Base-Induced Cyclization of α-Chloro β,γ-Unsaturated Ketones. Facile Synthesis of Tri- and Tetrasubstituted 2-Cyclopenten-1-ones

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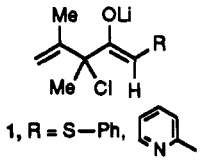
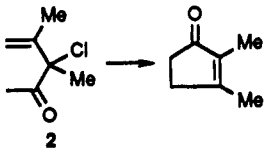
Base-induced cyclization of fully substituted α-chloro β,γ-unsaturated ketones results in substituted cyclopentenones. Potassium *tert*-butoxide, lithium diisopropylamide, sodium hydroxide, and ammonium hydroxide can be used as the base for this process. In the case of ammonium hydroxide, it is proposed that initial formation of an enamine is followed by an intramolecular S_N2' reaction of the enamine carbon. For all other bases, the reaction most likely proceeds through a ketone enolate. Application of this novel cyclization has been extended to the synthesis of several 2,3-disubstituted, 2,3,5-trisubstituted, and 2,3,5-tetrasubstituted 2-cyclopenten-1-ones.

Nearly a decade ago, Wolinsky and co-workers[1,2] reported the synthesis of α-chloro β,γ-unsaturated ketones from α,β-unsaturated ketones and hypochlorous acid. The utility of these reagents in organic synthesis was demonstrated by the facile synthesis of (+)-menthofuran from (+)-pulegone by conversion with HOCl to 4-chloroisopulegone and then via acid- or base-catalyzed cyclization.[3]

Our own interest in α-chloro β,γ-unsaturated esters resulted in the discovery of a novel cyclopentenone annelation when these esters were allowed to react with sulfur and nitrogen-stabilized carbanions.[4-6] These facile annelations were proposed to proceed through an intermediate keto-enolate 1.



The cyclization of the keto-enolate 1 to cyclopentenone proceeded at low temperature (−78 °C), and neighboring group participation by sulfur and nitrogen was strongly implicated. We were, however, intrigued with the possibility of extending this novel cyclization to ketone enolates of fully substituted α-chloro β,γ-unsaturated ketones such as 2.



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Since ketones such as 2 are easily prepared from the corresponding α,β-unsaturated ketones using HOCl,[1,2] we investigated this possibility. Thus, exposure of 2 to 1 equiv of lithium diisopropylamide in tetrahydrofuran at −78 °C gave an orange solution of the keto-enolate. Aqueous acidic workup after 15 min at −70 °C gave only the starting ketone 2. Thus the ketone enolate derived from 2 unlike the heteroatom-stabilized enolate 1 fails to undergo this cyclization at low temperature, implying that the participation of the heteroatom is accelerating the rate of this cyclization. However, it was found that slowly warming a solution of the enolate derived from 2 to room temperature and aqueous acidic workup gave the expected cyclopentenone in acceptable yield. Furthermore, several other strong bases can effect this transformation in high yield in the presence of hexamethylphosphorous triamide as an added cosolvent.

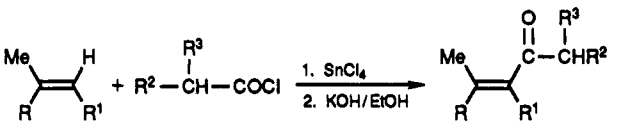
More importantly, it was found that this cyclization can also be effected with 4 N NaOH under phase-transfer conditions in excellent yields. This result is important from an economical point of view, since many of these cyclopentenones are commercially important products.[7] Quite by chance, it was also found that aqueous ammonium hydroxide can convert certain of these α-chloro β,γ-unsaturated ketones to cyclopentenones. This transformation probably proceeds through the initial formation

