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BRIEF COMMUNICATIONS

Hantzsch Reaction in Urea–Formaldehyde Resins

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Abstract—The effect of acetylacetone and ammonia in urea–formaldehyde resins on the reactions occurring in their presence was examined. The formation of 2,6-dimethyl-3,5-diacetyl-1,4-dihydropyridine in urea–formaldehyde resins was confirmed by ^{1}H NMR spectroscopy.

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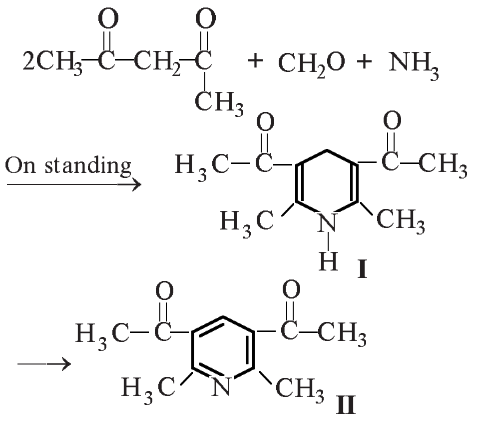
Structural studies of urea–formaldehyde (UF) resins and reduction of their free formaldehyde content are urgent problems [1–3]. Various additives and procedures decreasing the concentration of free formaldehyde have been reported. One of efficient methods is addition of β-diketones. Previously [4] we reported on a possible way to decrease the concentration of free formaldehyde in UF resin by adding acetylacetone and ammonia which enter into the Hantzsch reaction with formaldehyde:



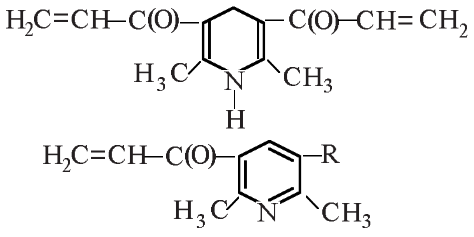
In this study we examined the mechanism of the Hantzsch reaction in UF resins by ^{1}H NMR spectroscopy.

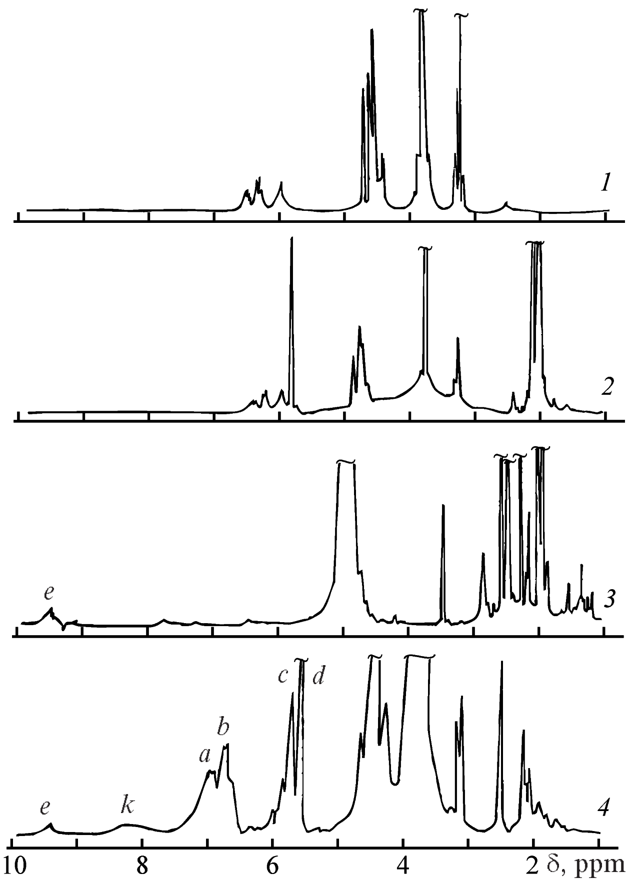
EXPERIMENTAL

Additives were introduced in amounts corresponding to the free formaldehyde content of UF resin [4]. The ^{1}H NMR spectra were recorded on a Gemini-200 spectrometer operating at 200 MHz in DMSO-d_6, reference TMS, 298 K. UF resin of the KF-MTS-15 brand [TU (Technical Specification) U-3,50-14 308 351-055–95 with revision 1] was used.

The reaction of acetylacetone and ammonia with formaldehyde, performed according to [5], yields 2,6-dimethyl-3,5-diacetyl-1,4-dihydropyridine **I**. According to published data [6, 7], in such compounds the chemical shift of the NH proton varies within 8.2–9.6 ppm depending on solvent, pH, and substituents. In the ^{1}H NMR spectrum of the reaction mixture, recorded 10 min after starting the reaction, there is a broadened NH signal at δ 9.4 ppm. Proton signals of the starting compounds (ketone, enol, formaldehyde) disappear (see figure, spectrum *2*). After 24 h, the NH proton signal disappears, and a signal appears at 7.4 ppm, which corresponds to the CH proton in the pyridine ring (compound **II**). These data show that, at pH > 7, the reaction occurs via 2,6-dimethyl-3,5-diacetyl-1,4-dihydropyridine.

