SULFUR DERIVATIVES OF 2-ACETYLFURAN

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A number of alkylthio derivatives of acetylfuran have been obtained by the replacement of the bromine in 2-acetyl-5-bromofuran. It has been shown by IR, NMR, and chemical studies that 2-acetyl-5-mercaptofuran exists in the thiol form in solutions and in the free state.

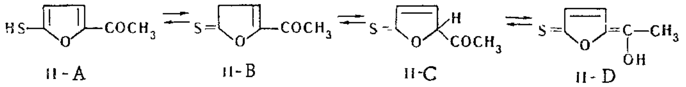
It has been shown in preceding investigations that 5-halogeno-2-acetylfurans readily react with sodium sulfide and sodium thioglycolate [1].

In a study of the mobility of a halogen atom in a furan ring, we found that 2-acetyl-5-bromofuran (I) readily exchanges the bromine for a thiomethyl, thioethyl, or thiophenyl group on being boiled with aqueous solutions of sodium methyl, ethyl, and phenyl sulfides, respectively.

As reported previously [1], the replacement of the halogen in a 5-halogeno-2-acetylfuran by a mercapto group forms the sodium salt of 2-acetyl-5-mercaptofuran (II). The acidification of this salt in an atmosphere of hydrogen gives an 87% yield of 2-acetyl-5-mercaptofuran (II-A). The reaction product is very unstable and darkens on standing. The oxidation of the sodium salt II by iodine in potassium iodide solution has given di(5-acetyl-2-furyl) disulfide (III). Its structure was confirmed by IR and NMR spectra.

The disulfide III is also formed by the acidification of the sodium salt II in the presence of atmospheric oxygen.

The hypothesis has been put forward previously [2] that 5-mercapto-2-acetylfuran (II-A) is capable of thione-thiol tautomerism:



However, the IR spectrum of II-A has an absorption band in the 1678 cm^{-1} region corresponding to the vibrations of a carbonyl group and lacks the absorption in the 3300 cm^{-1} region that is characteristic for chelates. These facts exclude the presence of form II-D.

The presence of forms II-B and II-C was excluded on the basis of a study of the NMR spectra of 2-acetyl-5-bromofuran (I) (Fig. 1) and a comparison of it with the NMR spectrum of 2-acetyl-5-methylthiofuran (IV). The NMR spectrum of II-A has four signals of two nonequivalent protons of the furan ring, which are characteristic for 2,5-disubstituted furans, the signal of the protons of the methyl group of an acetyl radical in the 2.57 ppm region, and the signal of the proton of a mercapto group in the 0.5 ppm region. If the tautomeric form II-B were present, the NMR spectrum would have the triplet of an olefinic proton and the doublet of the protons of a methylene group. If form II-C were present, the NMR spectrum of II-A would also be more complex. Thus, the IR and NMR spectra exclude the presence of forms II-B and II-D in solutions and show that there is only form II-A.

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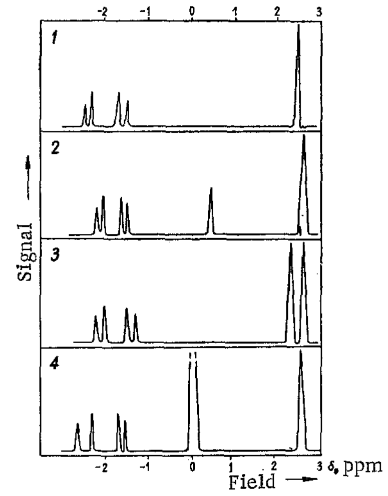
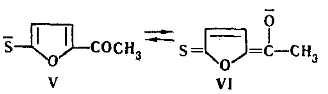


Fig. 1. NMR spectra: 1) di-(5-acetyl-2-furyl)disulfide; 2) 2-acetyl-5-mercaptofuran; 3) 2-acetyl-5-methylthiofuran; 4) sodium salt of 2-acetyl-5-methylthiofuran (20% aqueous solution) (others, 20% solutions in CCl_4; internal standard water; JNM instrument).

This conclusion is in harmony with the chemical properties of II-A. On being boiled with dilute acids, the furan ring is not opened, as would have been expected for forms II-B–II-D, since the latter have the thiolactone structure. Reaction with diazomethane in ethereal solution gave only 5-methylthio-2-acetofuran (XIV) in almost quantitative yield, its structure being shown by IR and NMR spectroscopy.