Table I. Synthesis of α,β-Unsaturated Ketones from Mesityl Oxide[8,9]

$$(Me)_2C{=}CHCOMe \xrightarrow[2.\ TsOH]{1.\ NaNH_2/RX} (Me)_2C{=}CRCOMe$$

R	X	product no.	yield, %
Me	I	3	74
$PhCH_2$	Cl	4	61
n-C_5H_{11}	I	5	66
$CH_2{=}CHCH_2$	Br	6	57

Table II. Synthesis of α,β-Unsaturated Ketones from Olefins[10,11]



R	R^1	R^2	R^3	product no.	yield, %
Me	Me	H	H	3	62
Me	Me	Me	H	7	71
Me	Me	Me	Me	8	68
Me	Me	$-(CH_2)_5-$		9	70
Me	Me	$-(CH_2)_3-$		10	64

[a] Isolated yield after flash column chromatography.

More importantly, it was found that this cyclization can also be effected with 4 N NaOH under phase-transfer conditions in excellent yields. This result is important from an economical point of view, since many of these cyclopentenones are commercially important products.[7] Quite by chance, it was also found that aqueous ammonium hydroxide can convert certain of these α-chloro β,γ-unsaturated ketones to cyclopentenones. This transformation probably proceeds through the initial formation

† This work was completed at Petrolite Corporation, St. Louis, MO, and is covered by a pending U.S. patent assigned to Petrolite.

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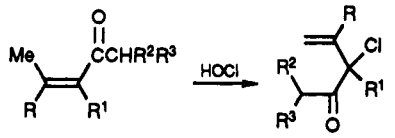
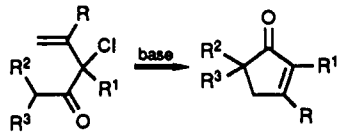
Table III. Synthesis of α-Chloro β,γ-Unsaturated Ketones



R	R^1	R^2	R^3	product	yield,[a] %
Me	Me	H	H	2	78
Me	Me	H	Me	11	81
Me	Me	Me	Me	12	74
Me	Me	$-(CH_2)_5-$		13	72
Me	Me	$-(CH_2)_3-$		14	65
Me	Bn	H	H	15	85
Me	n-C_5H_{11}	H	H	16	81

[a] Isolated yield after filtering through silica gel.

Table IV. Synthesis of Substituted Cyclopentenones



R	R^1	R^2	R^3	product	yield,[a] %	method[b]
Me	Me	H	H	17	61	B
					65	D
Me	Me	H	Me	18	56	C
					63	E
Me	Me	Me	Me	19	59	C
Me	Me	$-(CH_2)_5-$		20	66	C
Me	Me	$-(CH_2)_3-$		21	52	C
Me	Bn	H	H	22	68	A
					70	D
Me	n-C_5H_{11}	H	H	23	68	B

[a] Isolated yield after flash column chromatography. [b] Method A: KtBuO/THF/HMPA. Method B: LDA/THF/HMPA. Method C: $KN(Si(Me)_2)_2$/THF/HMPA. Method D: 4 N NaOH/THF/H_2O/n-$(Bu)_4NBr$. Method E: aqueous NH_4OH.

of an enamine. This aspect of the cyclization will be discussed later in the article.

It was found that a variety of fully substituted α,β-unsaturated ketones could be converted to substituted cyclopentenones in two steps. These α,β-unsaturated ketones were prepared by resorting to two methods in the literature. These are exemplified in Tables I and II.

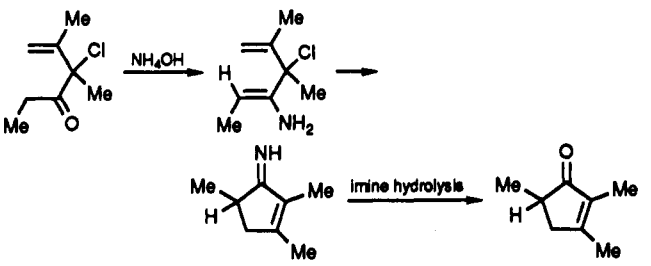
Although, this method allowed the preparation of several 3-alkyl-4-methyl-3-penten-2-ones in reasonably good yields, it is not suitable for the introduction of different groups at the 1- or 4-position. All of the unsaturated ketones listed in Tables I and II reacted with HOCl (generated with calcium hypochlorite/acetic acid) at 0 °C to give the allylic chlorides listed in Table III in fair to good yield.

