

REACTION OF CARBONYL-STABILIZED ALLYL SULFOXONIUM
YLIDES WITH MICHAEL ACCEPTORS¹

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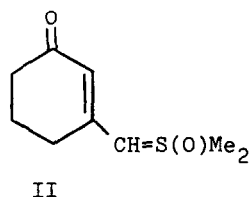
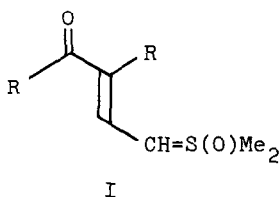
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The role of carbonyl-stabilized sulfonium and sulfoxonium ylides in synthesis has become quite prominent in the last decade.² While the acyl-, diacyl- and carbethoxy-stabilized sulfur ylides have been shown to form cyclopropanes readily with Michael acceptors,³ related vinyl sulfoxonium methylides (I) have not been studied under similar conditions.⁴ The conjugated double bond in this class of ylides offers numerous synthetic possibilities for its involvement prior to or subsequent to the known sulfur ylide reactions. We have been interested in utilizing allyl ylides in synthesizing vinyl cyclopropanes, and hence cyclopentenes, cycloheptadienes and their bicyclic counterparts.

We wish to report at this time on the reactions of dimethylsulfoxonium (3-oxo-1-cyclohexenyl) methyllide (II) with various Michael acceptors as an efficient entry into highly functionalized vinyl cyclopropanes.



Methylide (II) is a highly stable and crystalline sulfur ylide which was first prepared by Tamura and co-workers.⁵ When crystalline ylide II was treated with Michael acceptors (IIIa-f), an extremely clean addition took place to produce vinyl cyclopropane (IVa-f) in high yield.

The reaction conditions and yields are shown in Table A.

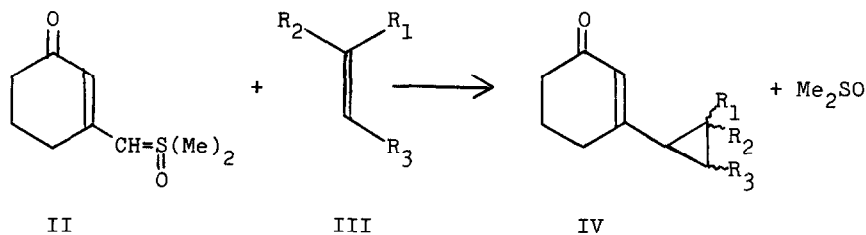


Table A

	III ^a			Solvent	Temp.	Time	Yield
	R ₁	R ₂	R ₃				
a	H	CHO	H	CH ₃ CN	R.T.	5 hr	85-90%
b	H	COCH ₃	H	CH ₃ CN	56	4	87%
c	H	CHO	CH ₃	CH ₃ CN	56	8	87%
d	H	NO ₂	H	(CH ₃) ₂ CO	R.T.	4	55% ^b
e	Br	CO ₂ Et	H	(CH ₃) ₂ CO	R.T.	19	~50% ^b
f	H	CN	H	(CH ₃) ₂ CO	56	20	~50% ^b

^aAn excess of Michael acceptor (1.5 to 2.0 equivalents) was routinely used.

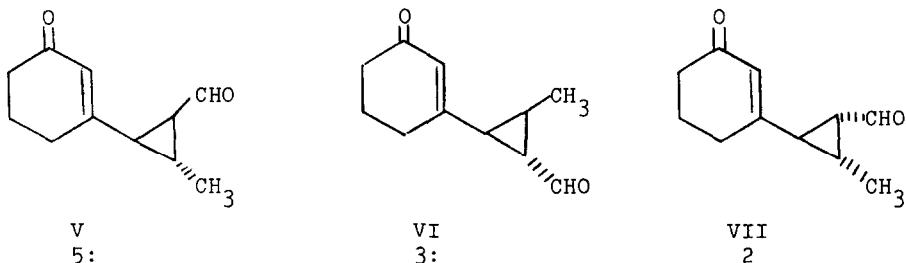
^bThese yields have not been maximized.

The products (IVa-c,e,f) were isolated in a very pure state by removing the reaction solvent, taking up the residue in a mixture of ethyl acetate and water, and evaporation of the ethyl acetate.

The structures of cyclopropanes (IVa-f) were consistent with their UV, IR, NMR and Mass Spectra.⁶ NMR data were primarily used to assign the stereochemistry of the products. As expected,^{2b,c} the cyclohexenone moiety and the R₂ group (IVa-c) had predominately trans stereochemistry. The product mixture from acrolein (IIIc) contained two isomeric products (4:1); the major isomer showed an aldehyde proton at 9.26 δ and a vinylic proton at 5.85 δ, while the minor compound had the corresponding peaks at 9.00 δ and 5.97 δ (60 MHz in

CDCl_3). Since the anisotropic effect of the enone moiety in the cis isomer was expected to shift the aldehyde proton upfield from that of the trans isomer, the minor isomer was assigned cis stereochemistry.

The methyl vinyl ketone adduct was 100% trans as evidenced by a single peak in VPC and by a single vinyl proton at 5.85 δ , a chemical shift consistent with the absence of a deshielding effect from the methyl ketone group. In the reaction of crotonaldehyde (V) with methylide (II), three isomeric cyclopropanes were isolated by v.p.c. in the ratio of 5:3:2. On the basis of NMR chemical shifts and anisotropic effects, they were assigned the following stereochemistry.⁷



The mildness and simplicity of the reactions outlined above contribute to the general utility of carbonyl-stabilized allyl sulfur ylides as a regioselective and largely stereospecific route to uniquely functionalized vinyl cyclopropanes, which are difficult to obtain otherwise. The latter class of compounds can be very useful intermediates in the synthesis of more complex ring systems, such as hydrindinones.⁸ In the following communication we also describe a very efficient and direct route to ring-fused cycloheptadienes from cyclopropane adduct IIIa. We shall report shortly on some additional transformations and new applications to syntheses of the above class of vinyl cyclopropanes.

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