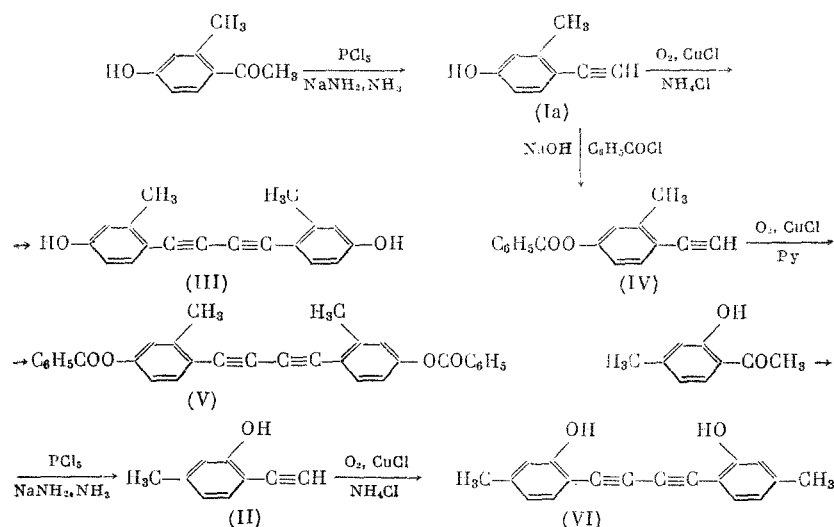


M. I. Bardamova, R. N. Myasnikova,
and I. L. Kotlyarevskii

UDC 547.554+547.566

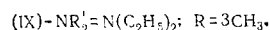
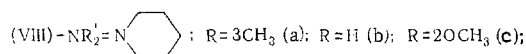
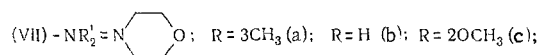
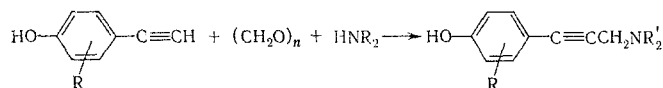
The chemical properties of the ethynylphenols, representing a new class of compounds [1-3], are interesting for studies involving the presence of several reaction centers in the molecule. The introduction of an electron-donor group into the nucleus should, on the one hand, sharply increase the reactivity of the nucleus, and on the other hand, it should exert an effect on the chemical behavior of the ethynyl group. The reactivity of the ethynylphenols in reactions involving the acetylenic hydrogen should be greatly reduced due to the introduction of donor groups into the nucleus, if the mechanism of these reactions is correct, postulating the initial dissociation of acetylene into proton and acetylide ion. In the present paper this postulation is confirmed on the examples of the Mannich reaction between a number of ethynylphenols, formaldehyde and various secondary amines, and conditions for running these reactions were ascertained, under which the hydrogen atoms of the nucleus do not react. As the ethynylphenols we used 3-methyl-4-ethynylphenol (Ia), 4-ethynylphenol (Ib) and 2-methoxy-4-ethynylphenol (Ic). (Ia), synthesized by replacing the carbonyl oxygen in 3-methyl-4-acetylphenol by chlorine using PCl_5 , and subsequent dehydrochlorination of the obtained chlorides using NaNH_2 , is an unstable compound, which was analyzed only as the benzoyl derivative (IV), obtained by the Schotten-Baumann procedure. The oxidation condensation of (Ia) leads to the unstable dehydro dimer (III), the structure of which was proved by the infrared spectrum and conversion to the dibenzoyl derivative (V). The latter was also obtained by the oxidative condensation of 2-methyl-4-benzoyloxyphenylacetylene (IV). 3-Methyl-6-ethynylphenol (II) was synthesized in the same manner as (Ia), and it also forms the dehydro dimer (VI).



In the absence of copper catalysts the ethynylphenols do not react in the Mannich sense under the usual conditions, and because of their instability they undergo polymerization before they have a chance to react with formaldehyde and the amines. In the presence of copper catalysts, which in the case of other arylacetylides assure completion of the Mannich reaction in 1 to 2 h [4 and 5], the (I) compounds react very slowly and the reaction is practically ended only after stirring the reaction mass for 30 h at 20-60°. A higher reaction temperature causes both polymerization of the starting (I) compounds and aminomethylation of the nucleus.

