# Cyclopentenones from the Acid-induced Ring Expansion of 1-Alkenylcyclopropanol Derivatives

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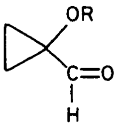
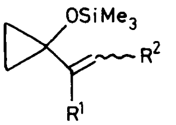
1-Alkenylcyclopropanols (**4a,b**) and (**5a,b**) underwent acid-induced ring expansion into cyclopentenones (**7**), *via* 2-alkenylcyclobutanones (**6**); the 2-methylcyclopropanols (**15a,b**) are also synthesised using the same method.

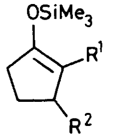
Cyclopropanecarbaldehyde derivatives (**1**) constitute useful building blocks for the construction of five-membered ring moieties as illustrated by the syntheses of jasmonoid,[1] spirovetivane,[2] and dicranenone[3] compounds. These syntheses are based on thermal vinylcyclopropane–cyclopentene ring expansion of the cyclopropanes (**2**), readily available from (**1**),[1–4] into the regiospecific cyclopentanone enol ethers (**3**) which then undergo either acidic and basic hydrolysis or dehydrosilation to provide the corresponding



(**1**)

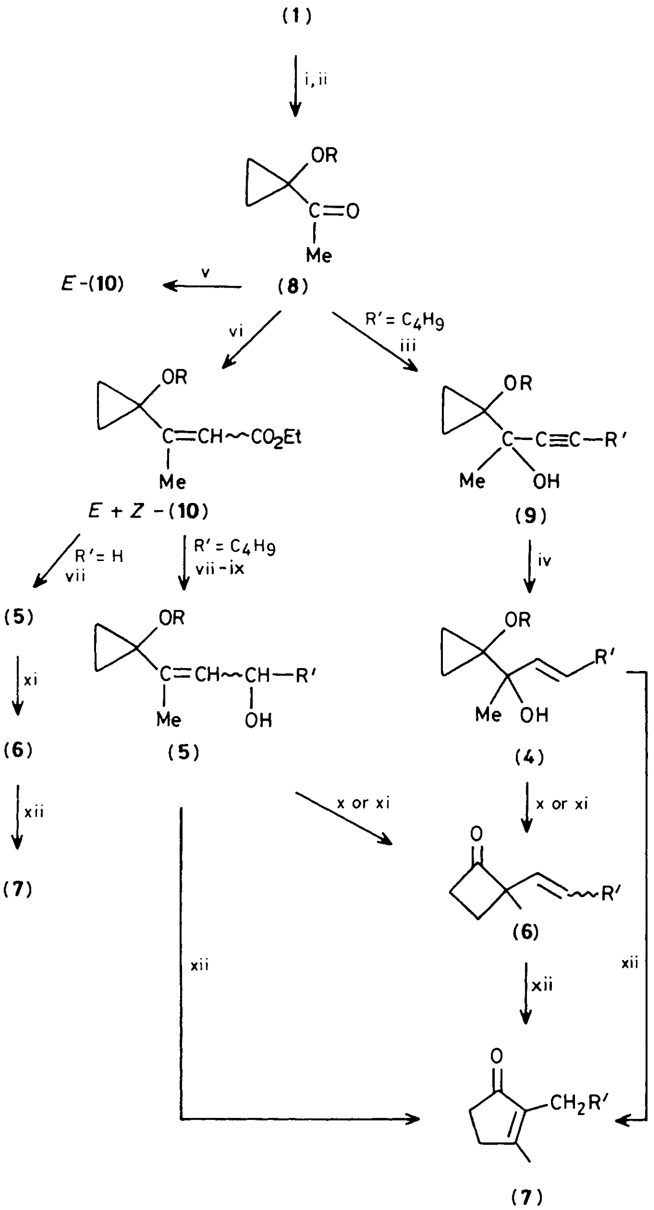


(**2**)



(**3**)

