CATALYTIC METHOD FOR OBTAINING 2-ARYL-SUBSTITUTED IMIDAZOLINES

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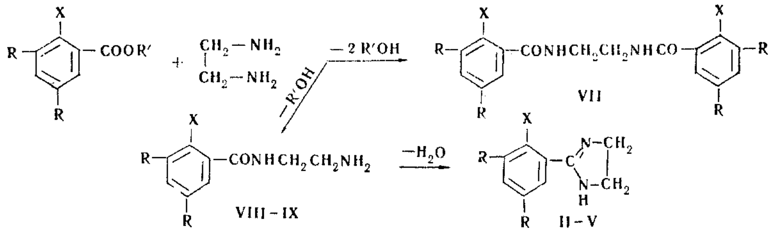
UDC 547.781.3: 542.97

2-Arylimidazolines were synthesized catalytically on KU-2 ion-exchange resin by condensation of esters of aromatic acids (benzoic, phenylacetic, anthranilic, salicylic, and 3,5-di-tert-butylsalicylic) with ethylenediamine. From 30 to 48% of the diamide is formed in addition to the corresponding imidazolines in the condensation of the esters of benzoic and phenylacetic acids with ethylenediamine. The condensation of the esters of salicylic and 3,5-di-tert-butylsalicylic acids with ethylenediamine gave quantitative yields of the monoamide, which is dehydrated to 2-arylimidazoline during vacuum distillation.

Methods for the synthesis of the simplest 2-alkylimidazolines from acids and their derivatives are described in the literature [1-3]. In contrast to the known thermal methods for the synthesis of 1,2-substituted imidazolines from acids and polyethylenepolyamines, the reaction proceeds under milder conditions and gives higher yields when ion-exchange resins are used [4, 5]. In the present paper, we report data on the synthesis of 2-arylimidazolines by the condensation of esters of aromatic acids (benzoic, phenylacetic, anthranilic, salicylic, and 3,5-di-tert-butylsalicylic) with ethylenediamine in the presence of KU-2 ion-exchange resin. In general form, the reaction can be expressed as follows:



II, VII R=X=H; III, VIII R=H, X=OH; IV, IX R=iso-C_4H_9, X=OH; V R=H, X=NH_2; R′=CH_3 or C_2H_5

2-Benzylimidazoline (I) and N,N′-bis(β-phenylacetyl)ethylenediamine (VI) were isolated and identified as a result of the condensation of ethyl phenylacetate and ethylenediamine. The effect of the molar ratios of ethyl phenylacetate to ethylenediamine and the reaction time and temperature on the yield of I was studied. The molar ratios of ethyl phenylacetate and ethylenediamine were varied from 1 : 1 to 1 : 5. Equimolecular amounts of the starting materials lead to the formation of considerable amounts of VI (48%), while the yield of I is 39%; when the ether–amine molar ratio was 1 : 5, I was isolated in 62.5% yield. The temperature was varied from 20 to 115°C. An increase in the temperature apparently promotes dehydration of the intermediate N-(β-phenylacetyl)ethylenediamine to I, which is in good agreement with the literature data [2], but the intermediate product could not be isolated in pure form. When the reaction time was increased from 3 to 10 h, the yield of I increased from 49 to 70%. Thus the optimum conditions for the synthesis of I are as follows: a reaction temperature of 115°, a reaction time of 5 h, and an ether–amine molar ratio of 1 : 5. Similar regularities were observed in the synthesis of 2-phenylimidazoline (II). N,N′-Dibenzoylethylenediamine (VII) was isolated in 39% yield as a side product.

I. M. Gubkin Moscow Institute of the Petrochemical and Gas Industry. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 383-385, March, 1972. Original article submitted October 20, 1970.

