INVESTIGATION OF VINYL ETHERS OF THE FURAN SERIES

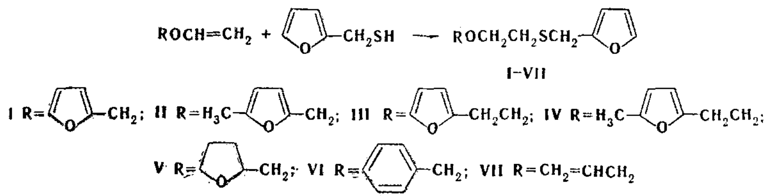
IX.* THIYLATION OF VINYL ETHERS OF FURFURYL ALCOHOLS WITH FURFURYL MERCAPTAN

G. G. Skvortsova, V. V. An,
L. M. An, and V. K. Voronov

UDC 547.279.1'722.2:541.67

The reaction of furfuryl mercaptan with several vinyl ethers of furan alcohols was studied. Nine new furan-substituted sulfides were synthesized. The structures of the compounds obtained were proved by PMR spectroscopy.

We have previously [1-3] reported the synthesis of vinyl ethers of several 5-substituted furfuryl alcohols and the electrophilic addition of alcohols to the vinyloxy group of these ethers. In the present paper we present data on the homolytic addition of furfuryl mercaptan (FM) to various vinyl ethers of furan-substituted alcohols and to vinyl tetrahydrofurfuryl ether (VTFE), vinyl benzyl ether (VBE), and vinyl allyl ether (VAE), which proceeds via the scheme



An example of the addition of butyl mercaptan to vinyl furfuryl ether (VFE) under both radical and electrophilic conditions is known [4]. Uvarova [4] demonstrated that α-addition of the mercaptan to the vinyloxy group is observed to a lesser degree along with β-addition during radical initiation. Our investigations demonstrated that sulfides I-VII are formed in good yields (66-84%) in the presence of 2,2'-azobisisobutyronitrile at 60°C; these are exclusively the products of β-addition. The course of the reaction was monitored via the mercuric chloride method [5] and thin-layer chromatography (TLC) on activity II Al_2O_3. An increase in the experimental temperature from 60° to 80° does not have a substantial effect on the yields of sulfide during heating for 8 h. The reactions were carried out in sealed glass ampules, previously treated with diethylamine. As in [4], when the thiylation of the vinyl ethers was carried out in vessels that had not been treated with base, the formation of small amounts of α-addition products was observed. We suppose that acidic agents on the walls of the reaction vessel play a large role in the formation of α-addition products. Thermal electrophilic α-addition of the mercaptans to the vinyl ethers is also possible. In order to verify this assumption, we studied the reaction of VTFE and FM without the addition of an initiator at 80° for 16 h. It is interesting to note that thiylation does not proceed completely when a small amount of hydroquinone is present in the reaction mixture. At the same time, the thermal reaction without an initiator and without hydroquinone gives 53% of the β-addition product after 8 h at 80°; the α-addition product is not observed.

---

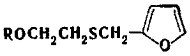
*See [6] for communication VIII.

Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1155-1158, September, 1972. Original article submitted July 28, 1971.

TABLE 1. Parameters of the PMR Spectra of VII and VIII

Compound	Chemical shifts, δ, ppm: furan ring H-2	H-3	H-4	$CH_2{=}CH{-}\overset{\vert}{\underset{\vert}{C}}{-}$	$-CH_2{-}O{-}CH_2-$	$-CH_2{-}S{-}CH_2-$	$-\overset{\vert}{\underset{\vert}{C}}{-}CH_2{-}\overset{\vert}{\underset{\vert}{C}}-$	Spin-spin coupling constants, J, Hz
VII	7,21	6,16	6,04	4,93—5,29 5,53—5,98	3,84 3,41	3,60 2,51	—	$J_{23}=1,9$ $J_{24}=0,8$ $J_{34}=3,3$ $J_{CH_2-CH_2}=6,4$
VIII	7,18	6,13	6,00	—	3,32 3,35	3,58 3,52 2,44 2,48	1,52	$J_{23}=1,9$ $J_{24}=0,8$ $J_{34}=3,2$ $J_{CH_2-CH_2}=7,0$

