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REARRANGEMENT OF 1-ALLYLOXY-2-ALLYLTHIO-4-METHYL-BENZENE TO 2,4-DIMETHYL-6-ALLYL-7-HYDROXY-2,3-DIHYDROBENZOTHIOPHENE

A. V. Anisimov, A. A. Grishkyan, Kh. A. Gaisina, and E. A. Viktorova

1-Allyloxy-2-allylthio-4-methylbenzene rearranges in N,N-diethylaniline at 215°C with migration of allyloxy and allylthio groups to form 2,4-dimethyl-6-allyl-7-hydroxy-2,3-dihydrobenzothiophene.

3,3-Sigmatropic rearrangements of allylaryl ethers and sulfides are one of the most generally useful methods for preparing oxygen and sulfur containing heterocyclic compounds [1-4]. In this work we have studied the thermal reactions of compounds occurring simultaneously as an allylaryl ether and sulfide (1-allyloxy-2-allylthio-4-methylbenzene) for which the only previously reported reaction was that with SCl_2 to give crown structured compounds [5]. Preliminary results had shown that diallyl compound I has a quite high thermal stability and undergoes reaction at a reasonable rate in alkylaryl amine media only above 195°C. The optimum temperature for the rearrangement was 215°C, above which strong tarring of the reaction product occurred.

Rearrangement of I was carried out at 215°C in N,N-diethylaniline. The reaction mixture was treated with Claisen base and was separated into two parts. The alkaline fraction (38% of the reaction mixture) was acidified and then purified on silica gel to give a material which was analyzed by ^1H NMR and IR spectroscopy and by mass spectrometry. The neutral fraction, insoluble in the Claisen base was analyzed separately.

The NMR spectrum of the material from the alkaline fraction showed an aromatic proton singlet at 6.95 ppm, two multiplets at 5.91 and 5.11 ppm for the allyl $=CH-$ and $=CH_2$, and signals at 3.41, 3.26, and 1.15 ppm, the position and appearance of which agreed with the presence of $-CH_2CH(CH_3)S$ as seen in 2-methyl-2,3-dihydrothiophene [6]. In addition, there was a methyl group at 2.15 ppm and an aryl bound $-CH_2-$ multiplet at 3.34 ppm. The IR spectrum showed a broad 3000-3200 cm^{-1} band, typical of phenolic hydroxyl. The total data showed that the alkaline fraction contained a substance with an allyl and a hydroxyl group bound to the aryl ring. The structure proposed is the product of rearrangement of the starting diallyl derivative to a compound with migrated allyloxy and allylthio groups.

Our conclusion is based on the fact that, under the same conditions, allyl ethers form o-allylphenols whereas allylsulfides form cyclic products without separation of the intermediate allylthiophenols. The rearrangement of I was carried out in refluxing N,N-diethylaniline and, in these conditions, substituted allylaryl sulfides rearrange to give a mixture of 2,3-dihydrobenzothiophenes and thiochromans [4]. Thus, it might be expected that the present rearrangement would involve subsequent cyclization of the o-allylthiophenol II. The position and appearance of the NMR signals (in which characteristic thiochroman protons are absent) and mass spectral data showing the same mass ($M = 220$) for the product as for the starting I are the basis for our proposal that the product has the structure 2,4-dimethyl-6-allyl-7-hydroxy-2,3-dihydrobenzothiophene (III) (see top of the following page).

The neutral fraction of the rearrangement products not extracted by Claisen base consist mainly of starting I. This is based on the appearance of the NMR spectrum in which there are signals at 7.02 (aromatic protons), 5.85 (allyl methine), 5.01 (allyl CH_2), 4.51 and 3.39 (CH_2O and CH_2S), and 2.19 ppm (aromatic methyl protons).

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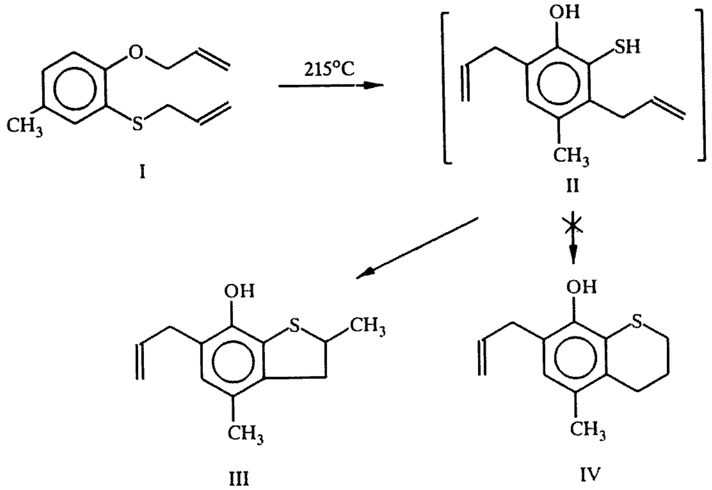

The IR spectrum of this compound showed the absence of a phenolic hydroxyl band and its mass spectrum agreed in detail with that of the starting material 1-allyloxy-2-allylthio-4-methylbenzene [5].

EXPERIMENTAL

^{1}H NMR Spectra were taken for 25% solutions on an AM-500 spectrometer using internal standard TMS with a chemical shift accuracy of ±0.01 ppm. GC-mass spectra were recorded on a Finnigan MAT-112S machine under electron impact conditions with an ionization energy of 80 eV, glass column (l = 50 m, d = 0.25 mm), stationary phase OV-101, and temperature program of 100 to 300°C. IR Spectra were taken on a UR-20 instrument as thin films.

1-Allyloxy-2-allylthio-4-methylbenzene was prepared as described in [5].

Thermal Rearrangement of 1-allyloxy-2-allylthio-4-methylbenzene (I). A solution of I (1.4 g) in N,N-diethylaniline (30 ml) was refluxed for 5 h in a round bottomed flask in an atmosphere of argon and fitted with a reflux condenser. After cooling, the mixture was washed five times with HCl solution (10%, 100 ml) to remove the diethylaniline and the residue was dissolved in ether. The ether layer was washed with Claisen base (KOH (35 g), CH_3OH (25 ml), and H_2O (100 ml)). The alkaline extract was acidified and the separated oil was extracted with ether. The ether layer was dried, solvent evaporated, and the residue purified by chromatography on silica gel (40/100) using CCl_4:hexane:ether (43:47:10) as eluent. The neutral fraction was dried, the solvent evaporated, and the residue chromatographed on 40/100 silica gel using hexane eluent.

2,4-Dimethyl-6-allyl-7-hydroxy-2,3-dihydrobenzothiophene (III). Yield 0.45 g (32%). PMR Spectrum ($CDCl_3$): 6.95 (1H, s, arom.); 5.91 (1H, m, $-CH=$); 5.11 (2H, m, $=CH_2$); 3.41 (1H, q, CHS); 3.26 (2H, d, CH_2); 3.34 (2H, m, CH_2); 2.15 (3H, s, CH_3); 1.15 ppm (3H, d, CH_3).

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