SYNTHESIS AND SPECTRAL STUDIES OF VINYL DERIVATIVES OF 2,2'-DIIMIDAZOLYL

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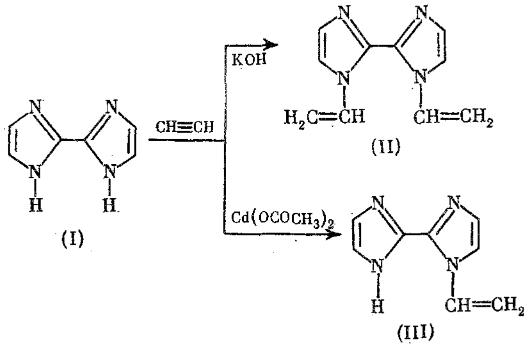
The known methods for obtaining 1-vinylimidazole, 1-vinylbenzimidazole, and 1-vinyltriazoles are based on the reaction of acetylene with the appropriate azoles [1-3], but information is lacking on the synthesis of the vinyl derivatives of 2,2'-biimidazolyl. In view of this, in the present paper a study was made of the reaction of 2,2'-biimidazolyl (I) with acetylene under pressure, as well as the spectral properties of the synthesized vinylbiimidzolyls.

The presence in the (I) molecule of two labile hydrogen atoms in the 1 and 1' positions determines the possibility of obtaining compounds with either two or one vinyl group. We studied the reaction of (I) with acetylene in the presence of various catalysts (KOH, $Cd(OAc)_2$, CuCl) in the range 140-220°C.



It proved that the use of KOH as the catalyst leads to the divinyl derivative (II).

The maximum yield of 1,1'-divinyl-2,2'-biimidazolyl (II) was obtained when the reaction was run in DMSO in the presence of 30% KOH for 4 h at 180°. Replacing the DMSO by α-methylpyrrolidone, as well as decreasing the temperature and time of the process, substantially lower the yield of (II), but they do not affect the direction of the reaction. The formation of the monovinyl derivative was not observed under these conditions.

The use of $Cd(OAc)_2$ in the vinylation of (I) changes the direction of the reaction and leads only to the monovinyl derivative, 1-vinyl-2,2'-biimidazolyl (III), in up to 20% yield. An attempt to increase the yield of (III) by varying the catalyst concentration, as well as the temperature and time of the process, was not successful.

The properties of the (II) and (III) derivatives are given in Table 1. The structure of (II) and (III) was confirmed by the elemental analysis and the PMR, IR, and UV spectral data.

The (II) derivative could not be obtained from (III) by vinylation in the presence of $Cd(OAc)_2$, and we were unable to detect even traces of the divinyl compound in the reaction product. At the same time, (II) is formed from (III) in 55% yield if the vinylation is run using KOH as the catalyst. It should be mentioned that the simultaneous formation of the mixture of (II) and (III), although in low yield, was observed when using 6% CuCl as the catalyst.

Compounds (II) and (III) easily add hydrogen to the double bonds of the vinyl groups to give the N-ethyl derivatives, which are given in Table 1.

The spectral characteristics of the synthesized compounds were determined employing the electronic, IR, and PMR spectral methods (Table 2).

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TABLE 1. 1-Vinyl and 1-Ethyl Derivatives of 2,2'-Biimidazolyl (I)

Compound	Yield, %	mp, °C	R_f	Found, %			Empirical formula	Calculated, %		
				C	H	N		C	H	N
1-Vinyl-2,2'-biimidazolyl	21	183–185	0,85	59,73	5,17	34,84	$C_8H_8N_4$	60,00	5,00	35,00
1,1'-Divinyl-2,2'-biimidazolyl	75	123–125	0,90	64,48	5,53	30,51	$C_{10}H_{10}N_4$	64,51	5,39	30,10
1-Ethyl-2,2'-biimidazolyl	63	132–134	0,86	59,01	6,25	34,63	$C_8H_{10}N_4$	59,25	6,17	34,57
1,1'-Diethyl-2,2'-biimidazolyl	68	38–39	0,91	63,08	7,03	29,87	$C_{10}H_{14}N_4$	63,10	7,31	29,48

