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A SYNTHESIS OF CIS-JASMONE

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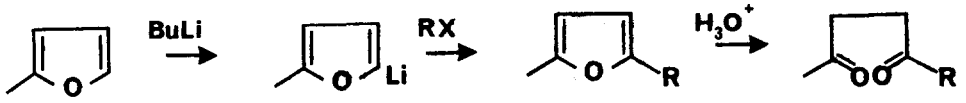
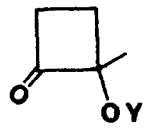
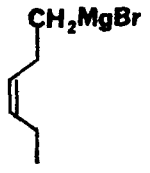
cis-Jasmone (6), an important constituent of the essential oil of jasmine, has been the object of a number of synthetic efforts in recent years.[2-6] The more successful approaches have involved cyclization of an appropriately substitued 1,4-diketone[7] to the jasmone cyclopentenone system.[2-6] Although several ingenious new methods for construction of 1,4-diketones have been reported,[2,5,6,8] one of the best routes to this system (Scheme I) involves lithiation of a furan, followed by alkylation and hydrolysis.[3] The major disadvantage of this route is the rather vigorous hydrolytic conditions necessary for opening the furan ring, sometimes resulting in undesired changes in the side chain. It appeared that a hydroxycyclobutanone might serve as the synthetic equivalent of 2-methylfuran, providing an alternative 1,4-diketone synthon.

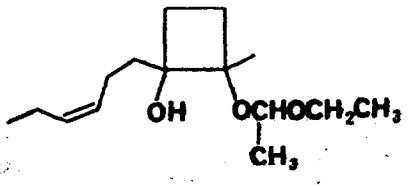
2-Hydroxy-2-methylcyclobutanone (1), readily available in quantitative yield by irradiation of 2,3-pentanedione,[9,10] was converted in 75% yield to a mixture of diastereomeric acetals 2 [ν_{max} film 1780 cm^{-1}] upon treatment with ethyl vinyl ether



Scheme I





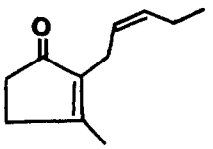


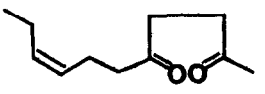
1 Y = H

2 Y = $CHOCH_2CH_3$ (CH_3)

3

4





6

5

in tetrahydrofuran solution in the presence of Dowex cation exchange resin. Addition of an ether solution of this mixture of acetals 2 to the Grignard reagent 3, prepared in ether from the corresponding bromide,[3] produced a diastereoisomeric mixture of alcohols 4. Without purification, this mixture was stirred overnight with periodic acid in aqueous tetrahydrofuran, giving the known diketone 5 (35% from 2). It had infrared and NMR spectra as described by Buchi[3] and Crombie[4]: ν_{max} $CHCl_3$ 1712, 1400 and 1360 cm^{-1}; NMR ($CDCl_3$) δ 5.4 (2H, m) 2.70 (4H, s), 2.5-1.5 (6H, m), 2.18 (3H, s), 0.98 (3H, s, J = 7.5 Hz).

Cyclization of diketone 5 with dilute sodium hydroxide[3,4,7] produced cis-jasmone (6) having infrared, ultraviolet and nuclear magnetic resonance spectra as reported.[3-5,11]

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