TABLE 1. Synthesis of Acetylenic Amines

Amines	Yield, %	M.p., °C	Found N, %	Empirical formula	Calc. N, %	Hydrochlorides			
						M.p., °C	found Cl, %	Empirical formula	calc. Cl, %
VIIb	53	103	6.12	C ₁₃ H ₁₅ NO ₂	6.45	156--7	14.18	C ₁₃ H ₁₆ NO ₂ Cl	13.98
VIIIb	45	163.5	6.60	C ₁₄ H ₁₇ NO	6.51				
VIIc	54	96--7	5.54	C ₁₄ H ₁₇ NO ₃	5.66	153--4	12.25	C ₁₄ H ₁₈ NO ₃ Cl	12.50
VIIIc	60	137	5.53	C ₁₅ H ₁₉ NO ₂	5.71	162--3	12.51	C ₁₅ H ₂₀ NO ₂ Cl	12.58
VIIa	30	129--9.5	6.06	C ₁₄ H ₁₇ NO ₂	6.04	176	13.34	C ₁₄ H ₁₈ NO ₂ Cl	13.24
VIIIa	35	124.5--5.0	5.99	C ₁₅ H ₁₉ NO	6.11	163--4	13.46	C ₁₅ H ₂₀ NOCl	13.34
IXa	20	Oil	9.33	C ₁₄ H ₁₉ NO	9.03				



The infrared spectra of all of the obtained compounds exhibit bands that correspond to the vibrations of the principal bonds present in the compounds. It should be mentioned that, in contrast to the previously obtained Mannich bases [5 and 6], the infrared spectra of the acetylenic amines (VII)–(IX) exhibit fairly intense absorption bands in the 2210–2245 cm⁻¹ region, which correspond to the stretching vibrations of the triple bond.

EXPERIMENTAL

3-Methyl-4-ethynylphenol (Ia). To 10 g of 3-methyl-4-acetylphenol in 40 ml of absolute benzene was added 17 g of PCl₅, the mixture was stirred for 2 h at 60°, and then it was added in 1.5 h to a suspension of sodium amide in liquid ammonia (from 17 g of Na in 500 ml of NH₃). After 4 h the mixture was decomposed with 37 g of NH₄Cl. Purification by chromatographing on Al₂O₃ gave 6.5 g of liquid (Ia), which darkened rapidly when exposed to the air or to light. Its benzoyl derivative (IV) was obtained in 60% yield by the Schotten-Baumann procedure, m. p. 60–61°. Found %: C 81.19; H 5.38; C₁₆H₁₂O₂. Calculated %: C 81.34; H 5.12. Infrared spectra, cm⁻¹: 1760 (> C ≡ O), 2177 (– C ≡ C–), 3293 (≡ C–H).

1,4-Bis(2'-methyl-4'-hydroxyphenyl)butadiyne (III). The compound was obtained by shaking a mixture of 5 g of (Ia) in 15 ml of methanol, 13 g of ammonium chloride, 15 ml of water, 1 drop of aqueous ammonia and 4 g of CuCl in an oxygen atmosphere. We isolated 3 g of (III), m. p. 180–185° (from ether). The material darkens rapidly. Infrared spectra, cm⁻¹: 2168 (– C ≡ C–), 3312 (–OH). The dibenzoyl derivative was obtained in 84% yield, m. p. 181–184° (from ether). Found %: C 81.18; H 5.04; C₃₂H₂₂O₄. Calculated %: C 81.68; H 4.71. Infrared spectra, cm⁻¹: 2168 (– C ≡ C–), 1770 (> C ≡ O).

3-Methyl-6-ethynylphenol (II), synthesized in the same manner as (Ia) in 70% yield, was obtained as a liquid that darkened rapidly. Infrared spectrum, cm⁻¹: 2129 (– C ≡ C–); 3579 (–OH). The dehydro dimer (VI) was obtained in 80% yield under the conditions of condensing (Ia) to give (III), m. p. 161–162° (from benzene). Found %: C 82.11; H 5.18; C₁₈H₁₄O₂. Calculated %: C 82.42; H 5.38. Infrared spectrum, cm⁻¹: 2158 (– C ≡ C–); 3511 (–OH).

1-(2'-Methyl-4'-hydroxyphenyl)-3-morpholinopropyne (VIIa). A mixture of 0.45 g of paraform and 1.31 g of morpholine in 20 ml of anhydrous dioxane was heated for 3 h at 30° in a stream of dry purified nitrogen. After cooling, 2 g of (Ia) in 20 ml of dioxane and 0.01 g of CuCl were added. The mixture was stirred for 4 h at 30–40°, 1 h at 60°, and 24 h at room temperature. Chromatographing on Al₂O₃ gave 1 g of amine (VIIa), m. p. 129–129.5° (from ether). Found %: N 6.06; C₁₄H₁₇NO₂. Calculated %: N 6.04. Infrared spectrum, cm⁻¹: 1130 (– C–N <), 2245 (– C ≡ C–), 3597 (–OH). The hydro-

chloride was obtained in quantitative yield by passing dry HCl through an ether solution of (VIIa), m. p. 176° (from ether).

Amines (VIIb), (VIIc), (VIIIa), (VIIIb), (VIIIc) and (IXa) were synthesized in a similar manner. The constants of the amines are given in Table 1.

CONCLUSIONS

1. 3-Methyl-4-ethynylphenol and 3-methyl-6-ethynylphenol were synthesized by us.
2. The conditions for the condensation of ethynylphenols with formaldehyde and secondary amines were ascertained.
3. The reactivity of the ethynylphenols in the Mannich reaction is lowered strongly due to the donor effect of the hydroxy group.

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