REACTION OF N-VINYLIMIDAZOLES WITH ALKYL HALIDES

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Quaternary salts of N-vinylimidazole and N-vinylbenzimidazole were synthesized. The structures of the products of quaternization of the N-vinylimidazoles were proved by IR and UV spectra. The distribution of the π-electron density in the N-vinylimidazole molecules was obtained by quantum-chemical calculation.

In a study of the halogenation and hydrohalogenation of N-vinylimidazole (I) and N-vinylbenzimidazole (II), we established their ability to form complexes with bromine, chlorine, and the corresponding hydrogen halides [1]. In contrast to I and II, N-vinylindole (III) polymerizes under similar conditions with the simultaneous formation of charge-transfer complexes [2]. It is shown that III also forms polymeric products, viz., quaternized salts, with alkyl halides.

Investigation of the reaction of alkyl halides with N-vinylazoles were continued in this paper in order to ascertain the participation of the double bond of the vinyl group and the ring heteroatoms of I and II under

TABLE 1. Quaternary Salts of N-Vinylimidazoles

Starting compounds		Synthesis cond.			mp	UV spectrum, λ max nm (log ε)*	Empirical formula	Yield, %	Halogen, %	
		AlkX, mole	temp.	time, h					found	calc.
N-Vinylimidazole (I)	CH_3I	2	37—40	2	85—86	—	$C_6H_9IN_2$	91	53,9	53,8
	C_2H_5I	3	75	2	101—104	224 (4,27)	$C_7H_{11}IN_2$	84	51,3	50,7
	$i\text{-}C_3H_7I$	3	90—91	2,5	90—91	—	$C_8H_{13}IN_2$	89	49,0	48,8
	C_2H_5Br	3	42—43	2	99—100	224 (4,0)	$C_7H_{11}BrN_2$	73	40,0	39,3
	C_3H_7Br	3	62—63	9	154—156	—	$C_8H_{13}BrN_2$	39	37,0	36,3
	C_4H_9Br	2	70	18	81—85	—	$C_9H_{15}BrN_2$	72	34,5	34,8
N-Vinylbenzimidazole (II)	CH_3I	3	45	20 min	200	216; 270 (4,38; 3,83)	$C_{10}H_{11}IN_2$	63	44,8	44,4
	C_2H_5I	3	70	2	236—237	218; 272 (4,50; 3,97)	$C_{11}H_{13}IN_2$	50	42,3	42,3
	$i\text{-}C_3H_7I$	3	91—94	3	195—200	218; 274 (4,58; 3,97)	$C_{12}H_{15}IN_2$	67	40,6	40,4
	C_4H_9I	3	96—100	2	140—142	—	$C_{13}H_{17}IN_2$	95	39,1	38,7
	C_2H_5Br	5	42—43	25	230—233	214; 272 (3,98; 3,70)	$C_{11}H_{13}BrN_2$	50	31,1	31,6
	C_3H_7Br	3	65—68	23	178—182	—	$C_{12}H_{15}BrN_2$	8	30,7	30,0
	C_4H_9Br	3	100—104	1	95—97	212; 272 (4,27; 3,98)	$C_{13}H_{17}BrN_2$	13	28,6	28,4

*UV spectrum: I, λ_{max}, 230 nm (log ε 4.09); II, λ_{max} 232, 280 nm (log ε 3.99, 3.48).

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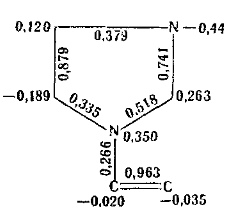
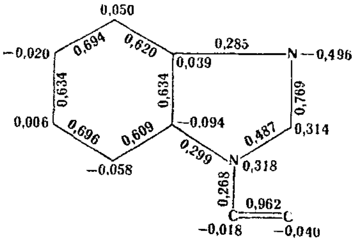
the conditions of the reaction under consideration. Information regarding the ability of imidazole and benzimidazole to complex with alkyl halides appeared only in papers that were published in the 1960's [3,4], and the quaternization of I became known recently from a communication [5]. We investigated the conditions of the reaction of I and II with methyl iodide, isopropyl and butyl iodides and bromides, and methylene chloride. The reaction proceeds without solvent in the presence of a two- to threefold molar excess of the alkyl halides at the boiling point of the reaction mixture to form the quaternary salts. It was found that N-vinylimidazole displays greater activity in the reaction with alkyl halides than N-vinylbenzimidazole; this is explained by its greater basicity. Alkyl iodides react more rapidly than alkyl bromides, and quaternary salts are formed in yields reaching 89-95% after 1-2 h. It was demonstrated that I and II do not react with alkyl chlorides.

