SYNTHESIS OF VINYL ETHERS OF FURFURYLIDENEAMINOPHENOLS

G. G. Skvortsova, Z. M. Garashchenko, V. V. An, N. N. Chipanina, and
L. M. An

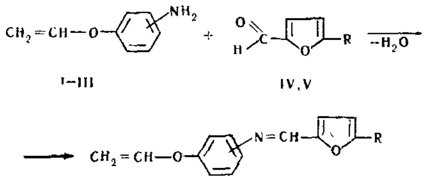
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 4, 588–591, 1968

UDC 547.724.2.07:542.953.4

The reaction of furfural and its homologs with vinyl and ethyl ethers of o-, m-, and p-aminophenols at room temperature without the addition of any catalyst whatever leads to the amine-aldehyde condensation with the formation of the corresponding ethers of furfurylideneaminophenols. The structure of the latter has been shown by hydrolysis, hydrogenation, and independent synthesis.

Vinyl ethers of aromatic amines containing furan rings in the molecule are very interesting new monomers with polyfunctional properties. We have studied the reaction of furfural and its homologs with vinyl ethers of o-, m-, and p-aminophenols (I–III). There is information in the literature on the condensation at 100–105° C of furfural with p-phenetidine [1] and with p-aminophenol [2]. In addition it is known that on reaction with aromatic amines furan aldehydes not infrequently undergo ring opening [3–6].

We have shown that vinyl ethers of aminophenols readily react with furfural (IV) and 5-methylfural (V) in equimolar amounts at room temperature. With all the isomeric vinyl ethers I–III the reactions take place very rapidly with the formation of an aldimine bond and the liberation of water in accordance with the equation



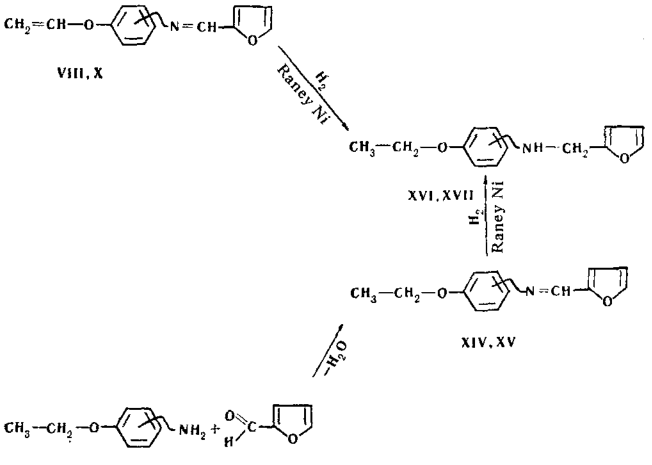
I–III IV,V

VIII–XIII

IV, VIII, IX, X R = H
V, XI–XIII R = CH_3

The ethyl ethers of o- and p-aminophenols (VI) and (VII) behave analogously. The yield of vinyl ethers of furfurylideneaminophenols VIII–XIII amounts to 80–90% and of the corresponding phenetidine derivatives—XIV–XV—85–95%. The initial furfural and ethers were recovered from the reaction mixtures in small amounts. No products whatever indicating a transformation or opening of the furan ring were found. All the vinyl and ethyl ethers of furfurylideneaminophenols synthesized are high-boiling liquids or crystalline substances soluble in alcohols, acetone, and hydrocarbons. They are fairly stable and do not decompose on distillation in vacuum. Their constants are given in the table. Determination of the refractive indices is difficult because of their intense fluorescence.

The structure of the vinyl ethers of the furfurylideneaminophenols is shown by the results of elementary analysis and infrared spectroscopy, by their hydrolytic decomposition and hydrogenation, and by independent synthesis, which was carried out in the following way:



VIII, X

XVI, XVII

XIV, XV

VI, VII

On acid hydrolysis, the vinyl ethers of the furfurylideneaminophenols form a brightly colored mixture of products containing mainly acetaldehyde and aminophenols with a small amount of furfural. The latter can also be detected on the hydrolytic cleavage of the ethyl ethers of the furfurylideneaminophenols under the conditions mentioned.

