REACTION OF 1-VINYLBENZOTRIAZOLE WITH ALKYL HALIDES AND DIALKYL SULFATES

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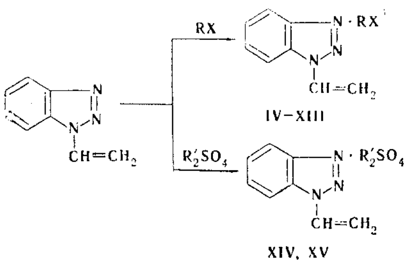
Adducts of alkyl halides and dialkyl sulfates with 1-vinylbenzyltriazole were synthesized, and their IR and UV spectra were investigated. The nitrogen atom in the 3 position is the coordination center in these quaternary nitrogen salts.

We have previously demonstrated [1] that 1-vinylbenzotriazole (I) forms complexes with bromine, chlorine, and the corresponding hydrogen halides. Addition to the vinyl group and simultaneous complexing are observed during bromination. The information on the quaternization of benzotriazole and its vinyl derivative is extremely limited. The synthesis of quaternary salts of benzotriazole has been described in patents [2,3] and the possibility of quaternization of I and its polymer in analogy with 1-vinylimidazole has been indicated in another patent [4].

In the present paper, we have investigated the reaction of I with alkyl halides [$C_nH_{2n+1}X$, where X = I (n = 1-9) and Br (n = 2,3,9)] and with dimethyl and diethyl sulfates. It was found that the reaction proceeds without a solvent in excess alkyl halide via the scheme



Under the conditions under consideration, I does not react with alkyl chloride; the reaction proceeds with alkyl bromides to give low yields of product. Alkyl iodides display considerably greater activity. The conditions for the synthesis of the alkiodides of I and their properties are presented in Table 1. The yields of the alkiodides of I increase as the reaction time increases, while raising the temperature shortens the reaction time, particularly for the lower alkyl halides. The optimum reaction temperature is close to the boiling point of the alkyl halides. Alkiodides IV-XIII are crystalline, colored substances that are soluble in most polar solvents.

The quaternization of I with dialkyl sulfates (Table 2) proceeds to give high yields at room temperature; raising the temperature to 90° promotes an increase in the reaction rate. The complexes obtained (XIV and XV) are white crystalline substances that are quite soluble in water and polar organic solvents.

The reaction of I, 1-vinylbenzimidazole (II), and 1-vinylindole (III) was investigated to compare their complexing abilities. It was shown that II reacts with dimethyl and diethyl sulfate more vigorously than I. We have previously [5] observed this sort of activity in a study of the action of alkyl halides on II.

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TABLE 1. 1-Vinylbenzotriazole Alkiodides

Comp.	R	Reaction conditions		mp, °C (from ethanol)	Empirical formula	Found, %			Calc., %			Yield, %
		temp. °C	time, h			C	H	I	C	H	I	
IV	CH_3	40—45	2	161—162	$C_9H_{10}IN_3$	37,0	3,4	44,4	37,6	3,5	44,2	66
V	C_2H_5	60—70	15	155—156	$C_{10}H_{12}IN_3$	39.8	4,0	42,4	39,8	4,0	42,1	48
VI	C_3H_7	60—70	20	168—169	$C_{11}H_{14}IN_3$	42,2	4,4	40,9	41,9	4,4	40,3	27
VII	i-C_3H_7	70	20	164—165	$C_{11}H_{14}IN_3$	41,9	4.5	40,3	41,9	4,4	40,3	32
VIII	C_4H_9	70—80	20	80—82	$C_{12}H_{16}IN_3$	43,2	4,9	39,2	43,7	4,8	38,6	35
IX	C_5H_{11}	60—70	10	120—121	$C_{18}H_{18}IN_3$	45,3	5,3	36,5	45,8	5,2	36,9	18
X	C_6H_{13}	60—70	20	50—51	$C_{14}H_{20}IN_3$	46,5	5,6	35,1	47,0	5,6	35,5	22
XI	C_7H_{15}	60—70	20	64—65	$C_{15}H_{22}IN_3$	49,2	6,1	33,7	48,5	5,9	34,4	24
XII	C_8H_{17}	70—80	10	71—72	$C_{16}H_{24}IN_3$	49,5	6,3	33,6	49.8	6,2	33,0	41
XIII	C_9H_{19}	70—80	20	73—74	$C_{17}H_{26}IN_3$	50,8	6,0	30,9	51,1	6,5	31,7	20

TABLE 2. Products of the Reaction of 1-Vinylbenzotriazole, 1-Vinylbenzimidazole, and 1-Vinylindole with Dialkyl Sulfates