Since these allylic halides partially decomposed during flash column chromatography the crude material was filtered through silica gel using hexane as the eluting solvent to remove polar impurities. The material thus obtained was characterized by ^1H and ^{13}C NMR spectra and used immediately for the cyclization.

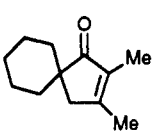
All of the allylic halides listed in Table III underwent base-induced cyclization to cyclopentenones in acceptable yields. The product yields and the method used for the cyclizations are listed in Table IV.

Despite several attempts starting materials were obtained when allylic halides **12**, **13**, and **14** were allowed to cyclize using methods A, D, or E. With these allylic halides it is logical to assume that there are steric interactions that inhibit the cyclization. Therefore, it is necessary to generate the enolate in high concentration using a strong base in a polar aprotic solvent. The synthesis of **20** from ketone

Scheme I



enolate of **13** under forcing reaction conditions is in marked contrast to the preparation of **24** from the reaction of 2-lithio-1,3-dithiane with ethyl 2-chloro-2,3-dimethyl-3-butenoate at −70 °C, which proceeds through a keto-thio enolate[5] **25**. This result provides further evidence for the proposed sulfur assisted S_N2' reaction of the keto-thio enolate. As is evident from Table IV, tetrasubstituted



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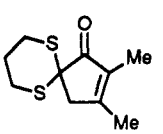

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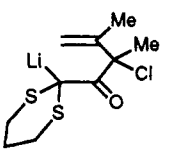

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cyclopentenones can be easily prepared from readily available starting materials in good yields. The present method complements the well-known synthesis of 5-substituted cyclopentenones by the internal acylation of vinylsilanes.[12] Although spiro[4.5]dec-2-en-1-ones similar to **21** can be prepared using the vinylsilane chemistry, this cannot be extended to the synthesis of 2,3-dialkyl-substituted ones. Trost[13] has recently reported the synthesis of several spirocycles by a novel cyclocontraction–spiroannulation reaction of vinyl keto sulfones with Lewis acid. However, this results in 2-unsubstituted spiro[4.5]dec-2-en-1-ones.

Dihydrojasmone (**23**) can be prepared in good yield starting from the readily available and inexpensive mesityl oxide in three steps. This is of importance in the manufacture of this perfumery ingredient.[14] However, all attempts to synthesize desoxyallethrolone using this chemistry were unsuccessful since hypochlorous acid conversion of the enone **6** to the allylic halide was accompanied by chlorohydrin formation of the isolated double bond. Similar problems were encountered in the attempted synthesis of *cis*-jasmone.

The reaction of these allylic halides with aqueous ammonia to generate cyclopentenones is very appealing since it does not require the use of a strong base. The reaction most likely proceeds through the initial formation of an enamine which undergoes an intramolecular S_N2' reaction on the enamine carbon (Scheme I).

Although intramolecular abnormal S_N2 cyclizations appear to have been not reported for enamines, the corresponding intermolecular S_N2' reaction is well documented.[15]

2,3-Dimethyl-2-cyclopenten-1-one (**17**) can be obtained in 44% overall yield in three steps starting from mesityl

(12) (a) Nakamura, E.; Fukuzaki, K.; Kuwajima, I. *J. Chem. Soc., Chem. Commun.* **1983**, 499. (b) For application of vinylsilane to synthesis of fused cyclopentenones, see: Cooke, F.; Moerck, R.; Schwindeman, J.; Magnus, P. *J. Org. Chem.* **1980**, *45*, 1046 and references therein.