The addition of hydrogen to the ethers VIII and X in the presence of a nickel catalyst takes place simultaneously at the vinyl and the nitrogen-carbon bonds, leading to the ethyl ethers of the furfurylaminophenols XVI and XVII with yields of 87–96%.

The latter was synthesized independently by the condensation of the phenetidines VI and VII with furfural and the subsequent hydrogenation of the ethers XIV and XV so obtained. The physicochemical constants of the products of the hydrogenation of XIV and XV agreed completely with the properties of XVI and XVII. Their IR spectra were completely identical; one of them is given in the figure (curve 6).

As can be seen from the figure, the spectra of the vinyl ethers VIII–XIII have intense bands of the stretching vibrations of a $CH_2=CH-$ group in the 1620–1630 cm^{-1} region, and the frequencies of the deformation nonplanar vibrations at 960 cm^{-1}. The ethyl ethers synthesized from the phenetidines and furfural and also the products of their hydrogenation XIV–XVII do not contain a band at 960 cm^{-1}. The absorption at 1390 and 2878 cm^{-1} corresponds to the deformation and stretching vibrations of the CH_3 groups of compounds XVI and XVII.

For the vinyl-group-containing compounds XVII–XIII studied, the accurate assignment of the absorption bands of the C=N group is difficult because superposition of the $CH_2=CH-$ vibrations takes place in the region of their stretching vibrations. This is confirmed

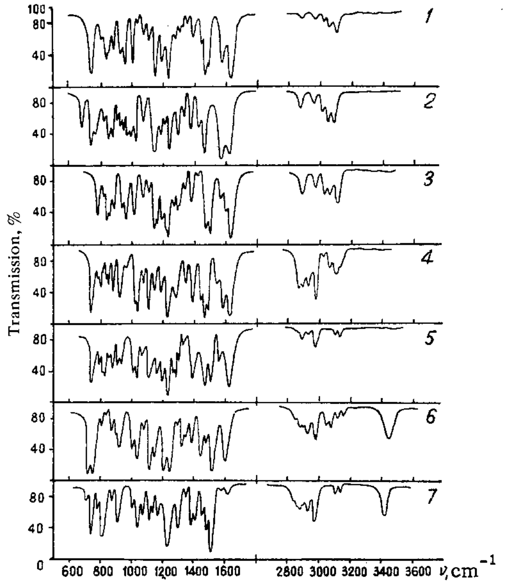
Properties of the Compounds Synthesized

Compound	Name	Bp °C (mm)	d_4^{20}	Empirical formula	Found, %			Calculated, %			Yield, %
					C	H	N	C	H	N	
VIII	Vinyl ether of o-furfurylideneaminophenol	141—142 (2)	1.1510	$C_{13}H_{11}NO_2$	73.18	5.23	6.83	73.22	5.20	6.57	81
IX	Vinyl ether of m-furfurylideneaminophenol	171,5 (5)	1.1407		73.23	5.22	6.74				84
X	Vinyl ether of p-furfurylideneaminophenol	163—164 (8)	1.1498		73.50	5.28	6.77				92
XI	Vinyl ether of o-(5-methylfurfurylideneamino)-phenol	144—145 (1)	1.1167	$C_{14}H_{13}NO_2$	—	—	6.44	73.99	5.77	6.16	89
XII	Vinyl ether of m-(5-methylfurfurylideneamino)-phenol	166—167 (1)	1.1183		—	—	6.25				85
XIII	Vinyl ether of p-(5-methylfurfurylideneamino)-phenol	166—167 (3)*	—		73.90	5.57	—				91
XIV	Ethyl ether of o-furfurylideneaminophenol	151—152 (2)	1.1467	$C_{13}H_{13}NO_2$	72.35	6.03	6.31	72.54	6.09	6.51	85
XV	Ethyl ether of p-furfurylideneaminophenol	164—166 (1)**	—		72.4	6.18	6.76				97
XVI	Ethyl ether of N-furfuryl-o-aminophenol	129—131 (2)	1.1067	$C_{13}H_{15}NO_2$	71.61	6.99	6.57	71.86	6.96	6.45	87
XVII	Ethyl ether of N-furfuryl-p-aminophenol	147—148 (2)***	—		71.53	6.84	6.70				96

