

2-LITHIO-2-PHENYLSULFONYL PROPANE AS EFFICIENT PRECURSOR OF
 GEM-DIMETHYL CYCLOPROPANE CARBOXYLIC ACIDS

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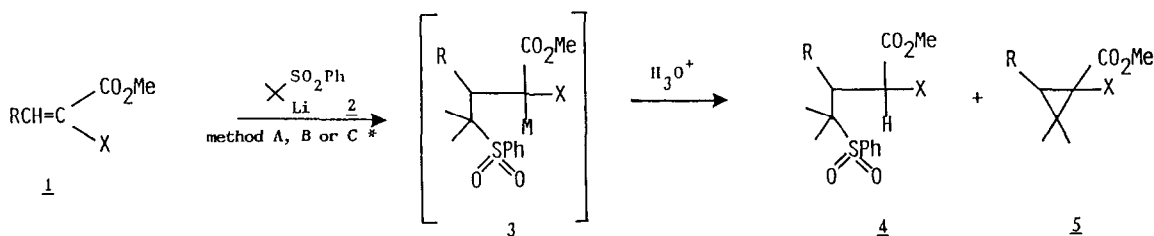
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2-Lithio-2-phenylsulfonyl propane has been successfully used for the cyclopropanation of electrophilic olefins and plays the role of an alkylidene transfer reagent.

The synthesis of cyclopropanoic esters from α -metallo allylsulfones and enoates¹ or alkylidene malonates² is a well established reaction, which is even used in an industrial synthesis of chrysanthemic acid¹ but has not yet been extended to other α -metallo alkyl phenylsulfones.

We now report that 2-lithio-2-phenylsulfonyl propane³ 2 adds at 20° in THF, across the carbon carbon double bond of methyl 2-hexenoate and mono alkyl substituted alkylidene malonates 1 to give after hydrolysis, the C₃ adduct 4 (method A). If DMSO or methanol is added and the resulting mixture is heated at 80° for 16 hrs before hydrolysis (methods B or C), the corresponding cyclopropanes are isolated from mono alkyl substituted alkylidene malonates. We were however unable to perform the same cyclopropanation from enoates (Scheme 1).

Scheme 1



R	X	Method A		Method B		Method C	
		4%	5%	4%	5%	4%	5%
Pent	H	50	--	50	--	--	--
Me	CO ₂ Me	84	--	--	45	--	--
Et	CO ₂ Me	91	--	--	63	--	64
iPr	CO ₂ Me	88	--	--	65	--	64

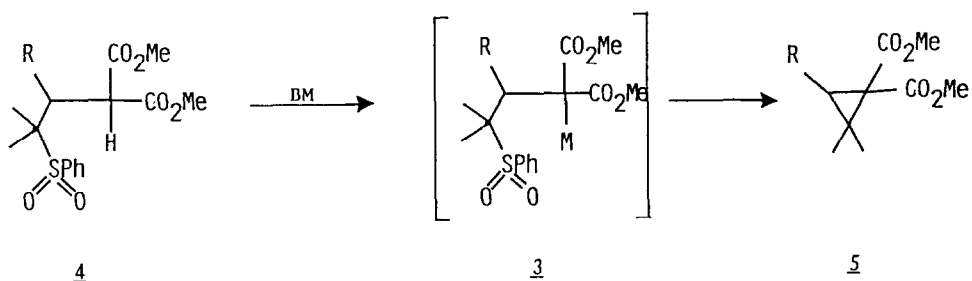
* Method A : THF 20°, 0.5h - Method B : THF 20°, 0.5h then DMSO 80°, 16h -
 Method C : THF 20°, 0.5h then methanol 70°, 16h.

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Surprisingly 2-lithio-2-sulfonylpropane reacts very sluggishly with alkylidene malonates if the reaction is directly performed in DMSO. This contrasts with our results involving 2-metallo-2-nitropropanes^{3,4} which in DMSO always produce cyclopropanes.

We have observed in a study which parallels the one just reported, that the cyclopropane diesters 5 are formed on treatment of γ -phenylsulfonyl malonates with bases in polar solvents (Scheme 2).

Scheme 2



	R	Conditions	
a	Et	1.1 MeSOCH ₂ K/DMSO, 80°, 4 h	97
b	iPr	1.1 KH/DMSO, 80°, 18 h	76
c		5 MeONa/DMF, 80°, 4 h	70
d		4 MeOLi or MeONa/MeOH, 65°, 4 or 15 h	66

Best results are observed when the reaction is carried out with dimethylpotassium or potassium hydride in DMSO at 80°, or with excess methanlates in DMF or more conveniently in methanol.

We are looking at the reactivity of α -metallo sulfonyl alkanes with other electrophilic olefins. The synthesis of chrysanthemic acid using this reaction is under way and will be reported soon.

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