(13) Trost, B. M.; Adams, B. R. *J. Am. Chem. Soc.* **1983**, *105*, 4849.

(14) For efficient synthesis of dihydrojasmone, see: (a) Stetter, H.; Kuhlmann, H.; Haese, W. *Org. Synth.* **1987**, *65*, 26. (b) Hosomi, A.; Shirahata, A.; Araki, Y.; Sakurai, H. *J. Org. Chem.* **1981**, *46*, 4631.

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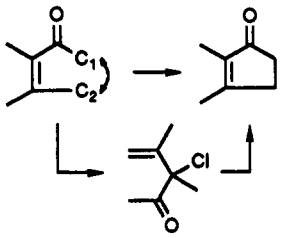
oxide and by using ammonium hydroxide cyclization of 2. Since enone 17 can be converted to the antibiotic methylenomycin-B by known literature methods[16] in high yield, the present method is comparable to previous efficient routes[17] for synthesis of this antibiotic. From a synthetic point of view, the key feature of this novel cyclization that makes it appealing is shown below.



The reaction simply involves connecting together of the carbons labeled 1 and 2 to give the product cyclopentenone. However, this is achieved in a masked fashion since the enone has to be converted to the allylic halide. This also implies that any fully substituted enone that can be converted to the allylic halide will undergo this transformation provided there is an enolizable hydrogen at the carbon labeled 1. Because of the biological importance and tremendous diversity of cyclopentanoid natural products, it is hoped that further application of this transformation can be put to test in organic synthesis.

Conclusions

Efficient syntheses of substituted cyclopentenones have been achieved by the base-induced cyclization of fully substituted α-chloro β,γ-unsaturated ketones. Although a wide range of bases can be used for this process, the use of aqueous ammonium hydroxide is particulary noteworthy. Using this novel route, rapid construction of the spiro[4.5]decane and spiro[3.4]octane ring systems has been been achieved.

Experimental Section

^{13}C NMR spectra were obtained at 15.04 MHz. ^1H NMR spectra were obtained at 90 or 300 MHz. NMR data were obtained in $CDCl_3$ solution. Flash column chromatography[18] was performed with silica gel 60 (230–440 mesh) purchased from Merck. All commercial chemicals were used as received. Tetrahydrofuran used was either distilled from $LiAlH_4$ or Gold Label anhydrous grade supplied by Aldrich Chemical Co. Reagent grade CH_2Cl_2, EtOAc, hexane, and ether were used. All reactions were done under nitrogen unless specified. All products obtained were liquids unless specified otherwise.

2,4,5-Trimethyl-4-hexen-3-one (8) was prepared from isobutyrl chloride and 3-methyl-2-butene following the general procedure.[10] This was purified by flash column chromatography (5% EtoAc/hexane). ^1H NMR: δ 2.96 (m, 1 H), 1.85 (s, 3 H), 1.73 (s, 3 H), 1.2 (s, 3 H), 1.02 (d, J = 7 Hz, 6 H). ^{13}C NMR: δ 212.12, 131.43, 113.24, 38.73, 22.26, 20.74, 18.21, 15.65, 14.13. IR (neat): 1700 cm^{-1}. Anal. Calcd for $C_9H_{14}O$: C, 78.26; H, 10.14. Found: C, 78.42; H, 10.27.

1-Cyclohexyl-2,3-dimethyl-2-buten-1-one (9) was prepared from cyclohexanecarbonyl chloride and 3-methyl-2-butene by the general procedure.[10] Purified by flash column chromatography (5% EtoAc/hexane). ^1H NMR: δ 2.60 (m, 1 H), 1.82 (s, 3 H), 1.70 (s, 6 H), 1.75 (m, 4 H), 1.25 (m, 6 H). ^{13}C NMR: δ 211.40, 134.76, 115.50, 49.04, 31.63, 28.63, 26.03, 25.89, 22.69, 22.11, 15.67, 14.88. IR: 1696 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O$: C, 80.01; H, 11.11. Found: C, 80.17; H, 11.24.