**a**; R = tetrahydropyran-2-yl
**b**; R = $SiMe_2Bu^t$

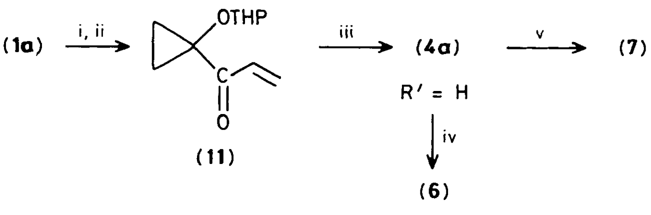


a; R = tetrahydropyran-2-yl
b; R = $SiMe_2Bu^t$

**Scheme 1.** *Reagents and conditions:* i, MeMgI, $Et_2O$ reflux, 2 h; ii, dimethylsulphoxide (DMSO)-$(COCl)_2$, $CH_2Cl_2$, −60 °C; iii, LiC≡C-$[CH_2]_3Me$, tetrahydrofuran (THF), 0 °C; iv, $LiAlH_4$, THF reflux, 3 h; v, $(EtO)_2P(O)CHCO_2Et$, THF reflux, 35% yield; vi, LiC-$(SiMe_3)HCO_2Et$, THF, −78 °C, 75%; vii, $Bu^i{}_2AlH$, toluene, −70 °C, 98%; viii, DMSO-$(COCl)_2$, $CH_2Cl_2$, −60 °C; ix, $Bu^nMgBr$, $Et_2O$ reflux, 2 h; x, $BF_3$-$Et_2O$ (0.1 mol equiv.), $CHCl_3$, room temp., 15 min; xi, 10 : 1 $MeSO_3H$-$P_2O_5$ (0.1 mol equiv.), $Et_2O$, room temp., 5 min; xii, $MeSO_3H$-$P_2O_5$ (17 equiv.), 6 h, room temp.

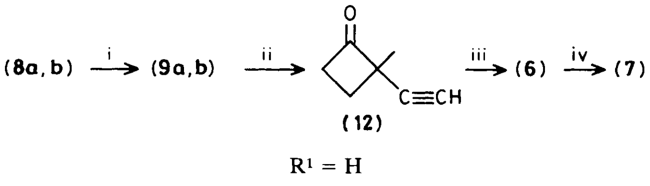
α,β-disubstituted cyclopentanones or cyclopentenones. This communication reports that (**1**) can also provide 1-alkenylcyclopropanol derivatives such as (**4**) and (**5**) which undergo acid induced ring expansion, *via* the intermediacy of the cyclobutanones (**6**), into cyclopentenone derivatives (**7**).

Addition of MeMgI to (**1a,b**) followed by oxidation[5] gave (**8a,b**) in 96% yield. Addition of hex-1-ynyl-lithium led to the octynols (**9a,b**) (R' = $C_4H_9$) which on reduction provided the *trans* vinyl alcohols (**4a,b**) (R' = $C_4H_9$) (90%). On the other hand, addition of triethylphosphonoacetate carbanion to (**8a,b**) gave the α,β-unsaturated *E*-ethyl carboxylates (**10a,b**),† while addition of ethyl lithiotrimethylsilylacetate[6] gave a mixture of *E*- and *Z*-(**10a,b**) (ratio 1 : 2).† Reduction of (**10a,b**) led to the allylic alcohol (**5a,b**) (R' = H). Then, DMSO-$(COCl)_2$ oxidation[5] and addition of $Bu^nMgBr$ provided the alcohols (**5a,b**) (R' = $C_4H_9$) (92.5%), Scheme 1.



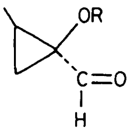
THP = tetrahydropyran-2-yl

**Scheme 2.** *Reagents and conditions:* i, $CH_2$=CHMgBr, THF, 20 °C; ii, DMSO-$(COCl)_2$, $CH_2Cl_2$, −60 °C; iii, MeMgBr, $Et_2O$, 0 °C, 50%; iv, $MeSO_3H$-$P_2O_5$ (0.1 equiv.), $Et_2O$, 5 min, 95%; v, $MeSO_3H$-$P_2O_5$ (15 equiv.), 55—68%.

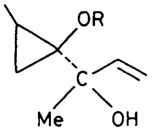


$R^1$ = H

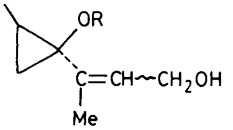
**Scheme 3.** *Reagents and conditions:* i, LiC≡CH-$NH_2CH_2CH_2NH_2$ (2 equiv.), THF, 20—40 °C, 70%; ii, $MeSO_3H$-$P_2O_5$ (0.1 equiv.), $Et_2O$, 83%; iii, Pd-$CaCO_3$, PbO, pentane; iv, $MeSO_3H$-$P_2O_5$ (17 equiv.), 6 h, room temp., 65%.



