

A VERSATILE SYNTHESIS OF  $\alpha, \beta$  -UNSATURATED ALDEHYDES  
FROM TOSYLHYDRAZONES.

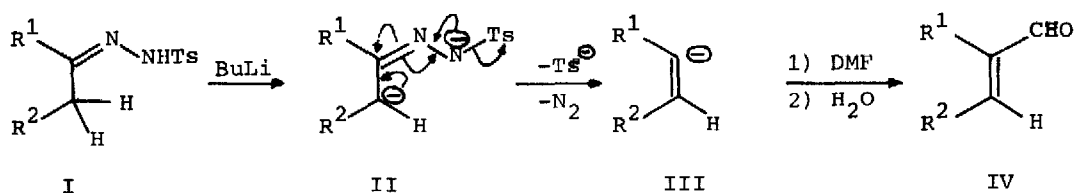
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The reaction of tosylhydrazones with alkyllithium derivatives provides an excellent route to a wide variety of substituted alkenes<sup>1,2</sup> (Bamford-Stevens reaction). Moreover, the reaction is highly regiospecific and affords exclusively the less substituted olefins<sup>3</sup>.

Although it has been known for a long time that alkenyllithium derivatives are intermediates in this reaction, effective trapping of these species with D<sub>2</sub>O to obtain specifically deuterated olefins has not been very successful<sup>1,2,4</sup>. Recently Bond and Stemke<sup>5</sup> introduced N,N,N',N'-tetramethylethylenediamine as a superior solvent providing deuterated olefins in improved yields up to 95%. In connection with our investigations on the Vilsmeier formylation of vinylcyclopropanes<sup>6,7</sup> and ketones<sup>8</sup> to obtain  $\alpha, \beta$  -unsaturated aldehydes we were interested to know whether these intermediate alkenyllithium species III can be trapped with dimethylformamide. This could provide another simple route to those aldehydes.



Trapping experiments were carried out with the appropriate tosylhydrazones according to the following procedure:

Commercial butyllithium in hexane (4 eq.) was added at  $-78^{\circ}$  to a suspension of the tosylhydrazone in N,N,N',N'-tetramethylethylenediamine. The clear red solution was allowed to reach room temperature. When the evolution of N<sub>2</sub> had ceased, dimethylformamide was added at  $0^{\circ}\text{C}$ , and the mixture was stirred for an additional hour. After the usual work up procedure the aldehydes were isolated by distillation in yields of 50 to 65%. As side products the corre-

sponding alkenes were obtained (normal Bamford-Stevens products).

In some cases the method is superior to Vilsmeier formylation. For instance the aldehydes 2-thujene-3-carbaldehyde (1) and 4-carene-4-carbaldehyde (2) can not be obtained by Vilsmeier formylation of 2-thujene<sup>7</sup> and 4-carene<sup>8</sup>, but via the new method they are obtainable in 60 and 55% yield respectively. Formylation of the tosylhydrazone of 4-acetyl-2-carene (3), affords in 60% yield the non-conjugated 2-(2-carene-4-yl)-2-propen-1-al and none of the conjugated dienal. Although this conjugated dienal can in principle easily be obtained from the non-conjugated aldehyde 3 by the action of strong base, no isomerisation takes place during the mild alkaline work up.

The reason that the tosylhydrazone of camphor gives such a low yield must be ascribed to steric hindrance in the approach of dimethylformamide. The sterically less demanding D<sub>2</sub>O offers no such problems and incorporation of deuterium proceeds almost quantitatively, thus illustrating the importance of steric effects.

No.	Hydrazone	Products	Yield	No.	Hydrazone	Products	Yield
1			60	4			65
2			55	5			54
3			60	6			57
				7			10

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