Compounds	Starting comp.	R′	Reaction condit.			mp, °C	Empirical formula	Found, %			Calc., %			Temp., °C
			molar ratio	temp., °C	time, h			C	H	S	C	H	S	
XIV	I	CH_3	1 : 2	20	48	99—100	$C_8H_7N_3 \cdot$ $\cdot (CH_3)_2SO_4$	44.4	5,1	11,5	44,3	4,8	11,7	97
XIV	I	CH_3	1 : 2	90	1	99—100	$C_8H_7N_3 \cdot$ $\cdot (C_2H_3)_2SO_4$	44,0	4,8	11,8	44,3	4,8	11,7	82
XV	I	C_2H_5	1 : 2	20	48	165—166	$C_8H_7N_3 \cdot$ $\cdot (C_2H_5)_2SO_4$	47,9	5,2	11,0	48,2	5,7	10,7	67
XVI	II	CH_3	1 : 1	20	0,25	189—190	$C_9H_8N_2 \cdot$ $\cdot (CH_3)_2SO_4$	48,0	5,1	11,9	48,8	5,1	11,8	64
XVII	II	C_2H_5	1 : 1	20	0,25	170—172	$C_9H_8N_2 \cdot$ $\cdot (C_2H_5)_2SO_4$	51,8	6,1	10,8	52,3	6,0	10,7	60
XVIII	III	CH_3	1 : 3	20	0,2	192—198	$(C_{10}H_9N)_{15} \cdot$ $\cdot (CH_3)_2SO_4$	80,3	6,2	1,4	80,2	6,3	1,4	90
XIX	III	C_2H_5	1 : 3	20	0,2	210—220	$(C_{10}H_9N)_{10} \cdot$ $\cdot (C_2H_5)_2SO_4$	77,8	6,2	1,9	78,7	6,3	2,0	90

In contrast to I and II, III is readily polymerized under these conditions to give polymeric complexes similar to those obtained by the action of bromine [6]. The complexes obtained (XVIII and XIX) are dark-red powders, and their composition was calculated from the results of elementary analysis (Table 2).

The bands of the vinyl group (1640 and 960 cm^{-1}) vanish in the IR spectra of the products of the reaction of III with dialkyl sulfates, and frequencies corresponding to the vibrations of alkyl groups (2930, 2970, and 3050 cm^{-1}) appear. The overall form of the spectra is similar to the spectrum of the polyvinylindole obtained under the influence of cationic catalysts. The bands of the stretching vibrations of the vinyl group at 1643-1645 cm^{-1} are retained in the spectra of the series of derivatives I, and bands at 1605 and 770 cm^{-1}, which are peculiar to the heteroring, are observed. The second band is shifted by 15-20 cm^{-1} to the shortwave region with respect to the absorption of I. The newly appearing maxima at 2870 and 2960 cm^{-1} are due to the presence of alkyl groups. The changes in the IR spectra of derivatives of II are similar. These data attest to the fact that the vinyl group does not participate in the reaction and that donor–acceptor complexes of I and II are formed with alkyl halides and dialkyl sulfates. This conclusion is in agreement with the results of measurements of the dipole moment of I (3.47 D) and of the product of reaction of I with $C_5H_{11}I$ (5.8 D). The considerable increase in the dipole moment is extremely characteristic for donor–acceptor complexes.

A small intensification of the absorption at both 220 and 270-290 nm (Figs. 1 and 2) is observed in the UV spectra of the investigated compounds. The size of the hydrocarbon chain in the alkyl iodides does not affect the character of the absorption. The ratio ($\varepsilon_1/\varepsilon_2$) of the molecular extinctions of the maxima of the first and second absorption bands changes in the order RI, RBr, R_2SO_4 but does not coincide for similar complexes of I and II.

This result renders probable the assumption of the common character of the investigated complexes and the identical nature of the complexing center for I and II (at the nitrogen atom in the 3 position). This was previously [7] proved for II on the basis of a study of the PMR spectra and an examination of the results of quantum-mechanical calculations.

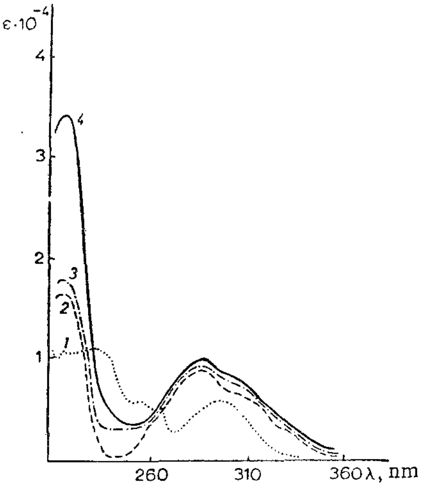


Fig. 1. UV spectra (in ethanol): 1) 1-vinylbenzotriazole (I); 2) 1-vinylbenzotriazole ethobromide; 3) 1-vinylbenzotriazole–diethyl sulfate complex (XV); 4) 1-vinylbenzotriazole ethiodide (V).

