ISOMERIZATION OF 2-(ALLYLOXYMETHYL)BENZOFURANS AND -BENZOTHIOPHENES IN THE PRESENCE OF POTASSIUM *tert*-BUTYLATE

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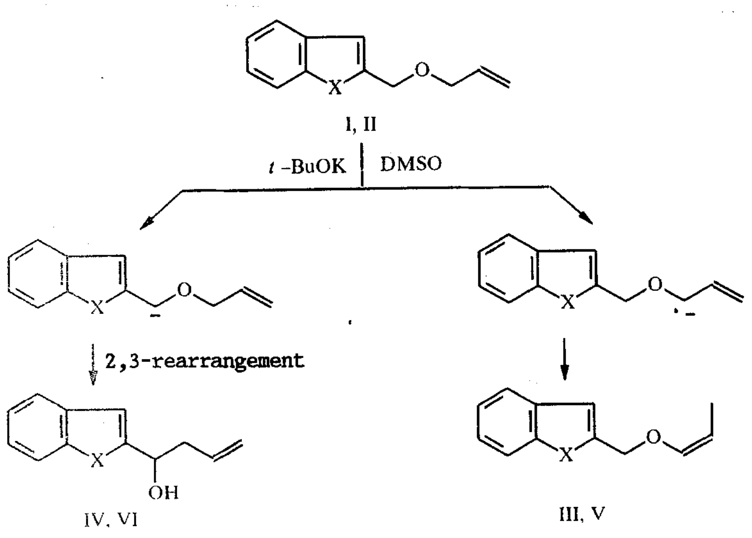
When 2-(allyloxymethyl)benzofurans and -benzothiophenes react with potassium tert-butylate in dimethyl sulfoxide (DMSO), they isomerize to the corresponding propenyl ethers and also undergo the Wittig rearrangement to isomeric butenols.

Alkali metal alcoholates are widely used for isomerization of allyl systems to propenyl ones, ensuring rather high stereoselectivity of the reaction [1-3]. For example, the use of potassium *tert*-butylate in DMSO has made it possible to carry out conversions of various allyl furyl and thienyl ethers to the corresponding *cis*-propenyl ethers in high yields with high selectivity [4].

In extending this method to 2-(allyloxymethyl)benzothiophene (I) and 2-(allyloxymethyl)benzofuran (II), we observed that the occurrence of isomerization is complicated by a number of side reactions, hindering the preparation of the expected propenyl ethers in high yield. Thus, in the reaction of a solution of potassium *tert*-butylate in DMSO with ether I, the product of its isomerization, 2-(propenyloxymethyl)benzothiophene (III), is formed in only insignificant amounts (5-7%) according to PMR-spectroscopic data, and most of the reaction mixture is consumed for the product of the Wittig rearrangement of ether I, 1-(2-benzothienyl)but-3-en-1-ol (IV).

Isomerization is also not the only direction of the reaction for 2-(allyloxymethyl)benzofuran (II): in that case, according to data of thin-layer chromatography and PMR, both isomerization of ether II to 2-(propenyloxymethyl)benzofuran (V) and the Wittig rearrangement to 1-(2-benzofuryl)but-3-en-1-ol (VI) occur:



I,III,IV X=S; II,V,VI X = O

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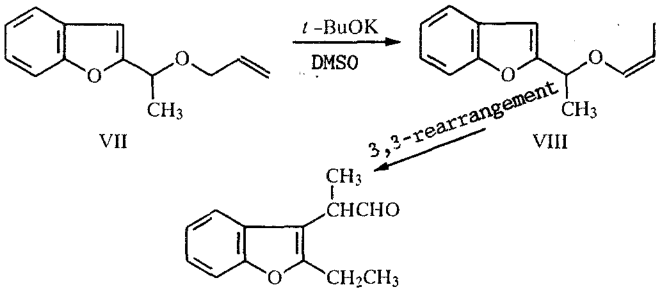
A similar course of the conversions of ethers I and II in the presence of potassium *tert*-butylate is related to the possibility of deprotonation of both methylene groups, which is due not only to the rather high C—H acidity of the protons in the allyl position, but also of the protons of the methylene group that is directly bonded to the heterocycle. This assumption is confirmed by data on the isomerization of (2-benzofuryl)ethyl allyl ether (VII): in that case, in ether II, methyl-group substitution of one hydrogen atom in the methylene group bonded to the heterocycle lowers the acidity of that proton and creates in ether VII specific steric hindrances for approach of a *tert*-butoxy anion. The virtually complete absence of the corresponding alcohol, a product of the Wittig rearrangement, in the reaction mixture is also probably related to that.



IX

It should be noted that for ether VII the yield of its isomerization product propenyl ether VIII, did not exceed 10-15%. In an attempt to purify ether VIII by vacuum distillation, it underwent partial 3,3-sigmatropic rearrangement to aldehyde IX, as indicated by the fact that the PMR spectrum of ether VIII showed a decrease of the integrated intensity of the peak of the β proton of the furan ring and the appearance of a peak of an aldehyde proton in the region of 9.66 ppm.