1-Cyclobutyl-2,3-dimethyl-2-buten-1-one (10) was prepared from cyclobutanecarbonyl chloride and 3-methyl-2-butene by the general procedure.[10] ^1H NMR: δ 3.40 (m, 1 H), 2.20–1.70 (m, 6 H), 1.85 (s, 3 H), 1.70 (s, 6 H). IR (neat) 1690, 1610 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O$: C, 78.94; H, 10.52. Found: C, 78.76; H, 10.63.

3-Benzyl-4-methyl-3-penten-2-one (4) was prepared by a modification of the literature method.[8,9] To a stirred solution of sodium amide (60 mmol, prepared from sodium (1.4 g, 60 mmol) and ammonia) in liquid ammonia (100 mL) was added dropwise mesityl oxide (6.0 g, 60 mmol) in ether (10 mL). After 20 min, benzyl chloride (7.7 g, 61 mmol) in ether (4 mL) was added. The pale green suspension was then stirred for 1 h, and then the ammonia was allowed to evaporate while ether was added. The resulting slurry was stirred with water (25 mL), and the organic layer was separated. The organic layer was washed with 5% HCl (20 mL) and processed to give a yellow oil (9 g). This was mixed with p-toluenesulfonic acid (200 mg) and refluxed for 20 min. Flash column chromatography of the cooled reaction mixture (eluting with 5% EtOAc/hexane) gave the enone 4 (6.2 g, 61%). ^1H NMR: δ 7.20 (m, 5 H), 3.65 (s, 2 H), 2.15 (s, 3 H), 1.90 (s, 3 H), 1.80 (s, 3 H). ^{13}C NMR: δ 206.56, 141.50, 131.59, 130.18, 129.68, 127.96, 117.50, 36.85, 31.84, 23.96, 23.11. IR (neat) 1695, 1620 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O$: C, 82.97; H, 8.51. Found: C, 82.76; H, 8.43.

4-Methyl-3-pentyl-3-penten-2-one (5) was prepared by the above method using pentyl bromide as the alkylating agent. ^1H NMR: δ 2.25 (s, 3 H), 2.15 (t, J = 6 Hz, 2 H), 1.80 (s, 3 H), 1.70 (s, 3 H), 1.25 (m, 6 H), 0.85 (t, J = 6 Hz, 3 H). ^{13}C NMR: δ 206.50, 139.23, 116.05, 32.87, 30.98, 29.87, 28.24, 23.65, 23.61, 22.44, 15.08. Anal. Calcd for $C_{11}H_{20}O$: C, 78.57; H, 11.90. Found: C, 78.42; H, 11.78.

3-Chloro-3,4-dimethyl-4-penten-2-one (2). To a stirred ice-cold solution of **3**[9] (11.2 g, 100 mmol) in CH_2Cl_2 (500 mL) was added $Ca(OCl)_2$ (10.6 g, 74.6 mmol) and water (50 mL). Glacial acetic acid (6.0 g, 100 mmol) was added dropwise at such a rate so that the internal temperature did not exceed 5 °C. After stirring at this temperature for 20 min the mixture was diluted with water (100 mL). The organic layer was separated, washed with $NaHCO_3$ (100 mL) and water (100 mL), and dried over $CaCl_2$ and $MgSO_4$. Evaporation of solvents at 25 °C under vacuum gave crude yellow oil. This was filtered through silica gel (20 g), eluting with hexane. The colorless solution was evaporated to give allylic halide **2** as an oil sufficiently pure for the cyclization. ^1H NMR: δ 5.30 (s, 1 H), 5.10 (s, 1 H), 2.25 (s, 3 H), 1.85 (s, 3 H), 1.75 (s, 3 H). ^{13}C NMR: δ 205.76, 120.05, 115.20, 57.45, 26.17, 24.69, 19.48.

