

CONVERSIONS OF ALLYL ARYL SULFOXIDES UNDER PUMMERER  
REARRANGEMENT CONDITIONS

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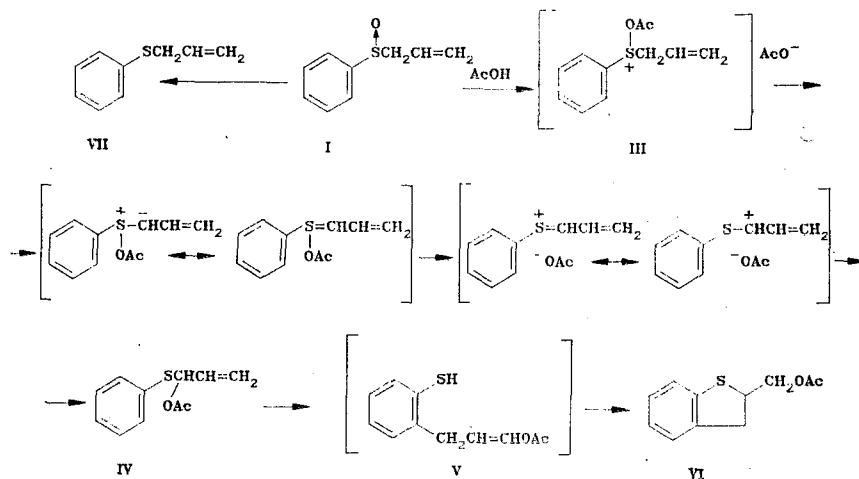
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In the presence of acetic acid, allyl phenyl sulfoxide forms  $\alpha$ -acetoxyallyl phenyl sulfide and 2-acetoxymethyl-2,3-dihydrobenzothiophene; under the same conditions allyl 1-naphthyl sulfoxide gives 2-methyl-2,3-dihydronaphtho-[1,2-b]thiophenoxide.

Of the known cases [1-6] of the Pummerer rearrangement of unsaturated sulfoxides to  $\alpha$ -acetoxy substituted sulfides, only [5, 6] describe the conversion of sulfoxides containing an aromatic and an unsaturated group. The conversion of such sulfides by a Pummerer type rearrangement with subsequent [3,3]sigmatropic rearrangement may be a method for synthesizing various heterocyclic sulfur compounds containing functional groups in the heterocycle [5].

We have carried out the rearrangement of allyl phenyl sulfoxide (I) and allyl 1-naphthyl sulfoxide (II) at 130°C in the presence of glacial acetic acid, i.e., under conditions where the Pummerer rearrangement and the thio-Claisen rearrangement can take place.

From the reaction mixture obtained in the conversion of I, we separated  $\alpha$ -acetoxyallyl phenyl sulfide (IV), 39%; 2-acetoxymethyl-2,3-dihydrobenzothiophene (VI), 5%; and allyl phenyl sulfide (VII), 11%. The formation of IV and VI indicates the stepwise character of the conversion of I; the first stage is a Pummerer rearrangement, which is followed by conversion of IV by a scheme consistent with a [3,3]sigmatropic shift to the intermediate thiol V, which then cyclizes to the dihydrobenzthiophene VI:

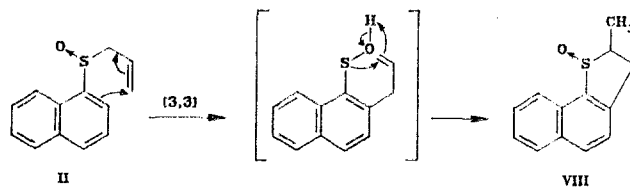


The formation of sulfide VII is apparently related to the partial reduction of sulfoxide I.

When sulfoxide II rearranges, the only reaction product is 2-methyl-2,3-dihydronaphtho [1,2-b]thiophene-1-oxide (VIII), 63%. (See structure on following page).

The assumption that a compound of similar structure is formed in the rearrangement of allyl 2-naphthyl sulfoxide has been expressed [5]. The appearance of VIII in the rearrangement of II and the absence of the corresponding  $\alpha$ -acetoxyallyl 1-naphthyl sulfide is evidence that conversion of II by the [3,3]sigmatropic shift is preferred over the Pummerer rearrange-

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ment. Such a reaction path is related to the greater mobility of the  $\pi$ -electrons of the electron system of the naphthalene ring, which are involved in the six-membered transition state of the [3,3]sigmatropic rearrangement, over that of the  $\pi$ -electrons of the benzene ring in I. Our data are in good agreement with the results of the thio-Claisen rearrangement of various allyl aryl sulfides [7].

#### EXPERIMENTAL

PMR spectra were obtained in  $\text{CCl}_4$  with a Varian T-60 spectrometer, with TMS internal standard. IR spectra were obtained in film on a IKS-22 apparatus. Chromato-mass spectra were measured on a Finnigan MAT-112S apparatus at 80 eV ionization energy with a OV-101 glass capillary column ( $l = 25$  m,  $d = 0.25$  cm) under isothermal conditions at  $210^\circ$ .

The allyl phenyl and allyl naphthyl sulfides were obtained by the procedure of [8], by the reaction of allyl bromide with the respective thiolates. Sulfoxides I and VII were synthesized by oxidation of the respective sulfides with hydrogen peroxide in acetic acid [9] in 97-98% yield.

The sulfoxides were rearranged in anhydrous *o*-xylene in an argon atmosphere at  $130^\circ$  for 5 min. The initial molar ratio of sulfoxide to glacial acetic acid was 1:2. At the end of the reaction *o*-xylene and the remaining acetic acid were distilled off. The purity of the starting compounds and the course of the reaction were monitored by TLC on Silufol plates. Products were separated and purified on an unmounted silica gel layer, 40/100  $\mu\text{m}$ , in 40:43:10 hexane- $\text{CCl}_4$ -ether.