---

*Mp 33° C **Mp 72°. ***Mp 57° C.

by a comparison of the spectra of the vinyl ethers with the spectra of the ethyl ethers of the furfurylideneaminophenols XIV and XV in which bands with frequencies of 1630 and 1625 cm^{-1}, respectively, are well defined.



IR spectra: 1) vinyl ether of o-furfurylideneaminophenol (VIII); 2) vinyl ether of m-furfurylideneaminophenol (IX); 3) vinyl ether of p-furfurylideneaminophenol (X); 4) ethyl ether of o-furfurylideneaminophenol (XIV); 5) ethyl ether of p-furfurylideneaminophenol (XV); 6) ethyl ether of N-furfuryl-o-aminophenol (XVI); 7) ethyl ether of N-furfuryl-p-aminophenol (XVII).

According to literature data, the band of the stretching vibrations of C=N groups should be located at 1690–1640 cm^{-1} [7]. The displacement of these bands to the low-frequency end of the range can apparently be explained by the presence in compounds XIII–XV of conjugation of the C=N bond with aromatic and furan rings. The same effect has been observed by other authors for a whole series of systems conjugated with aromatic rings, limiting the interval mentioned to 1660–1630 cm^{-1} [8].

After the hydrogenation of XIV and XV, the bands at 1630 and 1625 cm^{-1} disappear and characteristic bands of a secondary amino group with frequencies of 3435 and 3410 cm^{-1}, respectively for XVI and XVII, appear.

Thus, the structure of the substances synthesized is not a matter of doubt and shows the occurrence of amino-aldehyde condensation.

EXPERIMENTAL

Starting materials. The vinyl ethers of o-, m-, and p-aminophenols (I–III) were obtained from acetylene and the aminophenols [9]: I, bp 69°–70° C (2mm), d_4^{20} 1.0676, n_D^{20} 1.5715; II, bp 92°–93° C (2 mm), d_4^{20} 1.0760, n_D^{20} 1.5825; III bp 94° C (5 mm), d_4^{20} 1.0759, n_D^{20} 1.5767. The o-phenetidine (VI) was obtained by reducing the ether I over a nickel catalyst [9]: bp 81°–82° C (1 mm); n_D^{20} 1.5545. The 5-methylfurfural (V), with bp 64° C (5 mm), d_4^{20} 1.1012, n_D^{20} 1.5310 was synthesized by the formylation of sylvane with dimethylformamide [10]. The p-phenetidine (VII), bp 110°–111° C (1 mm), n_D^{20} 1.5635 and the furfural (IV), bp 61°–62° C (18 mm), n_D^{20} 1.5260 were commercial reagents purified by vacuum distillation.

Condensation of the vinyl ether of o-aminophenol with furfural. A three-necked flask with a reflux condenser was charged with 5.2 g (65 mole) of furfural and then, with stirring, 7.3 g (54 mM) of the ether I was added dropwise. The reaction took place with the evolution of heat and was complete after 30–40 min. The water was eliminated from the turbid reaction mixture under vacuum and the residue was distilled. This gave 9.3 g of the vinyl ether of o-furfurylideneaminophenol (VIII) in the form of a greenish-yellow oily liquid strongly fluorescent in the light. Compounds IX–XIII were obtained similarly; their properties are given in the table.

