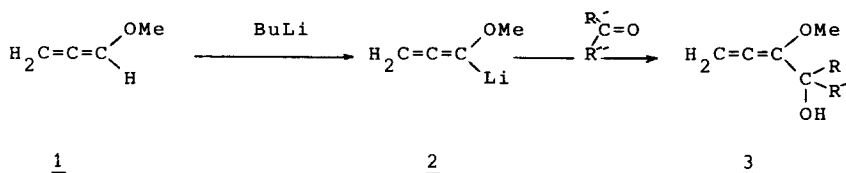


A NEW ROUTE TO 2-ALKYL - AND 2-ARYL -3-METHOXY -1,3- DIENES AND  $\alpha$ -ALKYLIDENE-KETONES . APPLICATION OF ORGANOCOPPER(I) REAGENTS IN ALLYLIC 1,3- SUBSTITUTION REACTIONS .

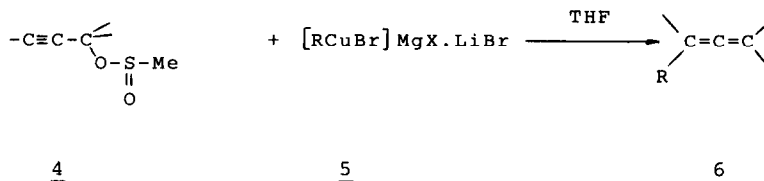
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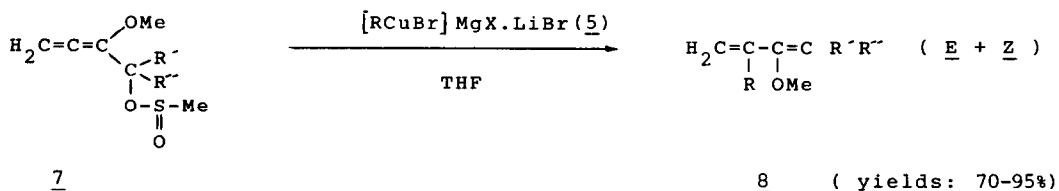
The easily available compound methoxypropadiene (1) has successfully been used in a number of syntheses <sup>1-4</sup> . Some years ago Hoff *et al.* reported on its excellent conversion into the  $\alpha$  - lithiated compound 2 <sup>5</sup> , from which the  $\alpha$  - allenic alcohols 3 could be obtained in a good yield <sup>6</sup> :



If in 3 the hydroxyl group is transformed into a smooth leaving group , organometallic compounds R-M could induce a 1,3-substitution reaction leading to 1,3-dienic products of type 8 . Such 3-alkoxy-1,3-dienes are useful compounds in synthesis. They have for instance been applied to the preparation of *Cecropia* juvenile hormone <sup>7</sup> and ( 2R,3'E,7'E ) - $\alpha$  - Tocotrienol <sup>8</sup> . Recently we found that allenic hydrocarbons (6) can be obtained in high yields from propargylic methanesulfinic esters (4) and organoheterocuprates (5) in tetrahydrofuran ( THF ) <sup>9</sup>:



In this communication we wish to report that the methanesulfinic ester group is also an excellent leaving group when it is present in the esters 7 derived from 3.



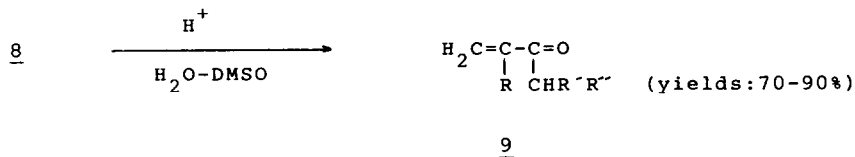
The fact that the conversion of primary, secondary as well as tertiary alcohols into the corresponding methanesulfinic esters can be achieved almost quantitatively (yields > 95%), makes this route to 8 to a very attractive one.

Addition of lithium bromide in the preparation of 5 from RMgX and copper(I) bromide shortened the reaction time needed for the complete formation of the cuprate, although its presence did not influence the yield of 8. Homocuprates -  $\text{R}_2\text{CuMgX}$  - could not be used for transformation of 7 into 8, because these reagents preferentially gave attack on the sulfur atom in 7 with the formation of  $\text{R-S(O)-Me}$  and 3. This phenomenon was also observed when 4 was reacted with homocuprates<sup>9</sup>.