Thus, a consideration of both the chemical and the physical properties of 2-acetyl-5-mercaptofuran shows the absence of tautomeric transformations.

It follows from a comparison of the NMR spectra of II-A and its sodium salt that on dissolution in alkalies the signal of the methyl group of the acetyl radical is shifted very slightly downfield – by 0.07 ppm – while the signals of the protons of the furan ring are shifted downfield considerably more strongly: by 0.51 and 0.21 ppm. This probably shows that in the anion of 2-acetyl-5-mercaptofuran the contribution of the mesomeric structure VI is very small in comparison with that of structure V.



Otherwise, the negative charge on the oxygen atom would lead to a change in the screening of the proton of the methyl group and to a shift in its NMR signal.

EXPERIMENTAL

2-Acetyl-5-mercaptofuran (II-A). With stirring and cooling in a current of nitrogen, 30 ml of 10% hydrochloric acid was added to the sodium salt of 2-acetyl-5-mercaptofuran (II) obtained from 8.9 g (0.047 mole) of 2-acetyl-5-bromofuran (I) and 11.5 g of sodium sulfide. The oil that deposited was separated off, and the aqueous layer was extracted with ether; after the ether had been driven off, the residue was distilled in vacuum in an atmosphere of nitrogen. This gave 4.1 g of II-A, bp 98°C (12 mm); yellow crystals, mp. 45°C. Found %: S 22.28; 22.37. $C_6H_6O_2S$. Calculated %: S 22.55.

2-Acetyl-5-mercaptofuran-2,4-dinitrophenylhydrazone, mp 212°C (from ethanol). Found %: N 17.25; 17.33. $C_{12}H_{10}N_4SO_5$. Calculated, %: N 17.41.

Di(5-aceto-2-furyl) disulfide (III). With stirring, 25 g of iodine in a solution of 40 g of potassium iodide in 100 ml of water was added to the sodium salt obtained from 19 g (0.1 mole) of I, 60 ml of water, and 24 g of sodium sulfide. The crystals that deposited were filtered off. Yield 10.7 g (76%), mp 126°C (from ethanol). Found, %: S 22.86; 22.97. $C_{12}H_{10}O_4S_2$. Calculated, %: S 22.74.

2-Acetyl-5-methylthiofuran (IV). a. With cooling to 0°C, 4.8 g (0.1 mole) of methanethiol and 7.6 g (0.04 mole) of I were added to a solution of 2 g of caustic soda in 25 ml of water. The mixture was heated in a sealed tube at 80°C for 6 h. After cooling, the tube was opened and the crystals that had deposited were filtered off and recrystallized from aqueous ethanol. Yield 59%, mp 44°C. It gave no depression of the melting point with an authentic sample [1].

b. A solution of 3.2 g (0.017 mole) of II in ether was treated with a 50% excess of diazomethane in ether, and the residue after the evaporation of the ether was crystallized from ethanol; mp 44-45°C. It gave no depression of the melting point with the II obtained previously [1].

2-Acetyl-5-ethylthiofuran (VII). With cooling and stirring, 6.2 g (0.1 mole) of ethanethiol, followed by 15.2 g (0.8 mole) of I were added to a solution of 4.5 g of caustic soda in 50 ml of water. The mixture was boiled for 4 h. After cooling, the crystals that had deposited were filtered off, giving 13.6 g (83%) of 2-acetyl-5-ethylthiofuran, mp 49°C (from aqueous ethanol). Found, %: S 18.64; 18.72. $C_8H_{10}SO_2$. Calculated, %: S 18.86.

2-Acetyl-5-ethylthiofuran 2,4-Dinitrophenylhydrazone, mp 209°C (from ethanol). Found, %: N 13.93; 13.75. $C_{18}H_{14}N_4O_5S$. Calculated, %: N 14.09.

2-Acetyl-5-phenylthiofuran (VIII). This was obtained in a similar manner to VII with a yield 85%, mp. 66°C (from aqueous ethanol). Found, %: S 14.68; 14.53. $C_{12}H_{10}O_2S$. Calculated, %: S 14.71.

LITERATURE CITED

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