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RING OPENING OF CYCLOPROPYL KETONES ASSISTED BY THE TRIMETHYLSILYL GROUP

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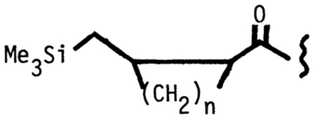
Cyclopropyl ketones 2 were smoothly cleaved with boron trifluoride-acetic acid under mild reaction conditions by the assistance of trimethylsilyl group to give γ,δ-enones in good yields and the reaction was applied to the formal total synthesis of *cis*-jasmone.

Cyclopropanes are attractive synthetic intermediates because of their ready availability and reactivity. It is well-known that cyclopropyl ketones are cleaved by a reductive process[1] 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 paper[4] 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.



A n = 1
B n = 2

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 conditions[6]: 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-C$_5$H$_{11}$, R^2 = H), a precursor of dihydrojasmone,[7] by palladium catalyzed oxidation reaction.[8]

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

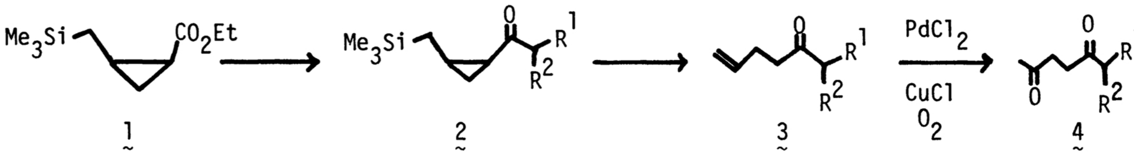
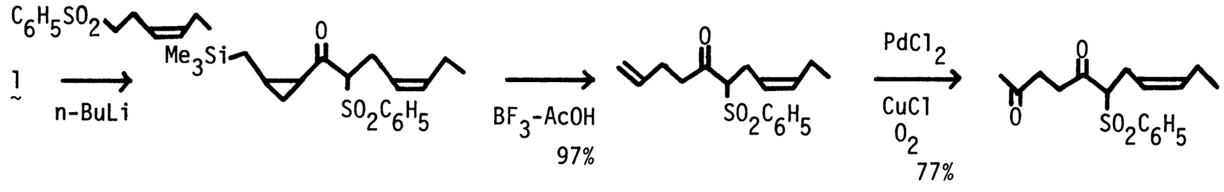


Table Ring opening of cyclopropyl ketones 4 using boron trifluoride-acetic acid in CH_2Cl_2

		Cyclopropyl Ketone	γ,δ-Enone	% Yield[a]
R^1 = H,	R^2 = $C_6H_5SO_2$	2a	3a	67
R^1 = n-C_5H_{11},	R^2 = $C_6H_5SO_2$	2b	3b	97
R^1 = n-C_5H_{11},	R^2 = H	2c	3c	79
R^1 = H	R^2 = $MeSO_2$	2d	3d	72
R^1 = Me,	R^2 = $C_6H_5SO_2$	2e	3e	84
R^1 = C_6H_5,	R^2 = H	2f[b]	3f	81

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

dilithio derivative of *cis*-3-hexen-1-yl phenyl sulfone[11] 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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9) 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 (R^1 = C_6H_5, R^2 = $C_6H_5SO_2$) in 56% yield. Cyclopropyl ketone 2f was obtained by the reductive cleavage of carbon-sulfur bond of 2g using Na/Hg in 96% yield.

10) 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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