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REACTION OF S-VINYL SULFILIMINES WITH CARBANIONS
SYNTHESIS OF β-SUBSTITUTED VINYL SULFIDES

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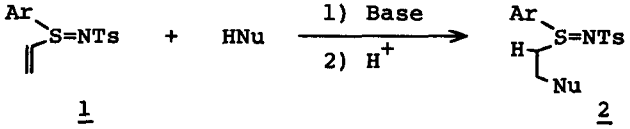
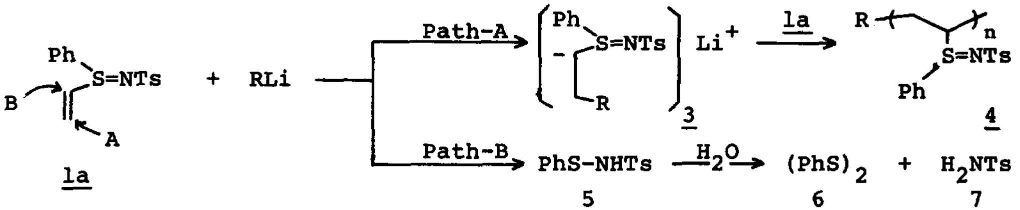
In the previous paper,[1] we described that S-vinyl sulfilimines(1) react with protic nucleophiles(HNu) such as alcohols, thiols, secondary aromatic amines and active methylenes to give Michael type adducts(2).



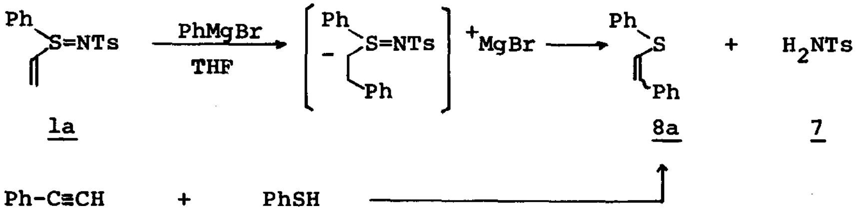
For the extension of this reaction to the aprotic nucleophiles as organometallic compounds, we examined the reactions of 1 with organo-lithium and -magnesium reagents.

The reaction of 1 with an alkyllithium gave polymer(4) of 1, sulfenamide(5), diphenyl disulfide(6) and tosylamide(7). Thus, 3 mmol of S-phenyl-N-tosyl-S-vinyl sulfilimine(1a) in 20 ml of dried THF was treated with 3 mmol of n-butyllithium in 2 ml of n-hexane at -70°C for 1 hr and worked-up as described in the previous paper[1] to give 4 (32%) as one of the products. The IR spectrum of 4 was identical with that of the polymer containing S=N structure which was derived from poly(vinyl chloride)[2] (965(S=N), 1140, 1284, 1296(SO_2) cm^{-1}, KBr disk). At the same time, 5 (11%), 6 (22%) and 7 (33%) were isolated.

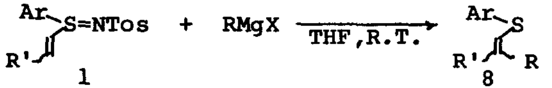


Contrary to our expectation, the reaction of 1a with n-butyllithium gives 5 and derived products thereof via Path-B as well as 4 via Path-A, probably due to the strong nucleophilicity of these carbanions (n-butyl and 3) which pair with lithium cation.

As the less nucleophilic reagents than the lithium compound, Grignard reagents were examined for this reaction. For example, to 3 mmol of 1a in 20 ml of dried THF was added 4 mmol of phenylmagnesium bromide in 5 ml of ether at 20°C, and the mixture was stirred for 6 hr. After the reaction, the resulting mixture was treated as the case of n-butyllithium to give phenylstyryl sulfide(8a)(58%, main product) and 7. 8a seems to be formed by the way of Michael type addition and following elimination of 7. The structure of 8a was identified by comparison of IR and NMR spectra with the authentic sample which was prepared by the reaction between phenylacetylene and thiophenol.3) The use of HMPA as solvent resulted in the formation of 4 (e.g. PhMgBr/1a=1/20; yield; 82%, M.W.; ca. 4200) exclusively.



Similarly the reactions between 1 and Grignard reagents gave corresponding β-substituted vinyl sulfides (8). The results were summarized in the Table.



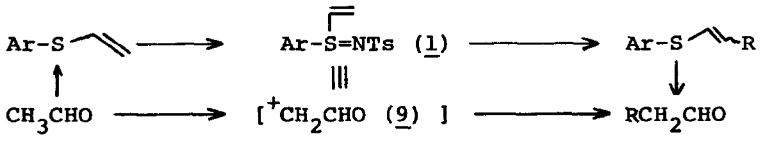
	Ar	R	R'	Y%	trans : cis **)
8a	C_6H_5	C_6H_5	H	58	13 : 8
8b	p-tol	C_6H_5	H	79	13 : 4
8c	p-tol	4-MeOC_6H_4	H	76	1 : 1
8d	C_6H_5	C_2H_5	H	71	
8e	C_6H_5	C_5H_{11}	H	66	
8f	C_6H_5	i-Pr*)	H	45	
8g	C_6H_5	C_6H_{11}	H	54	
8h	C_6H_5	C_6H_5	Me	21	

*) Reaction temperature : -70°C

**) Determined by NMR

The mechanism of this reaction is now under investigation, but the occurrence of Michael type reaction between 1 and Grignard reagents may be indispensable. By use of corresponging Grignard reagents, arbitrary substituents (alkyl and aryl) could be easily introduced to the β-position of vinyl sulfides and, consequently, the present reaction is useful as a route to β-substituted vinyl sulfides.

Moreover, since vinyl sulfides can be converted to the corresponding aldehydes,4) 1 is regarded as synthon of 9 as depicted below.



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