Ethyl ethers of furfurylideneaminophenols. At room temperature (18°–20° C) with continuous stirring, 3.16 g (23 mM) of o-phenetidine was slowly added to 2.32 g (30 mM) of furfural. The reaction mixture was treated as in the preceding cases. Distillation yielded 2.89 g of the ether XIV in the form of a yellow-green liquid. The crystalline compound XV (table) was obtained similarly. According to the literature, the ether XV has mp 72°–73° C.

Hydrolysis of the vinyl ether of p-furfurylideneaminophenol.(X). A mixture 0.57 g of the ether X and 20 ml of 2% H_2SO_4 was heated in a 50-ml tube in the boiling water bath for 2 hr. After cooling, the tube was opened, 10 ml of sodium bisulfite solution was added to the reaction mixture, and the excess of it was back-titrated with 0.1 N iodine solution. Calculated from the aldehyde liberated, 89.4% hydrolysis had taken place.

Hydrogenation of the vinyl ether of p-furfurylideneaminophenol (X). 2.45 g of the ether X was added to 0.4 g of Raney nickel catalyst in 28 ml of absolute ethanol and reduction was carried out. After 12 hr, 615 ml of hydrogen had been absorbed, the theoretical amount being 601.2 ml. Vacuum distillation yielded thecethyl ether of N-furfuryl-p-aminophenol (XVII) in the form of crystals with mp 56°–57° C, weight 2.38 g. When 1.62 g of the ethyl ether of p-furfurylideneaminophenol (XV) was hydrogenated, the absorption of hydrogen ceased after 6 hr. The total absorbed was 203 ml and the theoretical amount 192.7 ml. This yielded 1.59 g of compound XVII. A mixture of the first and second sets of crystals gave no depression of the melting point.

Ethyl ether of N-furfuryl-o-aminophenol (XVI). When 2.70 g of substance XIV was hydrogenated in 30 ml of ethanol in the presence of Raney nickel, 342.0 ml of hydrogen (20° C, 716 mm) was absorbed, the theoretical amount being 328.2 ml. The ether XVI, 2.2 g, was obtained in the form of an oil which crystallized on standing, mp 37°–38.5° C, bp 145°–147° C (8–9 mm); d_4^{20} 1.1067, n_D^{20} 1.5628. Found: MR_D 63.66. Calculated for $C_{13}H_{13}NO_2$: MR_D 63.15.

The reduction of 2.95 g of the vinyl ether VIII gave an 86% yield of the ether XVI, mp 37.5° C (table), the amount of hydrogen consumed being 782 ml and the theoretical amount 765.4 ml.

The IR spectra of the compounds VIII–XVII synthesized were recorded on a UR-10 spectrophotometer in the 700–3600 cm^{-1} region in a microlayer or, for the crystalline substances, in tables with potassium bromide.

REFERENCES

1. R. Ehrhardt, Ber., 30, 2014, 1897.
2. V. I. Isagulyants and G. M. Egorova, The Chemistry of Petroleum [in Russian], Gostoptekhizdat, 1949.
3. H. Schiff, Lieb. Ann., 201, 355, 1880.
4. W. König, J. pr. Chem., (2) 88, 193, 1913.
5. J. Stenhouse, Lieb. Ann., 156, 197, 1870.
6. H. Schiff, Lieb. Ann., 239, 349, 1887.
7. K. Nakanishi, Infrared Spectra. Practical [Russian translation], Mir, Moscow, p. 45, 1965.
8. Khorana, Chem. Rev., 53, 145, 1953.
9. M. F. Shostakovskii, G. G. Skvortsova, and M. Ya. Samoilova, ZhOKh, 31, 3226, 1961.
10. V. J. Fraynelis, J. J. Miskel, and J. R. Sowa, J. Org. Chem., 22, 1269, 1957.

20 June 1966

Irkutsk Institute of Organic
Chemistry, Siberian Division,
AS USSR