 6.96 (dt, *J* = 15.6, 6.9 Hz, 1 H), 8.09 (d, *J* = 1.3 Hz, 1 H). Anal. ($C_9H_{12}O$) C, H.

2-(cis-1-Hexenyl)cyclopropenone (46). *Rf* 0.30 (3% acetone in CH_2Cl_2); IR (neat) 3050, 1830, 1630, 1570; ^1H NMR ($CDCl_3$, 200 MHz) 0.92 (t, *J* = 7.6 Hz, 3 H), 1.22-1.60 (m, 4 H), 2.63 (br q, *J* = 7.6 Hz, 2 H), 6.18 (dq, *J* = 9.9, 1.8 Hz, 1 H), 6.59 (dt, *J* = 9.9, 7.6 Hz, 1 H), 8.19 (d, *J* = 1.8 Hz, 1 H). Anal. ($C_9H_{12}O$): C, H.

2-(1-Cyclooctenyl)cyclopropenone (47). *Rf* 0.30 (5% acetone in CH_2Cl_2); IR (neat) 1830, 1640, 1580; ^1H NMR ($CDCl_3$, 200 MHz) 1.43-1.71 (m, 8 H), 2.34-2.62 (m, 2 H), 2.51 (m, 2 H), 6.93 (t, *J* = 8.5 Hz, 1 H), 8.11 (s, 1 H). Anal. ($C_{11}H_{14}O \cdot 0.70H_2O$): C, H.

2-(1-Cyclohexenyl)cyclopropenone (48). *Rf* 0.25 (4% acetone in CH_2Cl_2); IR (neat) 3050, 1820, 1640, 1570; ^1H NMR ($CDCl_3$, 200 MHz) 1.72 (m, 4 H), 2.34 (m, 4 H), 6.92 (m, 1 H), 8.09 (s, 1 H). Anal. ($C_9H_{10}O \cdot 0.37H_2O$): C, H.

2-Phenylcyclopropenone (49). *Rf* 0.20 (5% acetone in CH_2Cl_2); IR (neat) 3060, 2830, 2720, 2100, 1990, 1940, 1830, 1610, 1580; ^1H NMR ($CDCl_3$, 200 MHz) 7.50-7.70 (m, 3 H), 7.83-7.90 (m, 2 H), 8.55 (s, 1 H). Anal. (C_9H_6O): C, H.

2-(4-Methoxyphenyl)cyclopropenone (50). *Rf* 0.30 (5% acetone in hexane); IR (CCl_4) 3010, 1980, 1910, 1880, 1840, 1610, 1500, 1260; ^1H NMR ($CDCl_3$, 200 MHz) 3.88 (s, 3 H), 7.03 (d, *J* = 9.1 Hz, 2 H), 7.83 (d, *J* = 9.1 Hz, 2 H), 8.27 (s, 1 H). Anal. ($C_{10}H_8O_2$): C, H.

2,3-Dibutylcyclopropenone (52). *Rf* 0.35 (2% acetone in CH_2Cl_2); IR (neat) 2950, 2925, 2860, 1845, 1635, 1465; ^1H NMR ($CDCl_3$, 200 MHz) 0.74 (t, *J* = 7.6 Hz, 6 H), 1.43 (m, 4 H), 1.69 (m, 4 H), 2.62 (t, *J* = 7.2 Hz, 4 H). Anal. ($C_{10}H_{18}O$) C, H.

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References and Notes

1. Halton, B.; Banwell, M. G. in *The Chemistry of the Cyclopropyl Group*: Rappoport, Z. Ed; Wiley: New York, 1987; chapter 21.

2. Greenberg, A.; Tomkins, R. P. T.; Dobrovolny, M.; Liebman, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 6855.

3. Cf. Staley, W. S.; Nordon, T. D.; Taylor, W. H.; Harmony, M. D. *J. Am Chem. Soc.* **1987**, *109*, 7641.

4. Review on cyclopropenone chemistry: (a) Potts, K. T.; Baum, J. S. *Chem. Rev.* **1974**, *74*, 189. (b) Eicher, T.; Weber, J. L. *Topics Curr. Chem.* **1975**, *57*, 1 (c) Krebs, A. W. *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 10. (d) Billups, W. E.; Moorehead, A. W. In *The Chemistry of the Cyclopropyl Group*, Rappoport, Z. Ed; Wiley: New York; 1987; chapter 24.

5. (a) Okuda, T.; Yoneyama, U.; Fujiwara, A; Furumai, T. *J. Antibiotics* **1984**, *37*, 712. (b) Okuda, T.; Yokose, K.; Furumai, T.; Maruyama, H. B. *J. Antibiotics* **1984**, *37*, 718. (c) Okuda, T.; Shimma, N.; Furumai, T. *J. Antibiotics* **1984**, *37*, 723. (d) Okuda, T.; Furumai, T. *J. Antibiotics* **1985**, *38*, 631.

6. Bohlmann, F.; Jakupovic, J.; Mueller, L.; Schuster, A. *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 292.

7. (a) Dehmlow, E. V.; *Angew. Chem. Int. Ed. Engl.***1974**, *13*, 170. Dehmlow, E. V. *Chem. Ber.* **1967**, *100*, 3829. (b) Seyforce, D.; Damrauer. R. *J. Org. Chem.* **1966**, *31*, 1660.