TABLE 1. Physicochemical Constants of 2-Aryl-Substituted Imidazolines and N-Substituted Ethylenediamines

Compound	Name	Mp, °C	Bp, °C (press., mm)	Empirical formula	Found, %					Calc., %			
					C, %	H, %	N, %	N*, %	M	C, %	H, %	N, %	M
I	2-Benzylimidazoline	58	180—188 (20)	$C_{10}H_{12}N_2$	74,4	7,6	17,3	17,4	154	74,9	7,5	17,5	160
II	2-Phenylimidazoline	100	178—181 (20)	$C_9H_{10}N_2$	73,2	6,7	19,1	19,2	138	73,4	6,8	19,2	146
III	2-(o-Hydroxyphenyl)imidazoline	204	204—210 (20)	$C_9H_{10}N_2O$	66,2	6,3	17,4	17,2	166	66,6	6,2	17,3	162
IV	2-(o-Hydroxy-3,5-di-tert-butylphenyl)-imidazoline	135	194—202 (3)	$C_{17}H_{20}N_2O$	74,2	9,6	9,8	10,0	269	74,4	9,5	10,1	274
V	2-(o-Aminophenyl)imidazoline	50	174—186 (5)	$C_9H_{11}N_3$	69,7	6,6	25,9	—	160	70,3	6,9	26,0	161
VI	N,N'-Bis(β-phenylacetyl)ethylenediamine	202	—	$C_{18}H_{20}N_2O_2$	72,2	6,9	9,6	—	284	72,1	7,0	9,4	296
VII	N,N'-Dibenzoylethylenediamine	252	—	$C_{16}H_{16}N_2O_2$	71,0	6,2	9,9	—	256	71,5	6,0	10,4	268
VIII	N-(o-Hydroxybenzoyl)ethylenediamine	160	—	$C_9H_{12}N_2O_2$	59,2	6,4	15,7	—	178	59,9	6,7	15,5	180
IX	N-(o-Hydroxy-3,5,-di-tert-butylbenzoyl)-ethylenediamine	158	—	$C_{17}H_{28}N_2O_2$	70,0	9,9	9,0	—	—	69,8	9,7	9,6	292

* Determined by potentiometric titration.

When the synthesis of 2-(o-hydroxyphenyl)imidazoline (III) was carried out for 4 h at a methyl salicylate–ethylenediamine molar ratio of 1 : 5, N-(o-hydroxybenzoyl)ethylenediamine (VIII) was isolated in quantitative yield; vacuum distillation of VIII gave III in 85% yield. Identical results under the same reaction conditions were obtained for 2-(3,5-di-tert-butyl-o-hydroxyphenyl)imidazoline (IV), which was isolated in 77.4% yield; N-(o-hydroxy-3,5-di-tert-butylbenzoyl)ethylenediamine (IX) was obtained initially and was dehydrated to IV during vacuum distillation. 2-(o-Aminophenyl)imidazoline (V) was isolated in 40.5% yield in the condensation of methyl anthranilate with ethylenediamine after workup of the reaction mixture and vacuum distillation.

The compounds obtained were characterized from their physicochemical constants and IR absorption spectra. The percentage of nitrogen was determined by potentiometric titration.* The data are presented in Table 1.

Absorption bands are found at 1600-1610 (C=N), 3310 (N–H), and 1495 and 1605 cm^{-1} (benzene ring) [6] in the IR spectra of the synthesized imidazolines.

EXPERIMENTAL

The IR spectra of the imidazolines were recorded with an IKS-14 spectrophotometer. The potentiometric titration for the determination of the percentage of nitrogen in the 2-arylimidazolines was carried out with a standardized 0.1 N perchloric acid solution in glacial acetic acid with an LP-58 potentiometer.

2-Arylimidazolines. A flask was charged with KU-2 catalyst (30% of the weight of the corresponding aromatic acid ester) and 1 mole of anhydrous ethylenediamine, and 0.2 mole of the ester was added dropwise with stirring. The temperature was raised to 115°, and the mixture was stirred for 5 h. The mixture was filtered away from the cation-exchange resin, and the KU-2 was washed with alcohol. The alcohol and excess ethylenediamine were removed in vacuo with a water pump. Vacuum distillation of the residue gave the corresponding imidazoline.

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* This was performed jointly with L. P. Krylova.