Thus, unlike in the case of derivatives of furan and thiophene [4], isomerization of allyl ethers of 2-(hydroxymethyl)benzofuran and 2-(hydroxymethyl)benzothiophene to propenyl ethers is accompanied by their Wittig rearrangement to isomeric alcohols, and the propenyl ethers also undergo the Claisen rearrangement to an isomeric aldehyde.

EXPERIMENTAL

The PMR spectra were recorded with a Varian T-60 spectrometer, and the internal standard was TMS or HMDS. Charomatographic-mass-spectrometric analysis was carried out with a Finnigan MAT 112S instrument under electron-impact conditions at ionizing energy 80 eV with a glass capillary column with l = 25 m, d = 0.25 mm, an OV-101 stationary phase, temperature programming from 60 to 180°C, and a helium carrier gas.

Allyl ethers I, II, and VII were obtained by reaction of the corresponding alcohols with allyl bromide under phase-transfer catalysis conditions by the method of [5].

To a solution of 0.05 mole of 2-(hydroxymethyl)benzothiophene (benzofuran) in 50 ml of DMSO was added with stirring 50 ml of a 30% solution of KOH and tetraethylammonium bromide (3 wt.% per mole of alcohol). The mixture was heated for 15 min at 40°C, then 6.1 g (0.05 mole) of allyl bromide was added dropwise, and the whole was stirred for 3 h at 40°C. The reaction mixture was decomposed with water and extracted with ether, and the extract was dried with $CaCl_2$. After evaporation of the ether, the residue was distilled under vacuum or purified by chromatography on silica gel 40/100, and the eluent was 1:1 hexane—ether.

2-(Allyloxymethyl)benzothiophene (I). PMR spectrum (CCl_4):4.00 (2H, multiplet, OCH_2), 4.59 (2H, singlet, CH_2O), 5.55 (3H, multiplet, $CH{=}CH_2$), 7.03 (1H, singlet, β-H of thiophene), 7.43 ppm (4H, multiplet, arom.). Yield 63%.

2-(Allyloxymethyl)benzofuran (II). Boiling point 128-129°C (7 mm). PMR spectrum (CCl_4): 3.89 (2H, doublet, OCH_2), 4.43 (2H, singlet, CH_2O), 5.45 (3H, multiplet, $CH{=}CH_2$), 6.50 (1H, singlet, β-H of furan), 7.48 (4H, multiplet, arom.). Mass spectrum, m/z: 188(16), 160(8), 146(16), 132(36), 131(100), 106(12), 105(28), 104(12), 91(28), 85(64), 83(76), 77(40).

1-(2-Benzofuryl)ethyl Allyl Ether (VII). Boiling point 130-131°C (7 mm). PMR spectrum (CCl_4):CH=1.50 (3H, doublet, CH_3), 3.89 (2H, doublet, OCH_2), 4.56 (1H, quartet, CH), 5.55 (3H, multiplet, $CH{=}CH_2$), 6.46 (1H, singlet, β-H of furan), 7.45 ppm (4H, multiplet, arom.). Yield 50%.

Isomerization of Ethers I, II, and VII. Finely triturated potassium *tert*-blutylate (1.22 g, 0.012 mole) was dissolved in 15 ml of dry DMSO in a dry argon atmosphere, and then 0.01 mole of ether in 5 ml of DMSO was added with stirring. The reaction mixture was heated for 4 h at 40°C, water was added after completion of the reaction, the mixture was extracted with ether, and the extract was washed with water and dried with Na_2SO_4. After removal of the solvent, the reaction products were recovered by chromatography on silica gel 40/100, the eluent was hexane$-CCl_4-$ether, 47:43:10, and the purity of the compounds was monitored by thin-layer chromatography on Silufol UV-254 plates. The following compounds were recovered from the reaction mixtures:

2-(Propenyloxymethyl)benzothiophene (III). PMR spectrum (CCl_4): 1.13 (3H, singlet, CH_3), 4.69 (2H, singlet, CH_2O), 5.58 (2H, multiplet, CH═CH), 7.55 ppm (5H, multiplet, arom.).

1-(2-Benzothienyl)but-3-en-1-ol (IV). PMR spectrum (CCl_4): 2.67 (2H, multiplet, CH_2), 2.92 (1H, multiplet, OH), 3.36 (1H, quartet, CH), 5.59 (3H, multiplet, $CH{=}CH_2$), 7.55 ppm (5H, multiplet, arom.).

1-(2-Benzofuryl)but-3-en-1-ol (VI). PMR spectrum (CCl_4): 2.51 (2H, multiplet, CH_2), 2.95 (1H, multiplet, OH), 4.65 (1H, quartet, CH), 5.41 (3H, multiplet, $CH{=}CH_2$), 6.35 (1H, singlet, β-H of furan), 7.50 ppm (4H, multiplet, arom.).

1-(2-Benzofuryl)ethyl Propenyl Ether (VIII). PMR spectrum (CCl_4): 1.56 (3H, doublet, CH_3), 1.67 (3H, doublet, CH_3), 4.82 (1H, quartet, CH), 5.19 (1H, doublet, =CH), 5.98 (1H, double doublet, =CH−, J = 6 Hz), 6.07 (1H, doublet, β-H of furan), 7.26 (4H, multiplet, arom.).

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