

INVESTIGATIONS OF VINYL ETHERS OF THE FURAN SERIES

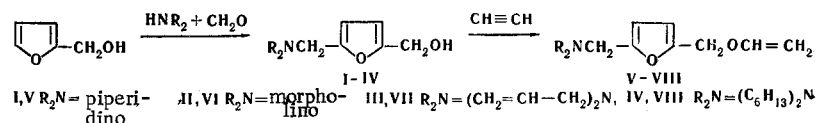
VI.* SYNTHESIS AND VINYLATION OF N,N-DISUBSTITUTED 5-AMINOMETHYLFURFURYL ALCOHOLS

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A number of 5-aminomethylfurfuryl alcohols were synthesized by the Mannich reaction from furfuryl alcohol, secondary amines, and paraformaldehyde. The corresponding vinyl ethers were obtained by reaction of these alcohols with acetylene. The PMR spectra of the vinyl ethers of 5-piperidino- and 5-diallylaminomethylfurfuryl alcohols are described.

It is well known that furfuryl alcohols are vinylated under comparatively mild conditions [1-3]. It was interesting to investigate the behavior of a number of other furfuryl alcohols which have a tertiary nitrogen atom in the side chain. For this, we synthesized N,N-disubstituted 5-aminomethylfurfuryl alcohols I-IV, of which II-IV were prepared for the first time, via the method in [4].



In so doing it was noted that dialkylamines undergo the Mannich reaction with furfuryl alcohol with difficulty, and the corresponding amino alcohols are isolated in low yields or are not obtained at all.

The amino alcohols obtained were subjected to reaction with acetylene under pressure in dioxane solutions in the presence of KOH.

Like the previously [1-3] investigated furfuryl alcohols, amino alcohols I-IV add to acetylene at 135°C forming vinyl ethers of N,N-disubstituted aminomethylfurfuryl alcohols (V-VIII), which are viscous liquids with specific gravities close to unity, have the characteristic odor of amines, and form azeotropes with the corresponding alcohols. They were freed from traces of the starting substances by column chromatography. Their structures were confirmed by their IR spectra and elementary analysis. Bands with frequencies of 1620-1630 and 1640-1660 cm^{-1} , which correspond to vibrations of the $-\text{O}-\text{CH}=\text{CH}_2$ group, are present in the IR spectra of all of the vinyl ethers obtained.





We also used PMR to elucidate the structure of ethers V and VII.† The PMR spectra of V and VII are readily interpreted from the first-order rules [5, 6], despite the significant number of resonance lines in them, allowing for the integral intensities. The weak-field quartet (6.40 ppm) in the PMR spectrum of VII (see Fig. 1) belongs to the proton of the $=\text{CH}$ vinyl group. However, the methylene protons of the vinyl group resonate in a stronger field with respect to the $=\text{CH}$ proton, during which the signal of the trans

*For Communication V, see [1].

†The PMR spectra were recorded with a JNM-4H-100 spectrometer at room temperature using carbon tetrachloride as the solvent and hexamethyldisiloxane as the internal standard.

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TABLE 1

Comp.	R ₂ N—	R'	bp, °C (mm)	n _D ²⁰	d ₄ ²⁰	MR _D		Empirical formula	Found, %			Calc., %			Yield, %		
						found	calc.		C	H	N	C	H	N			
I*		H	137 (3)	1,5135	—	—	—	C ₁₁ H ₁₇ O ₂ N	—	—	—	—	—	—	70		
II		H	192 (10)	1,5115	1,1486	51,37	51,79	C ₁₀ H ₁₅ O ₃ N	60,95	7,76	7,02	60,91	7,66	7,10	75		
III	(CH ₂ =CH—CH ₂) ₂ N	H	148 (3)	1,5110	1,0458	59,35	60,55	C ₁₂ H ₁₇ O ₂ N	69,75	8,29	6,76	69,53	8,27	6,75	72		
IV	(C ₆ H ₁₃) ₂ N	H	180—185 (5)	1,4685	0,9385	87,44	89,29	C ₁₈ H ₃₃ O ₂ N	—	—	5,17	—	—	4,74	40		
V		CH=CH ₂	139 (4)	1,5025	1,0293	63,40	63,65	C ₁₃ H ₁₉ O ₂ N	70,49	8,79	6,36	70,55	8,65	6,33	62		
VI		CH=CH ₂	152 (1)	1,5040	1,0918	60,68	60,40	C ₁₂ H ₁₇ O ₃ N	64,64	7,72	6,36	64,57	7,62	6,27	51		
VII	(CH ₂ =CH—CH ₂) ₂ N	CH=CH ₂	119 (5)	1,4939	0,9777	69,33	69,54	C ₁₄ H ₁₉ O ₂ N	72,40	8,52	6,20	72,07	8,21	6,00	37		
VIII	(C ₆ H ₁₃) ₂ N	CH=CH ₂	150 (1)	1,4651	0,9106	97,21	96,45	C ₂₀ H ₃₅ O ₂ N	74,88	11,12	4,59	74,76	10,90	4,86	17		

*bp 145° (2 mm), n_D²⁰ 1.5199 [4].

