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COMPLEX FORMATION OF 1-VINYLNAPHTHO-[2,3-*d*]IMIDAZOLE WITH HYDROGEN CHLORIDE AND ORGANIC ELECTRON ACCEPTORS

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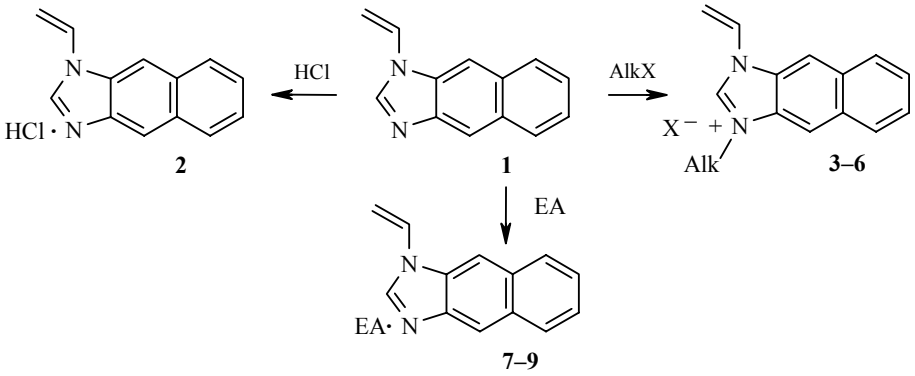
The reaction of 1-vinylnaphtho[2,3-d]imidazole with hydrogen chloride, alkyl halides, tetracyanoethylene, 2,4,7-trinitro-9-fluorenone, and p-chloranil giving the corresponding quaternary salts and charge-transfer complexes has been studied. The structure of the synthesized compounds has been confirmed from elemental analytical data and from IR and UV spectrometry.

Keywords: 3-alkyl-1-vinylnaphtho[2,3-*d*]imidazolium salts, 1-vinylnaphtho[2,3-*d*]imidazole, tetracyanoethylene, 2,4,7-trinitro-9-fluorenone, *p*-chloranil, alkylation, hydrohalogenation, complex formation.

Naphthoimidazoles are promising reagents for the synthesis of novel heterocyclic compounds [1, 2]. We have previously reported the reaction and properties of 1-vinylnaphtho[2,3-*d*]imidazole **1** and polymers based on it [3, 4].

In this work we have studied the reaction of 1-vinylnaphtho[2,3-*d*]imidazole **1** with hydrogen chloride and alkyl halides and also with organic electron acceptors (EA): tetracyanoethylene (TCNE), 2,4,7-trinitro-9-fluorenone (TNF), and with *p*-chloranil (CA).



2 **1** **3–6** **7–9**

3 Alk = Me, X = I; **4** Alk = Et, X = I; **5** Alk = Pr, X = I; **6** Alk = Et, X = Br;
7 EA = CA; **8** EA = TCNE; **9** EA = TNF

* Dedicated to Academician of the Russian Academy of Sciences B. A. Trofimov in his 70th jubilee.

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The reaction of compound **1** with hydrogen chloride occurs to give the hydrochloride **2**. According to the IR spectrum the vinyl group does not undergo a change in the hydrochloride, the C=C stretching absorptions being retained at 960 and 1648 cm^{-1}. The stretching bands for the naphthoimidazole ring are shifted to shorter wavelength (from 1510 to 1550 cm^{-1}) and a new band appears at 1170 cm^{-1} which points to a donor-acceptor interaction for the hydrogen chloride with the nitrogen atom at position 3. In fact this atom has the greatest negative electronic charge and is the center of complex formation [5]. The formation of hydrochloride **2** is also confirmed by its electronic absorption spectrum in which a characteristic band appears in the region 360-377 nm.

Refluxing compound **1** with a threefold excess of an alkyl iodide or bromide gives the quaternary alkylvinylnaphthoimidazolium salts **3-6** (Table 1) which are colored materials, soluble in alcohol, acetone, DMF, and CCl_4. A donor acceptor type interaction of compound **1** with alkyl halides also occurs at the nitrogen atom in position 3 as shown by the IR and UV spectrometric data. The IR spectra of salts **3-6** show absorption bands at 960 and 1648 cm^{-1} assigned to the vinyl group and do not undergo a change. A shift to the short wavelength region from 1500 to 1560 cm^{-1} is seen for the stretching absorption band of the naphthoimidazole ring and for the out of plane ring vibration (800 to 1100 cm^{-1}) and a new band appears at 1170 cm^{-1}. The quaternization of compound **1** by the alkyl halides to give the salts **3-6** is accompanied by changes in their UV spectra, *viz.* a hypsochromic shift of absorption band to the region 290-320 nm when compared with that of the base **1**.