4-Chloro-4,5-dimethyl-5-hexen-3-one (11). Following the general procedure, enone **7**[10] gave after flash column chromatography **11** as a pale yellow oil. ^1H NMR: δ 5.35 (s, 1 H), 5.15 (s, 1 H), 2.70 (q, J = 7 Hz, 2 H), 1.96 (s, 6 H), 1,15 (t, J = 7 Hz, 3 H). ^{13}C NMR: δ 205.67, 120.23, 117.65, 59.76, 28.56, 24.45, 19.76, 12.32. Anal. Calcd for $C_8H_{13}OCl$: C, 59,81; H, 8.09; Cl, 22.11. Found: C, 59.54; H, 7.86; Cl, 21.78.

4-Chloro-2,4,5-trimethyl-5-hexen-3-one (12): ^1H NMR: δ 5.34 (s, 1 H), 5.12 (s, 1 H), 3.31 (septet, J = 6 Hz, 1 H), 1.75 (s, 6 H), 1.14 (d, J = 6 Hz, 6 H). ^{13}C NMR: δ 205.89, 120.68, 116.78, 58.98, 36.34, 24.45, 19.67, 11.65. Anal. Calcd for $C_9H_{15}OCl$: C, 61.89; H, 8.59; Cl, 20.34. Found: C, 61.54; H, 8.37; Cl, 20.12.

2-Chloro-1-cyclohexyl-3-methyl-3-buten-1-one (13). ^1H NMR: δ 5.35 (s, 1 H), 5.10 (s, 1 H), 3.05 (m, 1 H), 1.80 (s, 3 H), 1.75 (s, 3 H), 1.65 (m, 4 H), 1.25 (m, 6 H). ^{13}C NMR: δ 208.84, 143.48, 115.65, 78.50, 45.46, 31.26, 30.73, 26.36, 25.84, 25.76, 19.97.

2-Chloro-1-cyclobutyl-3-methyl-3-buten-1-one (14). ^1H NMR: δ 5.25 (s, 1 H), 5.05 (s, 1 H), 3.70 (m, 1 H), 2.40–1.85 (m, 6 H), 1.80 (s, 3 H), 1.75 (s, 3 H). ^{13}C NMR: δ 206.48, 143.45, 114.52, 87.05, 40.90, 27.24, 26.11, 19.50, 18.14. Anal. Calcd for $C_{10}H_{15}OCl$: C, 64.34; H, 8.04; Cl, 19.03. Found: C, 64.07; H, 8.17; Cl, 19.24.

3-Benzyl-3-chloro-4-methyl-4-penten-2-one (15). ^1H NMR: δ 7.25 (m, 5 H), 5.15 (s, 1 H), 5.10 (s, 1 H), 3.35 (s, 2 H), 2.25 (s, 3 H), 1.80 (s, 3 H). ^{13}C NMR: δ 203.64, 141.70, 136.14, 131.43, 128.28, 127.36, 117.07, 81.35, 42.84, 25.80, 20.25. Mass spectrum: m/e 223, 187, 171.

3-Chloro-4-methyl-3-pentyl-4-penten-2-one (16). ^1H NMR: δ 5.40 (s, 1 H), 5.20 (s, 1 H), 2.25 (s, 3 H), 2.05 (m, 2 H), 1.80 (s, 3 H), 1.25 (m, 6 H), 0.90 (t, J = 7 Hz, 3 H). ^{13}C NMR: δ 206.45,

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138.98, 117.50, 81.50, 36.65, 31.24, 24.97, 23.88, 22.56, 19.63, 14.01. Mass spectrum: m/e 202, 167. Anal. Calcd for $C_{11}H_{19}OCl$: C, 65.18; H, 9.38; Cl, 17.53. Found: C, 64.86; H, 9.16; Cl, 17.27.