TABLE 2



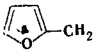
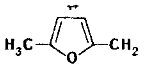
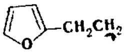
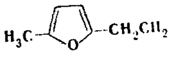
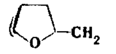
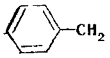
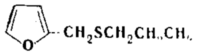
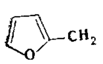
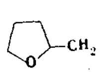
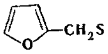
Comp.	R	bp, °C (mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.
I		139—140 (3)	1,1702	1,5378	63,60	64,28
II		152—154 (4)	1,1308	1,5280	68,62	68,90
III		150—151 (3)	1,1438	1,5308	68,14	68,89
IV		153—154 (3)	1,1197	1,5270	73,03	73,51
V		143 (3)	1,1355	1,5196	64,75	65,21
VI		160 (3)	1,1265	1,5582	71,00	71,40
VII	$CH_2{=}CHCH_2$	103 (3)	1,0722	1,5164	55,81	56,07
VIII		210—212 (3)	1,1678	1,5513	89,09	90,75
IX*		109 (3)	1,0290	1,4960	60,75	61,12
X*		116 (3)	0,9977	1,4290	61,97	62,08

TABLE 2 (continued)

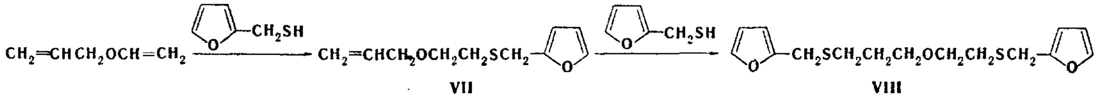
Comp.	Empirical formula	Found, % C	H	S	Calculated, % C	H	S	Yield, %
I	$C_{12}H_{14}O_3S$	60,2	5,9	13,7	60,5	5,9	13,5	84
II	$C_{13}H_{16}O_3S$	62,2	6,5	11,9	61,9	6,4	12,7	68
III	$C_{13}H_{16}O_3S$	61,8	6,4	13,0	61,9	6,4	12,7	82
IV	$C_{14}H_{18}O_3S$	63,0	7,0	12,0	63,1	6,8	12,0	66
V	$C_{12}H_{18}O_3S$	59,6	7,2	13,4	59,5	7,5	13,2	80
VI	$C_{14}H_{16}O_2S$	67,4	6,5	13,1	67,7	6,5	12,9	68
VII	$C_{10}H_{14}O_2S$	60,7	7,2	16,5	60,6	7,1	16,2	84
VIII	$C_{15}H_{20}O_3S_2$	—	—	—	—	—	—	13
IX*	$C_{11}H_{18}O_2S$	—	—	—	—	—	—	89
X*	$C_{11}H_{22}O_2S$	60,5	10,0	14,7	60,5	10,2	14,7	97

---

*Compounds IX and X contain C_4H_9S instead of the  grouping.

We accomplished the synthesis of the Markovnikov thiylation product from VFE and FM in the presence of SO_2 as the catalyst. The mercuric chloride method and thin-layer chromatography demonstrated that exclusively the α-addition product is obtained. The product is unstable and decomposes during vacuum distillation.

Despite the fact that vinyl ethers with considerably different substituents were used in the thiylation reaction, no substantial difference was observed in the yields of sulfides. The somewhat low yields of sulfides from the high-molecular-weight vinyl ethers is most likely explained by losses during isolation of the products. Sulfides are obtained in higher yields in the reaction of VFE and VTFE with butyl mercaptan than in the reaction with furfuryl mercaptan. Furfuryl mercaptan adds to both double bonds of VAE to give two addition products. The major product (84%) is β-allyloxyethyl furfuryl sulfide (VII). The other compound is the product of the addition of FM to both double bonds – 1,10-difuryl-2,9-dithia-5-oxadecane (VIII).



