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A Facile Preparation of Highly Functionalized Cyclopropanes and Their Conversion to Cyclopentanones and Furans

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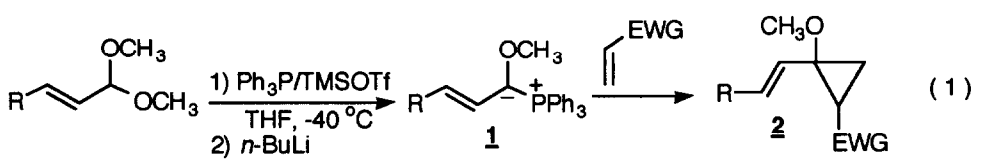
Abstract: It was found that cyclopentanones and furans were prepared from 1-alkenyl-1-methoxycyclopropane derivatives derived from the conjugate addition of 1-methoxy-2-alkenylidenephosphoranes to activated olefins.

Recent advances in the generation of three-membered rings have led to the steadily increasing usage of cyclopropyl derivatives as reagents for organic synthesis.[1] Especially, thermal rearrangement of vinylcyclopropane constitutes one of the commonly used methods for the annulation of functionalized cyclopentenes.[2] In this respect, cyclopropane formation via conjugate addition reaction of ylide to activated olefins have received considerable attention.[3] We report herein a new and experimentally convenient procedure for preparing functionalized cyclopentanes and furans using alkenylcyclopropanes containing anion stabilizing groups(Ph_3P-, $Ph_2P(O)$- and $PhSO_2$-). The reaction of 1-methoxy-2-alkenylidenephosphoranes **1**[4] with activated olefins proceeded cleanly to produce 1-alkenyl-1-methoxycyclopropane derivatives **2** which can be converted to larger rings via appropriate further reactions because electron withdrawing groups exist yet on the cyclopropane ring(eq 1).

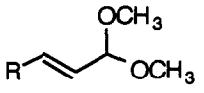
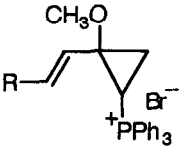
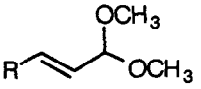
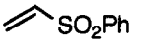
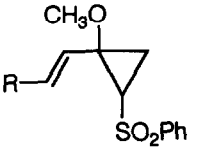
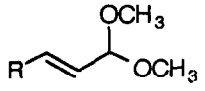
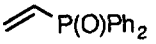
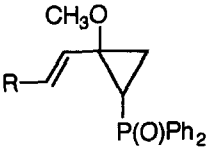


(1)

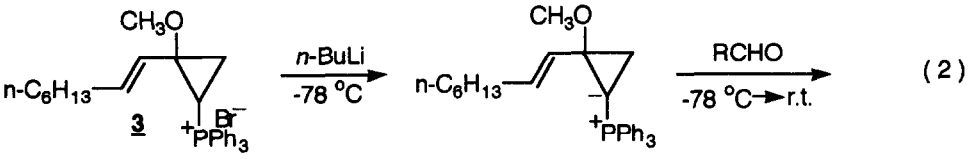
Some experimental results are shown in Table 1. Reaction of 1-methoxy-2-alkenylidenephosphoranes **1** with triphenylvinylphosphonium bromide afforded cyclopropyl triphenylphosphonium bromide **3** containing both alkoxy and alkenyl group on the cyclopropane ring. Apparently, this reaction would involve Michael addition and subsequent nucleophilic substitution. Also, phenyl vinyl sulfone and diphenylvinylphosphine oxide as Michael acceptors gave similar results, yielding **4** and **5** in moderate yields.

In connection with functionalization of cyclopropanes, methyl enol ethers of α-methylenecyclopentanones **7** were prepared from **3** through [3,3]-sigmatropic rearrangement of intermediates **6** accelerated by methoxy group.[5] Cyclopropylphosphonium bromide **3** is deprotonated with *n*-butyllithium at -78 °C and the reaction of ylide with 1.2 equiv of an aldehyde proceeds smoothly to afford **7** in moderate yields by six-step, one-pot procedure without isolation of any intermediates from α,β-unsaturated acetals[6](eq 2).

Table 1. Formation of 1-Alkenyl-1-methoxycyclopropane Derivatives

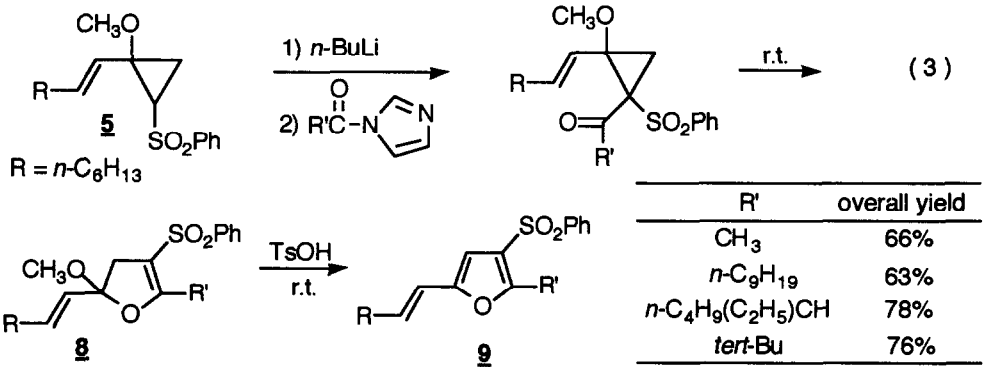
acetal	activated olefin	product	isolated yield(%) [a]
			