Base-Induced Cyclization Methods. Method A: Using Potassium *tert*-Butoxide in THF–HMPA. To a stirred solution of potassium *tert*-butoxide (1.12 g, 10 mmol) in THF (10 mL) at −70 °C was added hexamethylphosphortriamide (2 mL). A solution of the appropriate allylic halide (9 mmol) in THF (10 mL) was added dropwise in the course of 5 min, and the yellow solution was warmed to 25 °C in the course of 1 h (TLC monitoring indicated disappearance of starting material) and then quenched with aqueous NH_4Cl (10 mL) and extracted with ether (2 × 20 mL). The ether extracts were washed with water (10 mL) and dried. Evaporation gave the crude cyclopentenone, which can be purified by flash column chromatography. The best eluting solvent for these enones was found to be 20% EtOAc/hexane.

Method B: Using Lithium Diisopropylamide in THF–HMPA. To a stirred solution of diisopropylamine (2 g, 20 mmol) in THF (20 mL) at 0 °C was added 2.5 M *n*-BuLi in hexane (8 mL, 20 mmol) dropwise via syringe. After 30 min the yellow solution was cooled to −78 °C, and HMPA (2 mL) was added via syringe. Then a solution of the appropriate allylic halide (20 mmol) in THF (10 mL) was added dropwise via syringe in the course of 5 min. The deep yellow solution was warmed to room temperature in the course of 1 h (TLC monitoring indicated that the lower R_f product formed above 0 °C). The orange solution was now quenched with 1 N NH_4Cl (20 mL) and extracted with ether (2 × 20 mL). The ether extract washed with water (2 × 10 mL) and dried. Evaporation of solvent followed by flash column chromatography gave the appropriate cyclopentenone.

Method C: Using Potassium Hexamethyldisilazide in THF–HMPA. To a stirred solution of potassium bis(trimethylsilyl) amide (2 g, 10 mmol) in THF (10 mL) was added HMPA (2 mL). The deep yellow solution cooled to −78 °C, and a solution of the appropriate allylic halide (10 mmol) in THF (10 mL) was added dropwise in the course of 10 min. The orange solution was kept at −78 °C for 30 min and then slowly warmed to room temperature (~1 h). The red brown solution was then quenched with 1 N NH_4Cl (10 mL) and extracted with ether (2 × 20 mL). Usual processing followed by flash column chromatography gave the desired cyclopentenone.

Method D: Phase-Transfer Conditions. To a solution of the appropriate allylic halide (10 mmol) in THF (10 mL) was added tetrabutylammonium bromide (300 mg, cat.) and stirred rapidly at 25 °C while a solution of NaOH (0.4 g, 10 mmol) in water (1 mL) and THF (4 mL) was added dropwise in the course of 5 min. The resulting orange solution was stirred at 25 °C for 3 h, diluted with water (10 mL), and extracted with ether (2 × 10 mL). Usual processing and flash column chromatography gave the desired cyclopentenone.

Method E: Using Aqueous Ammonium Hydroxide. To a stirred solution of allylic halide (20 mmol) in THF (2 mL) was added 28% aqueous NH_4OH (50 mL), and the mixture was stirred under a closed system for 12 h. The yellow solution was diluted with water (100 mL) and extracted with ether (2 × 20 mL). The ether extract was washed with 1 N HCl (5 mL) and water (10 mL) and dried. Evaporation gave a mixture of the desired cyclopentenone and some unreacted starting material. Flash column chromatography gave the desired cyclopentenone.

2,3-Dimethyl-2-cyclopenten-1-one[5] (17). ^1H NMR: δ 2.38 (m, 4 H), 2.10 (s, 3 H), 1.70 (s, 3 H). ^{13}C NMR: δ 209.14, 169.30, 135.46, 33.50, 30.96, 16.10, 7.30. Mass spectrum: m/e 110 (M^+), 67 (base peak).