VII VIII

The structures of VII and VIII were confirmed by the PMR spectra (Table 1). The absence of signals from the protons of a vinyloxy group in the spectra of VII and VIII and of the signals of the protons of an allyl group ($CH_2{=}CH{-}C$) in the spectrum of VIII indicates that in the first case the addition occurred at the vinyloxy group, while addition occurred at both double bonds in the second case. In addition, the absence of the signals of a $>CH{-}CH_3$ group in the spectra of VII and VIII is evidence that the addition of mercaptan to both the vinyloxy and allyl groups was counter to the Markovnikov rules.

The physical constants, elementary analyses, and yields of the synthesized β-furfuryloxyethyl (I), β-(5-methylfurfuryl)oxyethyl (II), β-(β'-furylethyl)oxyethyl (III), β-(β'-5-methylfurylethyl)oxyethyl (IV), β-tetrahydrofurfuryloxyethyl (V), β-benzyloxyethyl (VI), and allyloxyethyl (VII) furfuryl sulfides, 1,10-difuryl-2,9-dithia-5-oxadecane (VIII), and β-furfuryloxyethyl (IX) and β-tetrahydrofurfuryloxyethyl (X) butyl sulfides are presented in Table 2. All of the sulfides obtained are transparent liquids with a characteristic sharp odor and are soluble in ether, acetone, and alcohol and insoluble in water.

EXPERIMENTAL

β-Furfuryloxyethyl Furfuryl Sulfide (I). A 3-g (24 mmole) sample of vinyl furfuryl ether, 3 g (26 mmole) of furfuryl mercaptan, and 0.03 g of 2,2'-azobisisobutyronitrile were placed in a diethylamine-treated glass ampule. The sealed ampule was held at 60° in a thermostat for 8 h. Vacuum distillation yielded 5 g (83.5%) of I with R_f 0.63 (activity II Al_2O_3, benzene). Sulfides II-X were similarly obtained.

Reaction of Vinyl Furfuryl Ether with Furfuryl Mercaptan in the Presence of SO_2. A stream of SO_2 was passed into a cooled (to –20°) solution of 3 g (24 mmole) of VFE in 3 g (26 mmole) of FM with stirring for 30 sec. The cooling bath was removed, and the temperature of the mixture was raised to 30°. Stirring was continued for another 2 h at room temperature to give a dark-gray solution. The mixture was subjected to thin-layer chromatography and gave two spots – one was the starting FM (R_f 0.79), the other was α-furfurylthioethyl furfuryl ether (R_f 0.38) (activity II Al_2O_3, benzene). The mixture gave a copious white precipitate on treatment with a 20% solution of mercuric chloride in alcohol. The reaction products resinified on attempts to distill them in vacuo.

The PMR spectra of CCl_4 solutions were recorded at room temperature with a BS-487 B spectrometer with hexamethyldisiloxane as the internal standard.

LITERATURE CITED

1. M. F. Shostakovskii, V. V. An, G. G. Skvortsova, and L. M. An, Khim. Geterotsikl. Soedin., No. 2, 93 (1970).
2. G. G. Skvortsova, V. V. An, L. M. An, and G. A. Rinkus, Khim. Geterotsikl. Soedin., No. 2, 97 (1970).
3. V. V. An, G. G. Skvortsova, L. M. An, and V. K. Voronov, Khim. Geterotsikl. Soedin., 1299 (1970).
4. N. I. Uvarova, Izv. Sibirsk. Otd. Akad. Nauk SSSR, 78 (1962).
5. E. N. Prilezhaeva, É. S. Shapiro, and M. F. Shostakovskii, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 438 (1951).
6. V. V. An, G. G. Skvortsova, and L. M. An, Khim. Geterotsikl. Soedin., 1593 (1971).