The reaction of compound **1** with the organic electron acceptors *p*-chloranil, tetracyanoethylene, and 2,4,6-trinitro-9-fluorenone gives the charge-transfer complexes **7-9**.

Complex formation is accompanied by a strong change in the color of the solutions and by the appearance in the electronic spectra of novel absorption bands with long wavelength maxima at 540, 613 (**1**-CA), 530, 580, and 625 (**1**-TCNE), and 526 nm (**1**-TNF). It was shown by the method of isomolar series that the complexes formed have the composition 1:1 [6]. Compounds **7-9** are promising for preparing photosensitive materials. We have previously shown that the 1-vinylnaphtho[2,3-*d*]imidazole **1** homopolymer possesses slight photosensitivity and this is increased by 10-45 times after its sensitization with CA, TCNE, and TNF [4].

Hence the complex formation and quaternization reactions of 1-vinylnaphtho[2,3-*d*]imidazole **1** with hydrogen chloride, alkyl halides, and organic electron acceptors gave novel compounds in whose molecules the vinyl group was preserved. This will subsequently lead to polymerization and to the preparation of novel polymers with a package of useful properties.

TABLE 1. Characteristics of the Compounds Synthesized

Compound	Empirical formula	$\frac{\text{Found Hal, \%}}{\text{Calculated Hal, \%}}$	mp, °C	Yield, %
1	$C_{13}H_{10}N_2$*	—	99-101	89
2	$C_{13}H_{11}ClN_2$	$\frac{16.04}{15.37}$	158-160	96
3	$C_{14}H_{13}IN_2$	$\frac{38.08}{37.75}$	216-220	55
4	$C_{15}H_{15}IN_2$	$\frac{36.87}{36.24}$	229-236	98
5	$C_{16}H_{17}IN_2$	$\frac{34.91}{34.84}$	137-140	73
6	$C_{15}H_{15}BrN_2$	$\frac{26.99}{26.35}$	154-156	94

* Found N, %: 13.80; Calculated N, %: 14.43.

EXPERIMENTAL

IR spectra were recorded on a Bruker IFS-25 spectrometer for KBr tablets. Absorption spectra were recorded on a Perkin-Elmer spectrometer (Lambda 35, UV-vis) as acetonitrile, ethanol, or chloroform solutions. Monitoring of the purity of the compounds obtained was carried out by TLC on Silufol UV-254 plates in the solvent system and revealed using UV light or iodine vapor. Melting points were taken on a compact Boetius heating block. The characteristics of the compounds are given in Table 1.

1-Vinylnaphtho[2,3-*d*]imidazole (1) was prepared by method [3].

Hydrochloride 2. A stream of dry hydrogen chloride was passed with stirring through a solution of compound **1** (0.6 g, 3 mmol) in anhydrous CCl_4 (10 ml) at -5ºC until absorption ceased (1.5 h). The precipitated colorless crystals of the hydrochloride **2** were filtered off, washed with absolute acetone, and dried *in vacuo* to constant mass, R_f 0.44 (acetone–benzene, 1:1). Hydrochloride **2** is soluble in water, alcohol, and DMSO.

3-Methyl-1-vinylnaphtho[2,3-*d*]imidazolium Iodide (3). Ethanol (1 ml) and methyl iodide (2 ml) were added to compound **1** (0.5 g, 1.5 mmol) and refluxed with a reflux condenser for 2 h. The precipitated salt formed after cooling was filtered off, washed with ether, and dried *in vacuo* to constant mass to give yellow needles of compound **3** (from ethanol) with R_f 0.65 (acetone–alcohol, 1:1).

3-Ethyl(propyl)-1-vinylnaphtho[2,3-*d*]imidazolium Iodides 4, 5 were prepared similarly to salt **3**. Trituration of the obtained oil with dry ether gave the salt **4** as yellow crystals with R_f 0.59 (acetone–alcohol, 1:1) and compound **5** as light-brown crystals with R_f 0.85 (acetone–alcohol, 1:1).

3-Ethyl-1-vinylnaphtho[2,3-*d*]imidazolium Bromide (6). A mixture of compound **1** (0.6 g, 3 mmol) and ethyl bromide (4 ml, 3 mmol) was refluxed for 6 h at 45ºC. The oil formed was triturated with dry ether and crystallized from ethanol to give compound **6** as brown needles with R_f 0.71 (acetone–alcohol, 1:1).

Complexes of Compound 1 with *p*-Chloranil (7), Tetracyanoethylene (8), and 2,4,7-Trinitro-9-fluorenone (9) (General Method). A solution of acceptor in chloroform ($c = 1.5\times10^{-2}$ g·mol/l) (10 ml) was added to a solution of compound **1** in chloroform ($c = 1.5\times10^{-2}$ g·mol/l) (10 ml). An intense color change of the solution occurred from light-yellow to dark-green (**7**), khaki (**8**), or dark-brown (**9**).

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