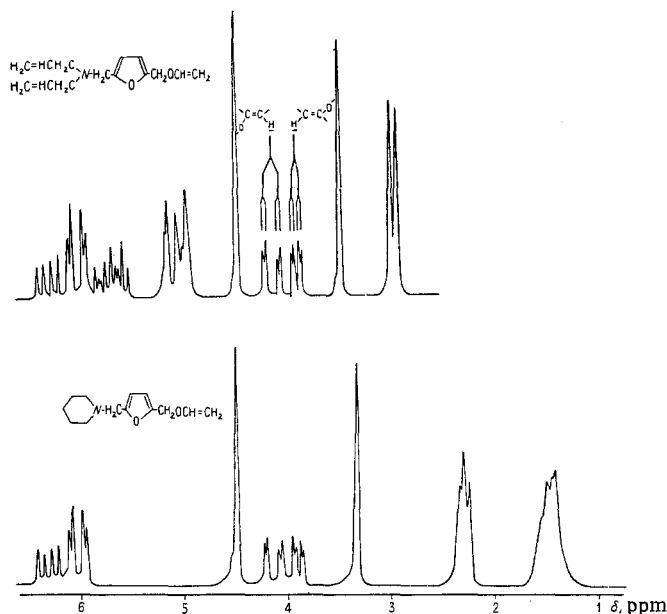


Fig. 1. PMR spectra of vinyl ethers of 5-piperidino- and 5-diallylaminomethylfurfuryl alcohols.

proton (with respect to the oxygen atom) has a chemical shift of 3.93 ppm, while the cis proton has a chemical shift of 4.16 ppm. The multiplicity (number of resonance lines) of the signals is due to spin-spin interaction of the methylene protons with each other and with the =CH proton. The protons of the furan ring form an AB system. Their signals appear as doublets with chemical shifts of 6.14 and 5.98 ppm. The signals of the protons of the methylene groups in the α position with respect to the oxygen atom of the furan ring appear as singlets. The protons of the $>N=CH_2$ group resonate at stronger fields (3.50 ppm) than the protons of the CH_2O group (4.51 ppm). The two methylene groups of the allyl radicals gave a doublet (2.97 ppm) which is due to spin-spin interaction with the neighboring =CH protons. Finally, the two multiplets remaining in the spectrum belong to the protons on the allyl double bonds; the multiplet from 4.90–5.27 ppm is due to the methylene protons, while that from 5.53–5.87 ppm is due to the =CH protons.

The spectrum of V is represented by nine groups of lines (see Fig. 1). Just as in the spectrum of VII, the weak-field quartet (6.32 ppm) belongs to the proton of the =CH vinyl group. The signals of the two other vinyl protons have chemical shifts of 4.13 ppm (signal of the cis proton with respect to the oxygen atom) and 3.92 ppm (signal of the trans proton). The signals of the protons of the methylene groups in the α position with respect to the oxygen atom of the furan ring, just as in the spectrum of compound VII, are represented by singlets and have chemical shifts of 4.52 ppm (CH_2O group) and 3.35 ppm ($=N-CH_2$ group). The signals of the protons of the furan ring are represented as two doublets with chemical shifts of 6.12 and 5.96 ppm. Finally, the unresolved multiplets at 1.18–1.73 and 2.18–2.53 ppm are due to the protons of the piperidine ring.

EXPERIMENTAL

N,N-Disubstituted 5-Aminomethylfurfuryl Alcohols (II-IV). These were synthesized in analogy with I [4] (see Table 1).

Vinyl Ether of 5-Piperidinomethylfurfuryl Alcohol (V). Compound I (10 g), 1 g of KOH, and 80 ml of dioxane were placed in a 1-liter rotating autoclave, acetylene was fed in at an initial pressure of 20 atm, and the mixture was heated at 135° for 1 h. After removal of the solvent the reaction product was distilled in vacuo to give 7 g (62%) of product. Ethers VI-VIII (Table 1) were similarly obtained.

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