(13)



(14)



(15)

**a**; R = THP
**b**; R = $SiMe_2Bu^t$

As recently reported, upon treatment in mild acidic conditions[4] octenols (**4a,b**) and (**5a,b**) (R' = $C_4H_9$) were converted quantitatively into the cyclobutanone (**6**) (R' = $C_4H_9$). Furthermore, treatment of neat (**4a,b**) or (**5a,b**) with methanesulphonic acid–phosphorus pentoxide[7] led directly to dihydrojasmone (**7**) (R' = $C_4H_9$) in 65—90% yields, as did (**6**) upon treatment under the same conditions (Scheme 1).[8,9]

Addition of vinylmagnesium bromide to (**1a**) followed by oxidation[5] gave (**11**) which, on treatment with MeMgBr gave (**4a**) (R' = H), Scheme 2. The butenol (**4a**) or (**5a,b**) (R' = H) could then undergo either $C_3 \rightarrow C_4$ ring expansion into the cyclobutanone (**6**) (R' = H) or $C_3 \rightarrow C_5$ ring expansion to cyclopentenone (**7**) (R' = H) (55—68%) a precursor of methylenomycin B,[10] Scheme 1.

Addition of lithiumacetylide–ethylenediamine complex[11] to (**8a,b**) provided the propynols (**9a,b**) (R' = H), which underwent $C_3 \rightarrow C_4$ ring expansion to (**12**). Then, partial hydrogenation of (**12**) led to (**6**) (R' = H), quantitatively, which was also prone to acid induced rearrangement into (**7**) (R' = H), Scheme 3.

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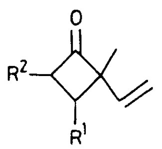
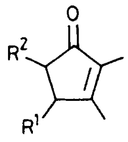
† As shown by the chemical shifts of the olefinic protons of *E*- and *Z*-(**10b**) at δ 5.80 and 5.22 respectively.



**(16)**



**(17)**

**a**; $R^1 = Me, R^2 = H$
**b**; $R^1 = H, R^2 = Me$

The aldehydes (**13a,b**), prepared from the readily available 1-hydroxy-2-methylcyclopropanecarboxylic acid,[12] allowed the synthesis of the alcohols (**14a,b**) and (**15a,b**), using the same route as for the formation of (**4a,b**) and (**5a,b**) from (**1a,b**). They also underwent acid-induced ring expansion, *via* the isomeric cyclobutanones (**16a,b**) into the cyclopent-2-en-1-ones (**17a**)[13] and (**17b**) (ratio 9 : 1) (50—70%).

This mild acid induced $C_3 \rightarrow C_4$ ring expansion of 1-alkenylcyclopropanol derivatives, into cyclobututanones[14] prone to $C_4 \rightarrow C_5$ ring enlargement[8,9] provides a convenient alternative pathway to five-membered ring compounds from 1-hydroxycyclopropanecarbaldehyde derivatives.

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## References

1 J. Salaün and Y. Almirantis, *Tetrahedron*, 1983, **39**, 2421.
2 J. P. Barnier and J. Salaün, *Tetrahedron Lett.*, 1984, **25**, 1273.
3 J. Ollivier and J. Salaün, *J. Chem. Soc., Chem. Commun.*, preceding communication.
4 J. Ollivier and J. Salaün, *Tetrahedron Lett.*, 1984, **25**, 1269.
5 A. J. Mancuso, S. L. Huang, and D. Swern, *J. Org. Chem.*, 1978, **43**, 2480.
6 S. L. Hartzell, D. F. Sullivan, and M. W. Rathke, *Tetrahedron Lett.*, 1974, 1403; K. Shimoji, H. Taguchi, K. Oshima, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, 1974, **96**, 1621.
7 P. E. Eaton, G. R. Carlson, and J. T. Lee, *J. Org. Chem.*, 1973, **38**, 4071.
8 J. R. Matz and T. Cohen, *Tetrahedron Lett.*, 1981, **22**, 2459.
9 D. A. Jackson, M. Rey, and A. S. Dreiding, *Helv. Chim. Acta*, 1985, **68**, 439.
10 J. Jernow, W. Tantz, P. Rosen, and T. H. Williams, *J. Org. Chem.*, 1979, **44**, 4212; M. Mikolajczyk, 'Current Trends in Organic Synthesis,' ed. H. Nozaki, Pergamon Press, Oxford and New York, 1983, p. 347.
11 O. F. Beumel and R. F. Harris, *J. Org. Chem.*, 1964, **29**, 1872.
12 H. G. Heine and D. Wendisch, *Liebigs Ann. Chem.*, 1976, 463.
13 S. Bernasconi, C. Capellini, and M. Sisti, *Synth. Commun.*, 1978, **8**, 71 and references cited therein.
14 For recent preparation of such 2-vinylcyclobutanones see Th. Cohen and J. R. Matz, *Tetrahedron Lett.*, 1981, **22**, 2455; D. A. Jackson, M. Rey, and A. S. Dreiding, *Helv. Chim. Acta*, 1983, **66**, 2330.