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# STUDIES ON THE MICHAEL-TYPE REACTION OF S-VINYL SULFILIMINE

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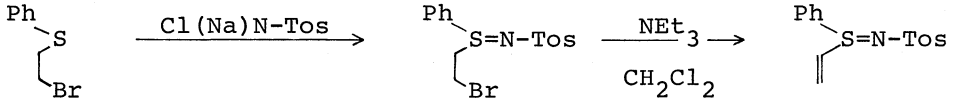
S-Phenyl-S-vinyl-N-tosyl-sulfilimine (3) was synthesized and the Michael type reactions of 3 with various nucleophiles such as thiols, dithiocarbamate, alcohols, amines and malononitrile were investigated. The adducts (4) obtained were pyrolyzed to give the vinyl compounds (7) together with sulfenamide (8) in good yield.

The Michael type addition to the vinyl groups adjacent to the cationic sulfur have been reported only on the cases of vinyl sulfonium salt[1] and vinyl sulfoxides[2]. As a part of our study on the reaction of sulfur-ylides[3], we herein investigated the Michael type addition of active hydrogen compounds to the S-vinyl-N-tosyl-sulfilimine which is isoelectronic to the vinyl sulfoxides and the pyrolysis of the resulting adduct which provides alternative method for the preparation of vinyl compounds. The synthesis of S-vinyl sulfilimine is also described briefly since there is no report on S-vinyl sulfilimines except for the sulfimination[4] which was attempted to identify the structure of divinyl sulfide.

## Preparation of S-vinyl sulfilimine

2-Bromoethyl phenyl sulfide ( 1, prepared from sodium thiophenoxide and large excess 1,2-dibromoethane[5]) was allowed to react with a small excess of chloramine T in methanol at room temperature. Working up the reaction mixture as usual gave S-2-bromoethyl-S-phenyl-N-tosyl-sulfilimine (2) in 62% yield based on the consumed 1.




1 2 3

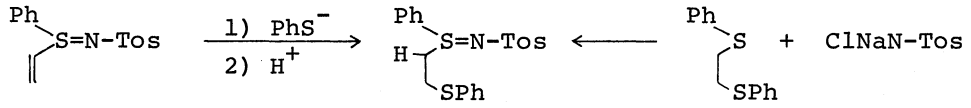
The yield was raised up to 90% by use of anhydrous chloramine T. The sulfilimine 2,

mp 98-99.5°C (from methylene chloride-ether), showed characteristic IR absorption at 1295-1280 ($\nu_{as}SO_2$), 1138 ($\nu_sSO_2$), 1085 and 985 $cm^{-1}$($\nu$S=N).

The sulfilimine 2 was treated with excess amounts of triethylamine at room temperature. S-phenyl-S-vinyl-N-tosyl-sulfilimine 3 was separated from the solution as white crystals, which showed mp 111-113°C (decomp.) after recrystallization (from methylene chloride-ether). This sulfilimine 3 is stable in air at room temperature and the structure was confirmed by elemental analysis and spectral data: IR (KBr), 3080 ($\nu$ =$CH_2$), 1285 ($\nu_{as}SO_2$),1140 ($\nu_sSO_2$), 1085 and 958 $cm^{-1}$($\nu$S=N); NMR ($CDCl_3$), $\delta$ 2.37(3H,s,$CH_3$), 5.99-6.58(3H,t.q,CH=$CH_2$), 7.3-7.7(5H,m,$C_6H_5$) and 7.12-7.75(4H,d.d,$C_6H_4$).

Michael type reaction of S-vinyl sulfilimine 3

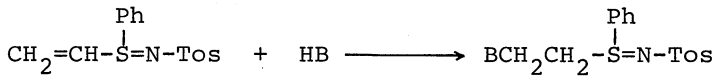
For example, an equimolar mixture of S-vinyl sulfilimine 3 and sodium thiophenoxide was allowed to stand in ethanol at room temperature for one day. After neutralization with acetic acid and working up as susal, the reaction mixture gave white crystals of S-phenyl-S-(2-phenylthioethyl)-N-tosyl-sulfilimine (4a) in 60% yield. The adduct 4a gave satisfactory elemental analysis, mp amd mixed mp 126-128°C and the IR spectrum was consistent in all respects with that of an authentic sample prepared from 1,2-bis(phenylthio)ethane and chloramine T ( yield, 60% ).