8. (a) Bird, C. W.; Harmer, A. F. *J. Chem. Soc. C* **1968**, 959. (b) Altman, L. J. *Diss. Abst.* **1966**, *26*, 5713.

9. (a) Breslow, R.; Altman, L. J.; Krebs, A.; Mohacsi, E.; Murata, I.; Peterson, R. A.; Posner, J. *J. Am. Chem. Soc.* **1965**, *87*, 1326 (b) McCorkindale, N. J.; Raphael, R. A.; Scott, W. T.; Zwanenburg, B. *J. Chem. Soc. Chem. Commun.* **1966**, 133.

10. (a) Tobey, S. W.; West, R. *J. Am. Chem. Soc.* **1964**, *86*, 4215. Zecher, D. C.; West, R. *J. Am. Chem. Soc.* **1967**, *89*, 153. West, R.; Zecher, D. C.; Goyert, W. *J. Am. Chem. Soc.* **1970**, *92*, 149. (b) Musigmann, K.; Mayr, H. ; de Meijere, A. *Tetrahedron Lett.* **1987**, *28*, 4517. (c) Musigmann, K.; Mayr, H. ; de Meijere, A. *Tetrahedron Lett.* **1990**, *31*, 1261.

11. Preliminary communications: (a) Isaka, M.; Matsuzawa, S.; Yamago, S.; Ejiri, S.; Miyachi, Y.; Nakamura, E. *J. Org. Chem.* **1989**, *54*, 4727. (b) Isaka, M.; Ando, R.; Morinaka, Y.; Nakamura, E. *Tetrahedron Lett.* **1991**, *32*, 1339.

12. Lithiation of simple cyclopropenes: (a) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1963**, *85*, 99. (b) Moiseenkov, A. M.; Czeskis, B. A.; Rudushevskaya, T. Yu.; Nesmayanova, O. A.; Semenovsky, A. V. *Tetrahedron Lett.* **1981**, *22*, 151; (c) Kirms, M. A.; Primke, H.; Stohlmeier, M.; de Meijere, A. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 462.

13. Breslow, R.; Pecoraro, J.; Sugimoto, T. *Organic Syntheses*; Wiley: New York, 1988; Collect. Vol. VI, p 361. See also ref 1.

14. (a) Dimethylacetal: Baucom, K. B.; Butler, G. B. *J. Org. Chem.* **1972**, *37*, 1730; Cook, G. A.; Butler, G. B. *J. Macromol. Sci-Chem.* **1985**, *A22*, 483. (b) Cyclic acetals: Butler, G. B.; Herring, K. H.; Lewis, P. L.; Sharpe, III, V. V.; Veazey, R. L. *J. Org. Chem.* **1977**, *42*, 679. (c) Boger, D. L.; Brotherton, C. E.; Georg, G. I. *Org. Synth.* **1987**, *65*, 32.

15. Boger, D. L.; Brotherton, C. E. *Advances in Cycloaddition*; JAI Press: Greenwich; 1990, Vol. II, p 147. Boger, D. L.; Brotherton, C. E. *J. Am. Chem. Soc.* **1986**, *108*, 6695.

16. **Note: During vacuum distillation of the dimethyl acetal of cyclopropenone, the residue in a distillation pot caught fire spontaneously in air a few minutes after the pot was removed from the distillation apparatus.** None of such events have been encountered with the much more stable 2,2-dimethyltrimethylene acetals.

17. Smith, III, A. B.; Branca, S. J.; Guuaciaro, A.; Wovkulick, P. M.; Korn, A. *Org. Synth.* **1983**, *61*, 65.

18. Stereochemistry was assigned by assuming that the addition took place in accordance with Cram's rule. Cram, D. J.; Abd Elhafez, F. A. *J. Am. Chem. Soc.* **1952**, *74*, 5828. Cram, D. J.; Kopecky, K. R. *J. Am. Chem. Soc.* **1959**, *81*, 2748. Cram, D. J.; Wilson, D. R. *J. Am. Chem. Soc.* **1963**, *85*, 1245.

19. Negishi, E.; Valente, L. F.; Kobayashi, M. *J. Am. Chem. Soc.* **1980**, *102*, 3298.

20. The resin neutralized with pyridine was too unreactive.

21. Sterzycki, R. *Synthesis*, **1979**, 794. Miyashita, M.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772.

22. Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* **1989**, *111*, 7285. Yamago, S.; Nakamura, E. *J. Org. Chem.* **1990**, *55*, 5553. Nakamura, E.; Yamago, S.; Ejiri, S.; Dorigo, A. E.; Morokuma, K. *J. Am. Chem. Soc.* **1991**, *113*, 3183.

23. Unpublished results by H. Tokuyama.

24. Nakamura, E.; Isaka, M.; Matsuzawa, S. *J. Am. Chem. Soc.* **1988**, *110*, 1297. Isaka, M.; Nakamura, E. *J. Am. Chem. Soc.* **1990**, *112*, 7248.