R = CH_3		R = CH_3	62
n-C_3H_7		*n*-C_3H_7	68
n-C_6H_{13}		*n*-C_6H_{13}	71
			
R = CH_3		R = CH_3	55
n-C_3H_7		*n*-C_3H_7	55
n-C_6H_{13}		*n*-C_6H_{13}	68
			
R = CH_3		R = CH_3	42
n-C_3H_7		*n*-C_3H_7	50
n-C_6H_{13}		*n*-C_6H_{13}	45

[a]The yields referred to isolated products based on α,β-unsaturated acetals.



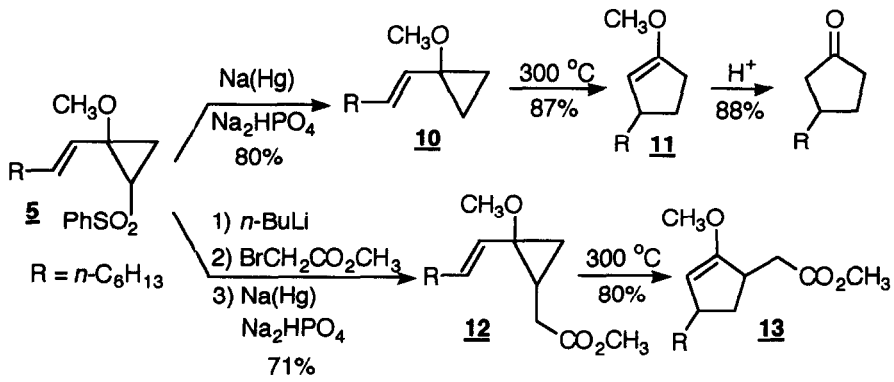
R	overall yield(*cis/trans*)
Ph	51% (1 : 15.8)
p-ClC$_6$H$_4$	40% (1 : 3.2)
n-C$_3$H$_7$	40% (*trans* only)
CO$_2$Et	45% (1 : 3.1)

We have studied the possibility of synthesizing furan derivatives via acylation of 2-alkenyl-2-methoxycyclopropyl phenyl sulfone **5**. The reaction of the sulfone stabilized anion derived from **5** and *n*-butyllithium with acyl chloride gave poor result under the present condition in which the starting material was recovered in 50% yield along with the predominant formation of several unidentified byproducts. However, the use of acyl imidazol gave **9** in good yields(eq 3): *n*-Butyllithium was added dropwise to a solution of **5** in THF at -78 ℃ to give yellow colored sulfone anion. The reaction mixture was stirred at -78 °C for 10 min and exposure to acyl imidazol generated α-acyl sulfone followed by rearrangement to form dihydrofuran **8**. Dihydrofuran was smoothly converted to furan **9** by virtue of *p*-toluenesulfonic acid or camphosulfonic acid at room temperature within 30 min.[6]



R'	overall yield
CH_3	66%
n-C$_9$H$_{19}$	63%
n-C$_4$H$_9$(C$_2$H$_5$)CH	78%
tert-Bu	76%

Ring enlargement via pyrolysis of **5** suffers from several drawbacks due to decomposition of sulfonyl group. Therefore, after sulfonyl group was removed with sodium/amalgam (3%, 4.0 equiv) in the presence of 4.0 equiv of disodium hydrogen phosphate, the complete conversion of alkenylcyclopropanes(**10** and **12**) to methyl enol ethers of cyclopentanones was done in a sealed tube at 300 °C within 2 h in good yields[6](eq 4). The noteworthy features of the present method include a facile preparation of functionalized cyclopropanes via conjugate addition reaction of ylides to activated olefins and a successful application of alkenylcyclopropanes for cyclopentanone and furan derivatives. Further investigations in the related area are in progress.



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6. **7** (*trans*, R=Ph): ^{1}H NMR ($CDCl_3$): 7.25-7.09 (m, 5H), 5.02 (d, *J*=2.55 Hz, 1H), 4.98 (s, 1H), 4.37 (s, 1H), 3.81 (s, 3H), 3.27 (dd, *J*=5.73, 2.76 Hz, 1H), 2.52 (m, 1H), 1.39-1.12 (m, 13H). **9** (R=*n*-C_6H_{13}, R'=CH_3): ^{1}H NMR ($CDCl_3$): 8.00-7.42 (m, 5H), 6.40-6.00 (m, 3H), 2.50 (s, 3H), 2.40-0.40 (br m, 13H). **11**: ^{1}H NMR ($CDCl_3$): 4.40-4.20 (m, 1H), 3.49 (s, 3H), 2.69 -1.80 (m, 3H), 1.50-0.80 (m, 15H). **13**: ^{1}H NMR ($CDCl_3$): 5.55-5.12 (m, 1H), 3.70 (s, 3H), 3.64 (s, 3H), 2.60-2.08 (m, 4H), 1.50-0.80 (m, 15H).

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