3 4a

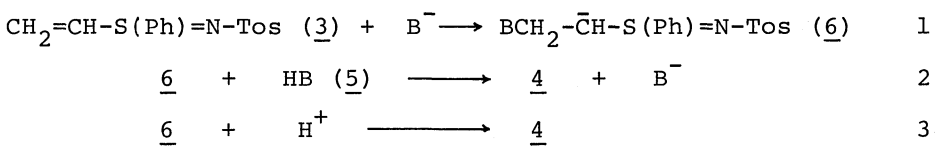
Similarly, various types of nucleophiles (active hydrogen compounds) were conveniently added to vinyl sulfilimine 3 and the results were summarized in Table 1. As can be seen from the Table 1, the mode of the reaction depends significantly on the nucleophilicity and basicity of the nucleophiles. The presence of base (sodium hydride) is necessary to make the reaction proceed except for the sodium salts, 5a and 5d. While the catalytic amounts (10 mol%) of base are enough for 5f in THF and for 5b, 5c, 5e and 5j in ethanol, more than the equivalent amounts are required for 5g, 5h and 5i in THF. This difference depends upon the basicity of the nucleophiles (BH). Thus the formers are so acidic as to be deprotonated by intermediary anion 6, consequently to circulate formulas 1 and 2. On the other hand, the latters are not so acidic as the circulation occurs, requiring an equimolar amonut of NaH to produce $B^-$. It is of interest that even the sterically hindered diphenylamine was added effectively.

Table 1. Michael type reaction of S-vinyl sulfilimine 3 [a]



| | 5 ( HB ) | Solvent | NaH[b] | 4[c] | Yield (%) | mp (°C) | IR ($cm^{-1}$) |
|---|---|---|---|---|---|---|---|
| a | $C_6H_5SNa$ | EtOH | —— | a | 60 | 126-128 | 982(νS=N) |
| b | p-$CH_3C_6H_4SH$ | EtOH | cat. | b | 95 | 124-126 | 985(νS=N) |
| c | 2-Mercaptoben-zothiazole | EtOH | cat. | c | 80 | oily | 948(νS=N) |
| d | $Et_2NCSSNa$ | THF | —— | d | 90 | 104-106[d] | 949(νS=N) |
| e | $C_2H_5OH$ | —— | cat. | e | 97 | 85.5-87 | 960(νS=N)1110(νC-O-C) |
| f | $C_6H_5CH_2OH$ | THF | cat. | f | 89 | oily | 964(νS=N)1100(νC-O-C) |
| g | $(C_6H_5)_2NH$ | THF | equimol. | g | 88 | 113-115 | 972(νS=N) |
| h | Carbazole | THF | equimol. | h | 87 | 130-132 | 951(νS=N) |
| | | THF | cat. | | 0 | | |
| | | EtOH | cat. | e | 83 | 85.5-87 | 960(νS=N)1100(νC-O-C) |
| i | Phenothiazine | THF | equimol. | i | 75 | 149-150 | 976(νS=N) |
| j | $CH_2(CN)_2$ | EtOH | cat. | j | 89 | 128-129 | 962(νS=N)2150(νC≡N) |

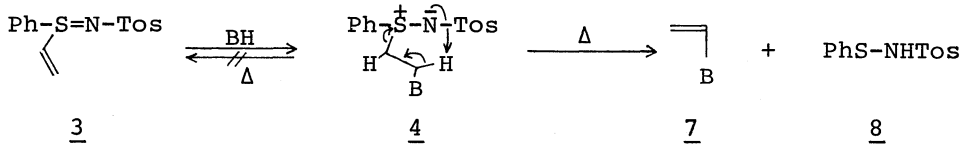
a) Reaction conditions: room temp.,1-3 days b) cat. means the use of catalytic amounts of NaH c) All of the adducts showed satisfactory results in elemental analyses d) Decomposed during recrystallization



The pyrolysis of the Michael adducts

In the pyrolysis of the Michael adducts 4, the elimination reaction 4 → 7 is expected to occur predominantly rather than the reverse course 4 → 3, probably due to the facility of intramolecular nucleophilic attack on β-H. In practice, for the cases of S,S-diethyl-sulfilimine ( $Et_2S$=NH )[6] and 4,B=alkyls[7], the formations of corresponding olefins upon pyrolysis have been reported. By application to our

case, the two-step course, addition to vinyl sulfilimine and successive pyrolysis of the adduct, seems to provide a promising method for the preparation of α-hetero-vinyl compounds.




3 4 7 8

For instance, the adduct 4a or 4b was heated (liquefied) at 130-140°C for 10 min followed by distillation in vacuo to give almost pure aryl vinyl sulfide ( 7, B=$C_6H_5S$ or p-$MeC_6H_4S$ ) in 95-98% yields ( estimated from NMR signal ). On the other hand, N-tosylbenzenesulfenamide (8), mp 112-114°C (from n-hexane-ether), was obtained quantitatively from the distillation residue. Similarly, the adduct 4f afforded benzyl vinyl ether ( 7, B=$OCH_2C_6H_5$, 63% yield ). For the carbazole adduct 4h, vinylcarbazole has not been obtained in a pure form. Upon pyrolysis, however, 4h gave sulfenamide 8 in good yield accompanied with a small amount of N-(2-phenylthio-1-tosyliminoethyl)carbazole and polymeric product. The formation of poly(vinylcarbazole) was independently proved by the reaction of vinylcarbazole and 8. Thus, the result may be explained that, while 4h also decomposed to vinylcarbazole in a similar fashion, the sulfenamide formed simultaneously would either add to or initiate the polymerization of highly reactive vinylcarbazole.

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