

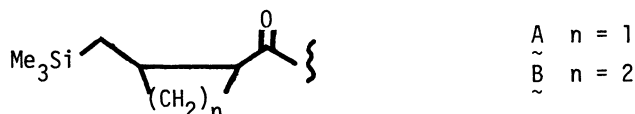
RING OPENING OF CYCLOPROPYL KETONES ASSISTED BY THE TRIMETHYLSILYL GROUP

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Cyclopropyl ketones **2** were smoothly cleaved with boron trifluoride-acetic acid under mild reaction conditions by the assistance of trimethylsilyl group to give γ,δ -enones in good yields and the reaction was applied to the formal total synthesis of *cis*-jasmone.

Cyclopropanes are attractive synthetic intermediates because of their ready availability and reactivity. It is well-known that cyclopropyl ketones are cleaved by a reductive process¹ or a variety of nucleophilic reactions.² For the acid catalyzed cleavage of cyclopropyl ketones drastic reaction conditions have usually been employed.³ In a previous paper⁴ we reported that cyclobutyl ketones **B** obtained by the cycloaddition of allylsilane to photoactivated double bond were smoothly cleaved by the assistance of trimethylsilyl group on treatment with boron trifluoride etherate at 0°C in dichloromethane. In this report we describe an extension of this ring opening reaction to cyclopropyl ketones of type **A** and its synthetic utility.



The required cyclopropyl ketone was prepared conveniently. Ester **1**⁵ (a mixture of E and Z isomers) on treatment with the sodium salt of methyl phenyl sulfone in glyme and DMSO gave β -keto sulfone **2a** in 91% yield. Its alkylation with *n*-amyl iodide and NaH in DMSO to **2b** (90%) followed by a reductive cleavage of carbon-sulfur bond with Na/Hg gave rise to a mixture of E and Z isomers of ketone **2c** in 92% yield.

Expectedly, the acid catalyzed ring opening of cyclopropyl ketone **2c** proceeded smoothly under mild reaction conditions⁶: on treatment with boron trifluoride-acetic acid complex in dichloromethane at 0°C for 20 min, **2c** gave γ,δ -enone **3c** in 79% yield. Ketone **3c** was converted into 1,4-diketone **4** ($R^1 = n\text{-C}_5\text{H}_{11}$, $R^2 = \text{H}$), a precursor of dihydrojasmone,⁷ by palladium catalyzed oxidation reaction.

In a similar manner, various kinds of cyclopropyl ketones **2**⁹ were cleaved smoothly,¹⁰ and the results are summarized in the Table.

As a synthetic application of the ring cleavage reaction, diketone **7**, which has been converted to *cis*-jasmone,¹¹ was synthesized. Ring opening of β -keto sulfone **5**, prepared from ester **1** and

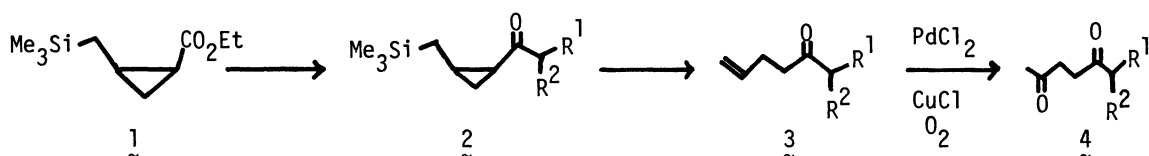
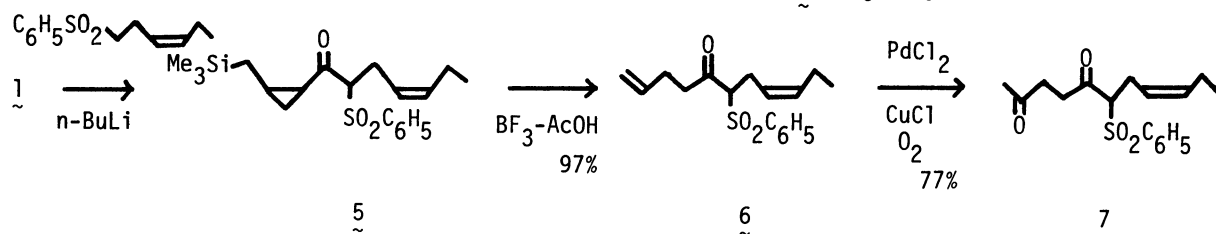


Table Ring opening of cyclopropyl ketones 4 using boron trifluoride-acetic acid in CH₂Cl₂

Cyclopropyl Ketone		γ,δ-Enone	% Yield ^a
R ¹ = H, R ² = C ₆ H ₅ SO ₂	<u>2a</u>	<u>3a</u>	67
R ¹ = n-C ₅ H ₁₁ , R ² = C ₆ H ₅ SO ₂	<u>2b</u>	<u>3b</u>	97
R ¹ = n-C ₅ H ₁₁ , R ² = H	<u>2c</u>	<u>3c</u>	79
R ¹ = H, R ² = MeSO ₂	<u>2d</u>	<u>3d</u>	72
R ¹ = Me, R ² = C ₆ H ₅ SO ₂	<u>2e</u>	<u>3e</u>	84
R ¹ = C ₆ H ₅ , R ² = H	<u>2f^b</u>	<u>3f</u>	81

a) Isolated yield. b) Chloroform was used as the solvent.

dilithio derivative of *cis*-3-hexen-1-yl phenyl sulfone¹¹ in 68% yield, gave γ,δ-enone 6 and then its palladium catalyzed oxidation afforded the desired diketone 7 in good yield.



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- Compound 2d was prepared from ester 1 in 43% yield in a similar manner as in the case of synthesis of 2a. Compound 2a on methylation with NaH and methyl iodide gave 2e in 89% yield. Ester 1 on treatment with the dilithio derivative of benzyl phenyl sulfone in THF gave β-keto sulfone 2g (R¹ = C₆H₅, R² = C₆H₅SO₂) in 56% yield. Cyclopropyl ketone 2f was obtained by the reductive cleavage of carbon-sulfur bond of 2g using Na/Hg in 96% yield.
- In contrast to the facile ring opening of ketones 2, ester 1 was recovered unchanged on its treatment with boron trifluoride-acetic acid complex in dichloromethane even under prolonged reflux.
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