TABLE 2. Parameters of UV, IR, and PMR Spectra of Vinyl and Ethyl Derivatives of 2,2'-Biimidazolyl (I)

Compound	λ, nm	ε, liter/mole • cm	δ, ppm	J, Hz
1,1'-Divinyl-2,2'-biimidazolyl	206 236 286	22 300 13 012 11 820	4,87 (H_A and $H_{A'}$), 5,17 (H_B and $H_{B'}$), 8,40 (H_X and $H_{X'}$)7,27 (H^5 and $H^{5'}$), 7,01 (H^4 and $H^{4'}$)	4,47 (AX), 8,12 (BX), 0,50 (AB)
1,1'-Diethyl-2,2'-biimidazolyl	253	11 820		
1-Vinyl-2,2'-biimidazolyl	– 225 284	– 10 361 15 209	4,99 (H_A), 5,35 (H_B), 8,68 (H_X), 7,06 (H_{NH}), 7,24 (H^4), 7,11 ($H^{4'}$), 7,65 (H^5)	4,40 (AX), 8,34 (BX), 0,55 (AB)
1-Ethyl-2,2'-biimidazolyl	272	16 141		

The electronic spectrum of (II) has three absorption bands. The bands at 206 and 236 nm, the same as in the spectrum of 1-vinylimidazole [4], are related to the π–π* electron transition, caused by the interaction between the electronic systems of the heterocycle and the vinyl group. The long-wave band in the spectrum of this compound is evidently related to the π–π* electronic transitions, caused by the conjugation between the azole rings. The long-wave band remains unchanged in the spectrum of (III), whereas the two short-wave bands exhibit hypsochromic shift, which can be explained as due to upsetting the coplanarity between the vinyl group and the azole ring. The 1-ethyl-2,2'-biimidazolyl molecule (IV) is characterized by one band with a maximum around 272 nm. An even greater hypsochromic shift of the maximum of this band to 253 nm occurs in the spectrum of 1,1'-diethyl-2,2'-biimidazolyl (V).

A hypsochromic shift of the bands at 236 nm to 225 nm, and at 206 nm to below 200 nm, is observed in the electronic spectrum of (II), taken in HCl solution. The position of the long-wave band remains unchanged, and only some decrease in its absorption coefficient occurs (ε 13,475). This testifies to the fact that it is the electronic transitions in each vinylazole fragment, and not the electronic transitions between the azolyl rings, that are most sensitive to protonation.

The values of the chemical shifts and SSCC of the olefinic protons, attached to the N atoms in the mono- and divinyl-2,2'-biimidazolyls, are characteristic [5]. The signal of the H^2 proton, which is present in the PMR spectrum of 1-vinylimidazole, is absent in the spectra of (II) and (III). If in the PMR spectrum of 1-vinylimidazole the signal of the H_X* protons (δH_X 6.88 ppm) is superimposed on the signals of the H^4 and H^5 ring protons, then in the spectrum (II) the signal of the H_X proton resonates further downfield. The H^4 and H^5 signals of the imidazolyl rings are represented by two singlets (see Table 2).

Similar to the IR spectrum of 1-vinylimidazole [4], the stretching vibrations of the heterocycle in the (II) and (III) derivatives appear in the 1500-1520 cm^{-1} region. In intensity they are substantially weaker, which is apparently related to an increase in the symmetry of the molecule as a whole.

The stretching vibrations of the disubstituted heterocycle in the spectra of (II) and (III) are also characterized by intense absorption bands at 1410 and 1440 cm^{-1}, respectively. Similar to 1-vinylimidazole, the absorption bands at 3050-3110 and 825 cm^{-1} in the spectra of its biimidazolyl derivatives correspond to νCH and δNCN of the heterocycle. The absorption bands at 1642-1645 and 955-960 cm^{-1} are related to the stretching and deformation vibrations of the C=C bonds of the vinyl groups. The integral intensities ($E_{\nu_1}^{\nu_2}$) of the absorption bands of each vinyl group in (II) make an additive contribution to the absorption band at 1645 cm^{-1} (E = 5435 liters/mole·cm^2), whose intensity is twice that of the band in the unsubstituted 1-vinylimidazole (E = 2722 liters/mole·cm^2).