Allyl Phenyl Sulfoxide (I). Bp  $109-111^\circ$  (2 mm),  $n_D^{20}$  1.5843. IR spectrum:  $1040\text{ cm}^{-1}$  (S=O). PMR spectrum: 3.50 (2H, d, SCH<sub>2</sub>); 5.31 (3H, m, CH=CH<sub>2</sub>); 7.48 m.d (5H, m arom.). Mass spectrum: \* 166 (M<sup>+</sup>, 1), 150 (1), 125 (77), 117 (27), 109 (10), 97 (13), 77 (26), 41 (100).

Allyl 1-Naphthyl Sulfoxide (II). Bp  $85-87^\circ$  (2 mm),  $n_D^{20}$  1.6362. IR spectrum:  $1030\text{ cm}^{-1}$  (S=O). PMR spectrum: 3.61 (2H, d, SCH<sub>2</sub>); 5.39 (3H, m, CH=CH<sub>2</sub>); 7.7 m.d (7H, m, arom.).

$\alpha$ -Acetoxyallyl Phenyl Sulfide (IV). Yield 28%. IR spectrum:  $1730\text{ cm}^{-1}$  (C=O). PMR spectrum: 2.1 (3H, s, CH<sub>3</sub>); 4.59 (2H, d, =CH<sub>2</sub>); 5.80 (1H, m, CH=); 6.68 (1H, d, S-CH); 7.30 m.d (5H, m, arom.). Mass spectrum: 208 (M<sup>+</sup>, 15), 165 (8), 152 (20), 149 (10), 147 (21), 137 (9), 110 (52), 99 (9), 77 (90), 43 (100).

2-Acetoxyethyl-2,3-dihydrobenzothiophene (VI). Yield 4%. PMR spectrum: 1.22 (2H, d, CH<sub>2</sub>O); 2.10 (3H, s, CH<sub>3</sub>); 3.51 (3H, m, CHCH<sub>2</sub>); 7.49 m.d (4H, m, arom.). Mass spectrum: 208 (M<sup>+</sup>, 20), 148 (86), 135 (100), 91 (33), 43 (77).

2-Methyl-2,3-dihydronaphthol[1,2-b]thiophene 1-Oxide (VIII). Yield 63%. IR spectrum:  $1040\text{ cm}^{-1}$  (S=O). PMR spectrum: 1.48 (3H, d, CH<sub>3</sub>); 3.39 (2H, m, CH<sub>2</sub>); 4.05 (1H, q, CH); 7.40 m.d (6H, m, arom.).

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\*Here and subsequently, are given  $m/z$  for the ion peaks, and the % intensity relative to the maximum in parentheses.

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## ELECTRON SPECTRA OF RADICAL CATIONS OF HETEROANALOGS

### OF INDENE

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The electron absorption spectra of the radical cations of indene heteroanalogs were studied by nanosecond laser photoexcitation. The absorption bands in the 450-650 nm region were assigned on the basis of absorption and photoelectron spectroscopy.

By means of nanosecond pulsed photoexcitation we have previously [1] studied the visible portion of the electron absorption spectra of indene (I), indole (II), 1-ethylindole (III), 2-methylindole (IV), 1-methylbenzimidazole (V), 2-ethylindazole (VI), and benzoxazole (VII). These molecules are characterized by absorption in the 450-650 nm region. From general considerations it follows that in this spectral range the radical cations of benzoxazole, indazole (VIII), benzimidazole (IX), and their derivatives (i.e., heterocyclic systems containing a pyridine nitrogen) can show two types of electron transitions, viz., the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  types. According to the data of [1] the absorption bands in the 450-650 nm region correspond only to  $\pi \rightarrow \pi^*$  transitions. This assignment is based on their quite high intensity at the absorption maximum ( $\log \epsilon > 3$ ) and the bathochromic shift of these bands when the dimensions of the  $\pi$ -system are increased. More detailed information about the nature and location of the long-wave transitions can be obtained from the concurrent application of electron spectroscopy of the radical cations and the photoelectric spectroscopy (PES) of the parent molecules.

The possible use of PES in this connection has been demonstrated in a number of studies, which have been discussed in part in [2]. The basis for comparing these spectral methods is the fact that the difference between the first and subsequent ionization potentials of a neutral molecule enables us to predict the energy ( $h\nu_{cr}$ ) of the electron excitation of a particular doublet state of a radical cation ( $\dot{X}-\dot{A}$  etc. [3]) (Fig. 1). Naturally it is difficult to expect a more precise correspondence, first of all because of the difference in ground-state equilibrium configurations of the radical cation and parent molecule, and also the difference in the phase states in which the respective experiments are most usually carried out [2]. Nevertheless it will be shown below that with indene and its heteroanalogs (planar heteroaromatic systems), PES enables us to determine both the energy and the type of radical-cation absorption bands that are located in the visible region.

Because information is lacking for compounds III, V, and VI concerning the energy gaps between the occupied molecular orbitals (MO), the photoelectron spectra of these molecules were studied. Assignment of transitions in the PES of these compounds was based on the linear correlation with the respective energies in the PES of the unsubstituted compounds II, VIII, and IX [4, 5], and with the electron transition energies ( $h\nu_{et}$ ) in the spectra of donor-acceptor complexes (Table 1). It is noteworthy that the donor-acceptor complexes of II-V with strong electron acceptors show two charge-transfer bands (CTB), the energies of

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