Tetrahedron Letters No. 7, pp 623 - 624.
0040-4039/79/0208-0623$02.00/0

REARRANGEMENT OF S-(2-SUBSTITUTED VINYL) SULFILIMINES TO N-ALLYLTOSYLAMIDES. APPLICATION TO TRANSFORMATION OF CARBONYL COMPOUNDS INTO N-ALLYLTOSYLAMIDES (ALLYLAMINES).

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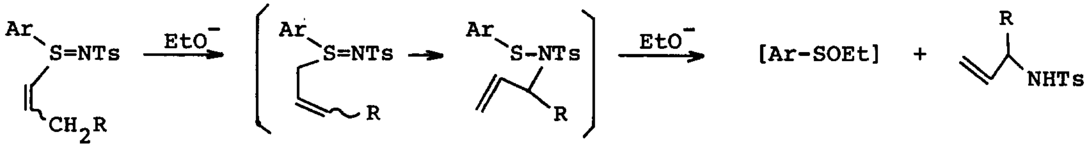
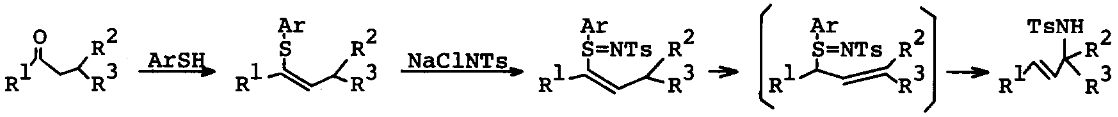
We have been studying on the syntheses and reactions of S-vinylsulfilimines for several years, and found that they behave as a good acceptor of Michael type reaction giving the corresponding adducts1) or 2-substituted vinyl sulfides derived from the Michael adducts2) with various nucleophiles.

Now we found S-(2-substituted vinyl)-N-tosylsulfilimines (1) rearranged easily to the corresponding N-allyltosylamides (3) in the presence of sodium ethoxide in ethanol. Thus S-phenyl-S-1-propenyl-N-tosylsulfilimine (1a) was treated with equimolar amount of sodium ethoxide in ethanol at 50°C for 3 hr. Usual work-up of the reaction mixture gave N-allyltosylamide (3a) in 69% yield, mp 64-65°C. The transformation (1→3) must be comprised the novel isomerization of 1 to S-allyl-S-phenyl-N-tosylsulfilimines (2) and following [2,3] sigmatropic rearrangement3).



1 2 3

The novel rearrangement (1→3) was applied to the transformation of carbonyl compounds into the corresponding N-allyltosylamides as outlined in following equation:



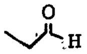
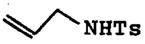
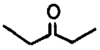
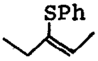
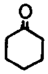
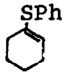
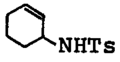
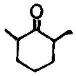
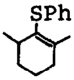
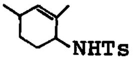
1 2 3

2-Substituted vinyl sulfides were prepared in good yield from the corresponding carbonyl compounds using benzenethiol and dehydrating systems

(P_2O_5 in dichloromethane4) or p-toluenesulfonic acid in azeotropically refluxing toluene5)). The sulfides obtained were converted to 1 in reasonable yield by the reaction with chloramine T. Transformation of 1 to 3 was carried out as described above. These results are summarized in Table 1.

The reaction of S-vinylsulfilimine (2-unsubstituted vinyl) with EtO^- gave Michael type adduct (4), S-(2-ethoxyethyl)sulfilimine quantitatively,1) while the reaction of 1a with EtO^- gave high yield of 3a with low yield (31%) of the adduct, S-(2-ethoxypropyl)-S-phenyl-N-tosylsulfilimine (4a). The selectivity of these reactions might depend on the steric effects of C_2 attacked by EtO^-. Thus the yields of the adducts 4 were 31%, 39%, 7%, 0%, and 0% from the corresponding sulfilimines, 1a, 1c, 1d, 1b, and 1e, respectively.

Table 1. Results of the transformation of carbonyl compounds to 3

	Carbonyl comp.	Vinyl sulfides	Y(%)	1 Y(%)	3	Mp(°C)	Y(%)
a			92	45		64-65	69
b			68	50		Oil	84
c			89	67		Oil	57
d			86	78		95-97	83
e			79	63		105-7	80

The structures of 1's were comfirmed by IR, NMR, and elemental analyses, and those of sulfides and 3's were comfirmed by IR and NMR. The sulfides are mainly composed of trans isomers.

Though the mechanism of the isomerization (1→2) and stereochemistry of obtained 3 are under investigation, it has become clear that some carbonyl compounds can be transformed feasibly to N-allyltosylamides and then allylamines6) using this method.

References:

1) T. Yamanoto and M. Okawara, Chemistry Letters, 1975, 581.
2) T. Yamamoto, M. Kakimoto, and M. Okawara, Tetrahedron Letters, 1977, 1659.
3) A. S. F. Ash, F. Challenger, and D. Greenwood, J. Chem. Soc., 1951, 1877.
4) The method was developed by the authers.
5) E. Benzing, U. S. Patent 3118002 (1960).
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(Received in Japan 22 November 1978)