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Preparation of β'-Phenylsulfonyl α,β-Unsaturated Ketones and Unsymmetric Dialkenyl Ketones from 2-Alkenyl-2-methoxycyclopropyl Phenyl Sulfones

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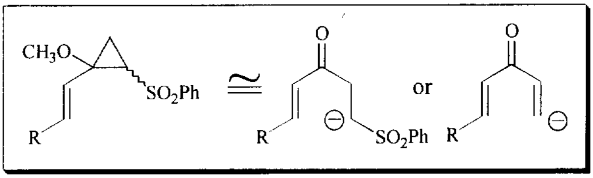
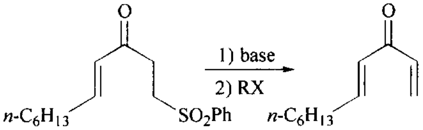
Abstract: β'-Phenylsulfonyl α,β-unsaturated ketones, which can be easily converted to unsymmetric dialkenyl ketones, were prepared *via* ring opening reactions of 2-alkenyl-2-methoxycyclopropyl phenyl sulfones. Copyright © 1996 Elsevier Science Ltd

Recent advances in the formation and ring opening reactions of three-membered rings have led to the steadily increasing utilization of cyclopropyl derivatives as reagents for organic synthesis.[1] In this respect, ring opening reactions of cyclopropanes have received considerable attention over the past years. Recently, we found that cyclopentanones and furans could be prepared from 1-alkenyl-1-methoxy cyclopropane derivatives containing anion stabilizing groups.[2] As part of our continuing effort to expand the synthetic utility of highly functionalized cyclopropanes, we now report a convenient procedure for preparing β'-phenylsulfonyl α,β-unsaturated ketones and unsymmetric dialkenyl ketones which are important building blocks for organic syntheses using 2-alkenyl-2-methoxycyclopropyl phenyl sulfones. The present method should strongly complement existing procedures for the synthesis of unsymmetric dialkenyl ketones, which are the precursors of choice for cyclopentanones by way of the Nazarov and related cationic cyclizations.[3]

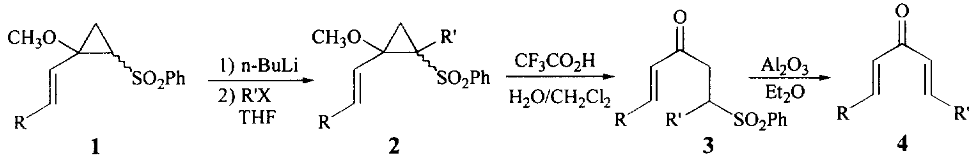
Initially, deprotonation of sulfone **1** leading to the sulfonyl carbanion was accomplished by treatment with *n*-butyllithium or LDA in THF. The sulfonyl carbanion reacted smoothly with reactive alkyl halides, 1°-alkyl bromides and trimethylsilyl chloride to give **2** in good yields as a mixture of *cis* and *trans* isomers. However, alkylation couldn't be achieved in case of isopropyl iodide, even when HMPA was used as additive. After examining a variety of acids to open the cyclopropane ring of **2**, it was found that 5 equivalents of trifluoroacetic acid was quite effective to produce the corresponding β'-phenylsulfonyl α,β-unsaturated ketones. In case of **2e** and **2j**, *p*-toluenesulfonic acid gave the better results.[4] In order to find the optimum conditions for the elimination reaction of phenylsulfonyl group from **3**, we began our study with **3j**. The use of triethylamine, Hunig's base, sodium bicarbonate or DBU gave **4j** in low yield along with other compounds.[5] However, treatment of **3j** with basic alumina in diethyl ether produced **4j** in 70% yield.[6] Some experimental results are shown in Table 1. The reaction of **5** with various bases followed by alkyl halides produced only **6** in *ca* 30% yield.[7] On the basis of these results, we can consider 2-alkenyl-2-methoxycyclopropyl phenyl sulfones as synthetic equivalents of sulfonyl carbanions or 3-oxo-1,4-alkadien-1-yl carbanions. The noteworthy features of the present method include a facile preparation of β'-phenylsulfonyl α,β-unsaturated ketones which can be converted to unsymmetric dialkenyl ketones *via* elimination of phenylsulfonyl group from **1**.





5 **6**

Table 1. Examples of Syntheses of β'-Phenylsulfonyl α,β-Unsaturated Ketones and Unsymmetric Dialkenyl Ketones from 2-Alkenyl-2-methoxycyclopropyl Phenyl Sulfones.



entry	R	R'X	isolated yield, %		
			2^a	3	4
a	CH_3	CH_3I	75(73)[b]	66	69
b		$CH_3(CH_2)_3CH_2Br$	74	80	80
c		$CH_2{=}CHCH_2Br$	82	55	72
d		$PhCH_2Br$	85	56	74
e		$(CH_3)_3SiCl$	76	75[c]	72
f	$CH_3(CH_2)_4CH_2$	CH_3I	84	82	73
g		$CH_3CH_2CH_2Br$	76	83	81
h		$CH_2{=}CHCH_2Br$	80	61	71
i		$PhCH_2Br$	86	72	75
j		$(CH_3)_3SiCl$	80	80[c]	70

[a]mixture of *cis* and *trans* form, [b]LDA was used, [c]*p*-TsOH was used.

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4. 5 Equivalents of *p*-TsOH in THF was used.
5. (*1,4E*)-Undecadien-3-one and 1-phenylsulfonyl-(*4E*)-undecen-3-one were produced as side products.
6. Vidal, J.; Huet, F. *Tetrahedron Lett.* **1986**, *27*, 3733-3736.
7. 1 or 2 Equivalents of triethylamine or LDA was used as a base and methyl iodide, ally bromide or benzyl bromide was used as an electrophile.

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