EXPERIMENTAL

The PMR spectra were measured on a Tesla BS-1878 spectrometer in CCl_4, CD_3OD, CD_3COCD_3, or DMSO solution relative to HMDS. The IR spectra were recorded on an UR-20 spectrophotometer either

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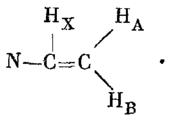

as KBr pellets or in ethanol solution. The electronic absorption spectra of the compounds in ethanol solution were obtained on a Specord UV-VIS spectrometer. The TLC was run using a loose layer of Al_2O_3 (II activity) in the system: 20:8:1 chloroform–benzene–ethanol. 2,2'-Biimidazolyl (I) was synthesized as described in [6]. The values of the integral intensities of the absorption bands ($E_{\nu_1}^{\nu_2}$) were measured as described in [7].

1-Vinyl-2,2'-biimidazolyl (III). A mixture of 5 g (0.031 mole) of (I) and 0.45 g (9%) of $Cd(OAc)_2$ in 60 ml of α-methylpyrrolidone was kept in an autoclave for 4 h at 180° and an acetylene pressure of 18 atm. The brown liquid was filtered and evaporated in vacuo in the presence of hydroquinone, and the residue was vacuum-distilled to give 1.23 g (21%) of (III), mp 183-185° (from alcohol).

1,1'-Divinyl-2,2'-biimidazolyl (II). A mixture of 5 g (0.026 mole) of (I) and 1.5 g (30%) of KOH in 60 ml of DMSO and 5 ml of water was kept in an autoclave for 4 h at 180° and an acetylene pressure of 18 atm. The dark-brown liquid was filtered and the solvent was distilled off under reduced pressure in the presence of hydroquinone. Distillation of the residue gave a viscous liquid with bp 165° (9 mm), which crystallized on standing. We obtained 5.2 g (75%) of (II), mp 123-125° (from alcohol).

1,1'-Diethyl-2,2'-biimidazolyl (V). A mixture of 4 g (0.021 mole) of (II) and 0.4 g (10%) of Raney Ni in 60 ml of abs. ethanol was kept in an autoclave for 24 h at 50° and a hydrogen pressure of 30 atm. The pale green liquid was filtered, the ethanol was evaporated, and the residue was distilled to give a colorless liquid with bp 143° (8 mm), which crystallized on standing. We obtained 2.6 g (64%) of (V), mp 38-39°.

CONCLUSIONS

1. A method was developed for the synthesis of 1,1'-divinyl-2,2'-biimidazolyl via the reaction of 2,2'-biimidazolyl with acetylene under pressure. Replacing the KOH catalyst by $Cd(OAc)_2$ facilitates the formation of 1-vinyl-2,2'-biimidazolyl.

2. The parameters of the electronic, IR, and PMR spectra of the vinyl derivatives of 2,2'-biimidazolyl were compared with the spectral parameters of 1-vinylimidazole.

LITERATURE CITED

1. M. F. Shostakovskii, G. G. Skvortsova, N. P. Glazkova, and E. S. Domnina, Khim. Geterotsikl. Soedin., 1969, 1070.
2. V. V. Kalmykov, I. B. Lopukh, and V. A. Ivanov, Zh. Prikl. Khim., 51, 2377 (1978).
3. M. F. Shostakovskii, G. G. Skvortsova, E. S. Domnina, and L. P. Makhno, Khim. Geterotsikl. Soedin., 1970, 1289.
4. N. N. Chipanina, N. A. Kazakova, Yu. L. Frolov, T. V. Kashik, S. M. Ponomareva, E. S. Domnina, G. G. Skvortsova, and M. G. Voronkov, Khim. Geterotsikl. Soedin., 1976, 828.
5. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, High-Resolution Nuclear Magnetic Resonance Spectroscopy [Russian translation], Vol. 2, Mir (1969).
6. H. Kölln, Liebigs Ann. Chem., 416, 231 (1918).
7. A. Weissberger, Technique of Organic Chemistry, Vol. 11, Part 1, Wiley-Interscience, New York (1963), p. 139.