As the reaction occurs in an alkaline solution, addition of formaldehyde to the OH group of the enol form of acetylacetone can be ruled out. Signals that could correspond to the CH protons at the double bond are absent. Compound **I** can subsequently react with formaldehyde to form substituted vinyl ketones [8]:





^{1}H NMR spectra. (δ) Chemical shift. (*1*) Aqueous formaldehyde solution (δ_{CH_3} 3.1–3.4, δ_{CH_2} 4.5–4.8, δ_{OH} 5.8–6.6 ppm); (*2*) mixture of acetylacetone and Formalin (acetylacetone occurs in DMSO-d_6 solution in keto and enol forms, δ_{CH_2} 3.8, δ_{CH} 5.8 ppm); (*3*) model composition (acetylacetone + Formalin + ammonia), 10 min after mixing (signal *e*, δ 9.4 ppm, corresponds to 2,6-dimethyl-3,5-diacetyl-1,4-dihydropyridine); and (*4*) UF resin with addition of acetylacetone and ammonia, 10 min after mixing (δ_{NH} 7.3–8.5 ppm, signal *k* corresponds to UF resin that has reacted with compound **I** or **II**).

In the ^{1}H NMR spectrum of the reaction mixture, we did not observe a multiplet that could correspond to CH_2=CH protons at a nonconjugated double bond (4.5–6.5 ppm) (see figure, spectrum *3*). Unfortunately, in the ^{1}H NMR spectra of the modified resin this region is obscured by the CH_2 and NH protons of the resin (see figure, spectrum *4*).

The ^{1}H NMR spectrum of the UF resin without modifying additives is fully consistent with the spectra given in [9]. In the range 4–7 ppm, it contains partially resolved signals of the NH groups in monomethylolurea, dimethylolurea, and oligomeric chains (range 6.2–7.3 ppm), and also of the NH_2 groups in oligomers and free urea (5.4–6.0 ppm).

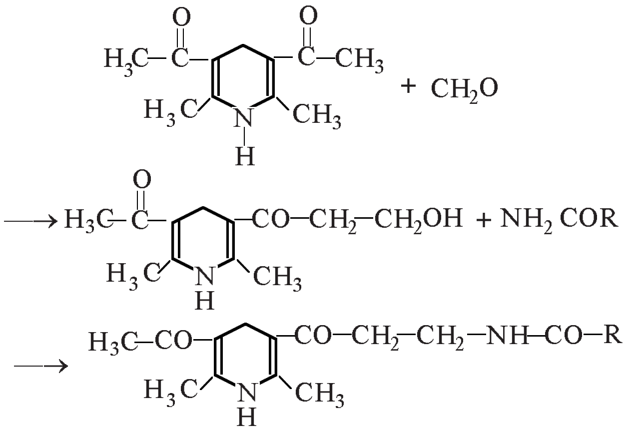
Relative content of NH_2 and NH fragments, according to ^{1}H NMR data

Range of δ, ppm	Structural fragment*	Relative content at indicated τ, min	
		10	40
5.4–6.0	NH_2 (*d*/*c*)	0.75	0.50
6.2–7.3	NH (*b*/*a*)	1.0	1.75
7.3–8.8	NH (*k*/*a*+*b*)	0.16	0.32

* (*d*) NH_2 group in free urea, (*c*) NH_2 group in oligomers, (*b*) NH group in oligomers, (*a*) NH group in monomethylolurea and dimethylolurea, and (*k*) NH group in components of the composition obtained by reaction with compound **I** or **II**. The designations are similar to those made in [9].

On introducing modifying additives (acetylacetone, ammonia) into the resin (see figure, spectrum *4*), a proton signal at δ 9.4 ppm, characteristic of the NH group of the dihydropyridine proton, and signals of methylene protons with the chemical shifts coinciding with those of the corresponding protons in the model compound (see figure, spectrum *3*) appear in the ^{1}H NMR spectrum. This fact confirms that the processes occurring in the modified resin are identical to the above-described reaction.

The table shows that the intensity of the signals from NH_2 and NH protons in oligomeric chains in the modified resin increases with time. Furthermore, chain lengthening in reactions of **I** or **II** with components of the composition is possible:



A downfield shift of the NH signal (δ_{NH} 7.3–8.8 ppm) is possible owing to a decrease in the electron density on the NH group under the influence of the electron-withdrawing C(O) group.

The signals of CH_3 groups observed in the region of methylol proton signals, as judged from the disappearance of the CH_2 and CH signals of the starting formaldehyde and acetylacetone, should be assigned to products of the above reactions (see figure, spectra *3*, *4*).

CONCLUSIONS

(1) The Hantzsch reaction performed in urea–formaldehyde resin initially yields 2,6-dimethyl-3,5-diacetyl-1,4-dihydropyridine.

(2) Compounds containing vinyl fragments were not detected in the model reaction.

(3) 2,6-Dimethyl-3,5-diacetyl-1,4-dihydropyridine and pyridine derivatives, formed in urea–formaldehyde resin in the presence of additives (acetylacetone and ammonia), can undergo chain lengthening.

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