All of the quaternization products obtained (Table 1) were purified by recrystallization from ethanol or by reprecipitation. They are colorless or slightly colored (iodides) crystalline substances that are soluble in water and polar solvents; some of them are hygroscopic.

The structures of the quaternary salts from I and II were confirmed by an investigation of their IR and UV spectra. The IR spectra contain absorption bands of the vinyl group at 1650 and 960 cm^{-1}. In addition, the bands corresponding to the vibration of the imidazole ring are shifted. Thus, bands at 1493 and 1510 cm^{-1}, which characterize the C=C and C=N vibrations, are raised to 1550 and 1570 cm^{-1}, respectively, while retaining the same intensity ratio. The frequencies of the out-of-plane vibrations of the ring C-H groups at 800-1100 cm^{-1} are also shifted to the short-wave region of the spectrum. A strong band appears at 1180 cm^{-1}. Such changes in the ring vibrations indicate donor-acceptor interaction during quaternization of the N-vinylimidazoles.



I



II

We confirmed the complexing center by quantum-chemical calculation of the I and II molecules via the Pople variant of the self-consistent-field MO LCAO method. This calculation demonstrates that the "pyridine" nitrogen atom has the greatest negative π-electron charge.

In contrast to the starting N-vinylimidazole, the band at 220-230 nm undergoes a hypsochromic shift with a simultaneous increase in the extinction coefficient in the UV spectra of the quaternized N-vinylimidazoles. A similar effect is observed for N-vinylbenzimidazoles, in which the quaternization is accompanied by a short-wave shift with a considerable increase in the intensity of both of these absorption bands. Thus, on the basis of an investigation of the structure of the products of the quaternization of N-vinylimidazoles by alkyl halides it has been shown that they contain a free vinyl group, owing to which the possibility of the synthesis of high-molecular-weight compounds from them is opened. The quaternary salts of polyvinylimidazoles can also be obtained by the action of alkyl halides on the polymers of I and II.

EXPERIMENTAL

N-Vinylimidazole Ethobromide. A mixture of 3 g (0.03 mole) of N-vinylimidazole and 10 g (0.1 mole) of ethyl bromide was refluxed for 2 h, and the resulting white, crystalline substance was isolated. The crystals were purified by repeated washing with ether and by crystallization from alcohol to give 4.72 g of N-vinylimidazole ethobromide. Found %: C 41.4; H 5.4; N 14.3. $C_7H_{11}BrN_2$. Calculated %: C 41.4; H 5.5; N 13.7.

N-Vinylbenzimidazole Ethiodide. A mixture of 3 g (0.02 mole) of N-vinylbenzimidazole and 10 g (0.06 mole) of ethyl iodide was refluxed for 2 h at 70° to give 3.07 g (49.5%) of N-vinylbenzimidazole ethiodide. Found %: C 43.8; H 4.3; N 9.9. $C_{11}H_{13}IN_2$. Calculated %: C 44.0; H 4.4; N 9.3.

Polyvinylbenzimidazole Methiodide. A 0.5 g sample of polyvinylbenzimidazole was dissolved in 2 ml of ethanol, and the solution was mixed in an ampule with 2 g (0.01 mole) of methyl iodide. The ampule was placed in a thermostat at 60°. A yellow precipitate formed after 0.5 h and was washed repeatedly on the filter with acetone and alcohol to give 0.83 g (92%) of a yellow powder with mp 288-303° that was soluble in dimethylformamide. Found %: I 40.0. $[(C_9H_8N_2)_5(CH_3I)_4]_n$. Calculated %: I 39.4.

The IR spectra of KBr pellets were recorded with a UR-20 spectrophotometer. The UV spectra of alcohol solutions ($1 \cdot 10^{-3}$ M) were recorded with an SF-4 spectrometer.

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