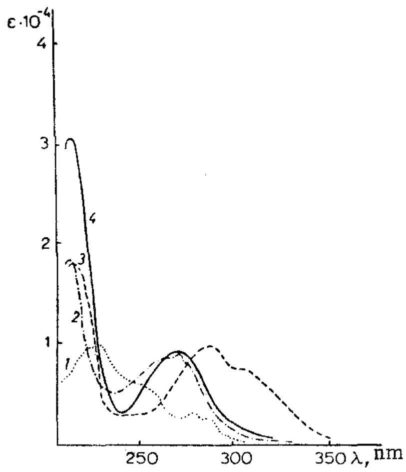
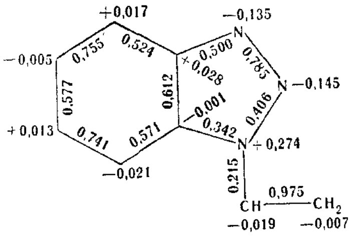


Fig. 2. UV spectra (in ethanol): 1) 1-vinylbenzimidazole (II); 2) 1-vinylbenzimidazole–diethyl sulfate complex (XVII); 3) 1-vinylbenzimidazole ethobromide; 4) 1-vinylbenzimidazole ethiodide.



The π-electron charges in I were found by calculation of the molecule with the Pople π-electron approximation.

As seen from the molecular diagram, the charges on the nitrogen atom in the 2 and 3 positions are close in magnitude. The quantum-mechanical polarizability of the nitrogen in the 3 position is higher than that of the nitrogen in the 2 position ($\pi_{22}^{\beta\beta} = 0.003$, $\pi_{33}^{\beta\beta} = 0.005$). This is evidence for predominant coordination at N_3 in the reaction of I with alkyl halides and dialkyl sulfates.

EXPERIMENTAL

1-Vinylbenzotriazole Methiodide (IV). A mixture of 3 g (0.02 mole) of I and 9 g (0.06 mole) of methyl iodide was refluxed at 42-43° for 2 h. The mixture was then cooled, and the shiny crystals were removed by filtration and washed repeatedly with ether to give 3.5 g of product (Table 1).

1-Vinylbenzotriazole Octiodide (XII). A mixture of 2 g (0.013 mole) of I and 7 g (0.03 mole) of octyl iodide was heated in a sealed ampule at 70° for 10 h in a thermostat. The mixture was then cooled to 0-5°, and ether was added to precipitate 2.2 g of yellow crystals with mp 71-72° (Table 1). Alkiodides V-XIII were similarly obtained (Table 1).

1-Vinylbenzotriazole Ethobromide. A mixture of 2 g (0.013 mole) of I and 4.5 g (0.039 mole) of ethyl bromide was refluxed at 40-45° for 30 h. The excess alkyl bromide was removed by evaporation in a stream of air, ether was added to the residue, and the resulting oil was triturated in ether to give 0.5 g (15%) of a white crystalline substance with mp 138-140° (from ethanol). Found, %: C 47.9; H 4.7; Br 31.1. $C_{10}H_{12}BrN_3$. Calculated, %: C 47.2; H 4.6; Br 31.1.

Polymeric Complex of 1-Vinylindole with Diethyl Sulfate (XIX). A 0.5-g (3 mmole) sample of diethyl sulfate was added with stirring and cooling to 0 to −5° to 0.5 g (3 mmole) of III in 3 ml of ether, and the resulting mass was triturated in ether and removed by filtration. The precipitate was washed with ether to give 0.9 g of a dark-red powder with mp 210-220° (Table 2).

Complex of 1-Vinylbenzotriazole with Dimethyl Sulfate (XIVb). A mixture of 0.5 g (3 mmole) of I and 1 g (1 mmole) of dimethyl sulfate was heated at 80° for 1.5 h, and the resulting dark viscous mass was treated with acetone. The resulting crystals were removed by filtration and washed on the filter with acetone to give 0.7 g of white crystals with mp 99-100°; the crystals were soluble in water and ethanol. Complexes (XVI and XVII) of 1-vinylbenzimidazole with dialkyl sulfates (Table 2) were similarly obtained.

The course of the reaction was monitored chromatographically by thin-layer ascending chromatography on a loose layer of activity II aluminum oxide with alcohol–ether (1 : 2). The IR spectra of KBr pellets were recorded with a UR-20 spectrophotometer. The UV spectra of ethanol solutions of the compounds were recorded with an SF-4A spectrophotometer. The calculations were performed with the BSÉM-4 VTs computer at Irkutsk State University from a program developed by N. M. Vitkovskaya and Yu. L. Frolov.

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