**Table 1.** Physical constants and yields of 8<sup>10</sup> obtained from 7 and 5<sup>11</sup>.

$\text{H}_2\text{C}=\text{C}(\text{R})-\text{C}(\text{OCH}_3)=\text{CR}'\text{R}''$ ( <u>8</u> )			<u>E/Z</u> -ratio <sup>12</sup>	Boiling p. (°C/mm Hg)	$n_D^{20}$	yield (%)
R	R'	R''				
Bu	H	H	-	65-66/20	1.4523	70
<u>t</u> -Bu	H	H	-	42-43/20	1.4380	80
<u>t</u> -Bu	H	Me	45 / 55	56-57/20	1.4420	75
Ph	H	Me	75 / 25	116-118/20	1.5414	95
Me	H	Ph	90 / 10	58-62 / 0.1	1.5583	90
<i>i</i> -Pr	H	Ph	> 95 / 5	66-68 / 0.1	1.5416	90
Et	Me	Me	-	44-45 / 20	1.4431	80
Ph	Me	Me	-	118-120/20	1.5396	95

The 1,3-dienes 8, which possess an enol ether unit, can easily be hydrolysed into the corresponding  $\alpha$ -alkyl- or  $\alpha$ -aryl-  $\alpha,\beta$ -unsaturated ketones 9 by treatment with a catalytic amount of acid in a mixture of water and dimethylsulfoxide (DMSO) :



Under these conditions migration of the other double bond did not take place. In our opinion this convenient route to 9 starting from 1 will be a method of choice for the preparation of  $\alpha$ -alkylidene ketones ( see for other methods reference 13 ).

Table 2 . Physical constants and yields of 9<sup>10</sup> obtained from 8 .

$\text{H}_2\text{C}=\text{C}(\text{R})-\text{CO}-\text{CHR}^{\sim}\text{R}^{\sim}$ ( <u>9</u> )			Boiling p. ( $^{\circ}\text{C}/\text{mm Hg}$ )	$n_{\text{D}}^{20}$	yield ( % )
R	R <sup>~</sup>	R <sup>~</sup>			
Bu	H	H	53-54 /18	1.4380	70
<u>t</u> -Bu	H	H	61-62 /48	1.4333	80
<u>t</u> -Bu	H	Me	75-76 /28	1.4358	70
Ph	H	Me	116-118/20	1.5386	70 <sup>14</sup>
Me	H	Ph	54-56 / 0.1	1.5366	80 <sup>14</sup>
<i>i</i> -Pr	H	Ph	56-59 /0.08	1.5124	90 <sup>14</sup>
Et	Me	Me	69-70 /48	1.4328	75
Ph	Me	Me	55-57 / 0.1	1.5294	95

#### Procedure

Preparation of 6 : To a stirred solution of CuBr ( 0.030 mole ) and LiBr ( 0.030 mole ) in THF ( 60 ml ) was added RMgX ( 0.030 mole ) in THF (  $\approx$  30 ml ) at  $-50^{\circ}$  ( R  $\neq$  Me or Ph ) or at  $-10^{\circ}$  ( R = Me or Ph ). After stirring the reaction mixture at  $-50^{\circ}$  and  $-10^{\circ}$  respectively ( 15 min ), a solution of 4 ( 0.025 mole )<sup>15</sup> in THF ( 5 ml ) was cautiously added at  $-50^{\circ}$  ( R  $\neq$  Me or Ph ) or at  $-10^{\circ}$  ( R = Me or Ph ). Subsequently the temperature of the reaction mixture was raised to  $20^{\circ}$  within 15 minutes and stirring was continued at this temperature ( 30 min ). After pouring the reaction mixture into a saturated aqueous solution of  $\text{NH}_4\text{Cl}$  ( 200 ml ) containing some NaCN ( 2 g ), 6 was isolated by extracting with pentane ( 3 x 50 ml ).

Preparation of 7 : The 1,3-diene 6 ( 0.030 mole ) was added to a stirred solution of 36 N  $H_2SO_4$  ( 2 ml ) in DMSO ( 60 ml ) and  $H_2O$  ( 12 ml ). The reaction mixture was stirred during 60 minutes at 50-70°. After adding  $H_2O$  ( 200 ml ) and cooling to 20° the ketones 7 were isolated by extraction with ether-pentane ( 1:1 (v/v); 3 x 50 ml ).

References and notes.

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10. The purity of 8 and 9 was at least 98 % ( based on  $^1H$ -NMR and GLC ).
11. The heterocuprates 5 were prepared from  $CuBr.LiBr$  and  $RMgCl$  ( R = Me, i-Pr, Bu or t-Bu ) or from  $CuBr.LiBr$  and  $RMgBr$  ( R = Et , Ph )
12. The E and Z configurations were determined from the chemical shifts of the vinylic protons, using the additive increments for the substituents according to :  
U.E.Matter, C.Pascual, E.Pretsch, A.Pross, W.Simon and S.Sternhall, Tetrahedron , 25, 691 (1969)
13. See for instance : F.Huet, M.Pellet and J.M.Conia , Tetrahedron Lett. 1977 , 3505 and other references cited therein.
14. The crude product was contaminated with an unknown impurity ( 7-9 % ), which was removed by chromatography (  $Al_2O_3$  / pentane ) prior to distillation .
15. The sulfinic esters 4 were prepared from 3 according to the method described in reference 9 and were used without purification .