2,3,5-Trimethyl-2-cyclopenten-1-one[19,20] (18). ^1H NMR: δ 2.90–2.20 (m, 3 H), 2.00 (s, 3 H), 1.65 (s, 3 H), 1.15 (d, J = 7 Hz, 3 H). ^{13}C NMR: δ 211.93, 167.91, 134.79, 40.64, 39.47, 16.62, 16.51, 8.05. Mass spectrum: m/e 124, 109. Anal. Calcd for $C_8H_{12}O$: C, 77.42; H, 9.67. Found: C, 77.38; H, 9.59. IR (neat): 1700, 1665 cm^{-1}.

2,3,5,5-Tetramethyl-2-cyclopenten-1-one[20] (19). ^1H NMR: δ 2.45 (br s, 2 H), 2.05 (s, 3 H), 1.70 (s, 3 H), 1.05 (s, 6 H). ^{13}C NMR: δ 213.82, 166.46, 133.37, 48.75, 42.68, 25.13, 16.95, 8.02. IR (neat): 1700, 1660 cm^{-1}. Anal. Calcd for $C_9H_{14}O$: C, 78.26; H, 10.14. Found: C, 78.36; H, 10.22.

2,3-Dimethylspiro[4.5]dec-2-en-1-one (20). ^1H NMR: δ 2.40 (s, 2 H), 2.04 (s, 3 H), 1.65 (s, 3 H), 1.50–1.80 (m, 4 H), 1.15–1.40 (m, 6 H). ^{13}C NMR: δ 214.51, 167.41, 134.42, 48.21, 45.48, 33.62, 25.50, 23.28, 17.03, 8.05. IR (neat): 1700, 1655 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O$: C, 80.89; H, 10.11. Found: C, 80.71; H, 10.16.

6,7-Dimethylspiro[3.4]oct-6-en-5-one[21] (21). ^1H NMR: δ 2.70 (s, 2 H), 2.40–1.80 (m, 6 H), 2.05 (s, 3 H), 1.80 (s, 3 H). ^{13}C NMR: δ 212.21, 166.56, 134.35, 48.29, 45.23, 31.47, 16.95, 16.19, 8.12. IR (neat): 1700, 1585 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O$: C, 80.01; H, 9.34. Found: C, 80.28; H, 9.52.

2-Benzyl-3-methyl-2-cyclopenten-1-one (22). ^1H NMR: δ 7.15 (m, 5 H), 3.50 (s, 2 H), 2.50 (m, 2 H), 2.35 (m, 2 H), 2.02 (s, 3 H). ^{13}C NMR: δ 209.34, 171.89, 140.05, 134.65, 128.50, 126.10, 34.00, 31.80, 28.50, 17.10. IR (neat) 1695, 1650 cm^{-1}. Anal. Calcd for $C_{13}H_{14}O$: C, 83.87; H, 7.52. Found: C, 83.66; H, 7.40.

3-Methyl-2-pentyl-2-cyclopenten-1-one (Dihydrojasmone, 23). ^1H NMR: δ 2.55 (m, 2 H), 2.34 (m, 2 H), 2.25 (t, J = 7 Hz, 2 H), 2.10 (s, 3 H), 1.38 (m, 6 H), 0.95 (t, J = 7 Hz, 3 H). ^{13}C NMR: δ 210.12, 170.24, 141.36, 34.50, 31.97, 28.18, 23.14, 22.61, 17.22, 14.05. IR (neat) 1700, 1650, 1400 cm^{-1}. Mass spectrum: m/e 166, 151, 137, 110. Anal. Calcd for $C_{11}H_{18}O$: C, 79.51; H, 10.84. Found: C, 79.62; H, 10.76.

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Supplementary Material Available: Proton NMR spectra of some intermediates (5 pages). Ordering information is given on any current masthead page.

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