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VINYLATION OF PYRROLES IN DIMETHYL SULFOXIDE

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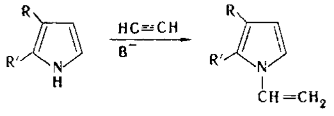
A number of 1-vinylpyrroles were obtained in up to 97% yields by base-catalyzed addition of substituted pyrroles to acetylene in dimethyl sulfoxide at 80-100°C.

N-Vinyl derivatives of heterocyclic compounds, which are valuable monomers and intermediates, find application in the manufacture of plastics and synthetic fibers, in radio technology, and in medicine (for example, see [1]). N-Vinylpyrroles are the most interesting derivatives of this sort but the least study has been devoted to them.

Methods for the synthesis of vinyl nitrogen heterocycles have been examined in a review [2]. They consist in dehydration of β-hydroxylethyl derivatives, dehydrohalogenation of haloethyl derivatives, or direct vinylation of heterocycles with an NH bond. Up until now the direct vinylation of nitrogen heterocycles has been accomplished at high temperatures (150-300°C) and pressures (20-40 atm) and has required a long time for completion [2].

Data from a study of the vinylation of a number of pyrroles obtained on the basis of the reaction of acetylene with ketoximes [3] are presented in this paper. 1-Vinylpyrroles I-XIV (table 1) were obtained in up to 97% yields:



I-XVI

R = H, alkyl, aryl; R' = alkyl, aryl

The reaction proceeds effectively in the presence of 30% KOH in aprotic polar solvents [dimethyl sulfoxide (DMSO), sulfolane, and hexamethylphosphoric triamide]; DMSO was found to be the best of the investigated solvents. The use of the latter made it possible to lower the reaction temperature to 80-100°, which is almost 100° lower than the temperature of classical vinylation of NH heterocycles, and 1-vinylpyrroles were obtained in practically quantitative yields. The use of DMSO makes it possible to carry out the vinylation of pyrroles at an acetylene pressure close to atmospheric (1.1-1.5 atm). It should be emphasized that up until now processes of this sort could not be put into practice because of the necessity of the use of acetylene under pressure and at high temperatures.

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TABLE 1. 1-Vinylpyrroles I-XVI

Compound	R	R′	bp, °C (mm)	d_4^{20}	n_D^{20}	Found, %			Empirical formula	Calc., %		
						C	H	N		C	H	N
I	H	CH_3	70 (40)	0,9308	1,5230	78,1	8,4	13,2	C_7H_9N	78,5	8,5	13,1
II	CH_3	CH_3	71 (20)	0,9297	1,5270	79,3	9,1	11,7	$C_8H_{11}N$	79,3	9,2	11,6
III	CH_3	C_2H_5	60 (6)	0,9112	1,5185	79,6	10,0	10,1	$C_9H_{13}N$	80,0	9,6	10,4
IV	H	n-C_4H_9	75 (5)	0,9108	1,5150	80,4	10,0	9,3	$C_{10}H_{15}N$	80,5	10,1	9,4
V	H	i-C_4H_9	74 (10)	0,9275	1,5130	80,6	10,3	9,1	$C_{10}H_{15}N$	80,5	10,1	9,4
VI	H	t-C_4H_9	63 (10)	0,9050	1,5115	80,5	10,4	9,2	$C_{10}H_{15}N$	80,5	10,1	9,4
VII	n-C_3H_7	n-C_4H_9	87 (2)	0,8925	1,5025	81,8	10,9	7,1	$C_{13}H_{21}N$	81,6	11,1	7,3
VIII	H	C_6H_{13}	113 (10)	0,8914	1,5040	81,8	10,5	7,8	$C_{12}H_{19}N$	81,4	10,7	7,9
IX	H	C_6H_5	104 (2)	1,0443	1,6180	85,2	6,6	8,1	$C_{12}H_{11}N$	85,2	6,5	8,3
X	CH_3	C_6H_5	110 (1,5)	1,0509	1,5960	85,2	7,1	7,7	$C_{13}H_{13}N$	85,3	7,2	7,6
XI	C_2H_5	C_6H_5	135 (5)	1,0192	1,5910	85,1	8,6	8,9	$C_{14}H_{15}N$	84,8	8,9	8,3
XII	n-C_3H_7	C_6H_5	140 (1)	0,9972	1,5780	84,1	7,6	7,5	$C_{15}H_{17}N$	84,5	7,9	7,1
XIII	C_6H_5	C_6H_5	—*	—	—	86,9	6,4	5,3	$C_{18}H_{15}N$	86,5	6,1	5,7
XIV	$-(CH_2)_4-$		92 (4)	1,0010	1,5570	81,5	9,1	9,4	$C_{10}H_{13}N$	81,6	8,9	9,5
XV	$-CH(CH_3)(CH_2)_3-$		69 (2)	0,9801	1,5465	82,1	9,4	8,5	$C_{11}H_{15}N$	82,0	9,4	8,7
XVI	$-(CH_2)_5-$		74 (1)	0,9937	1,5560	82,1	9,5	8,3	$C_{11}H_{15}N$	82,0	9,4	8,7

*This compound had mp 125°.

The individuality and structures of the synthesized compounds were proved by gas–liquid chromatography (GLC) and IR and PMR spectroscopy. The signals of the protons of the vinyl group in the PMR spectra of the chromatographically pure 1-vinylpyrroles are represented by three quartets at δ 6.67 ($-CH=$), 4.83 (the trans proton of the CH_2 group with respect to the CH proton), and 4.37 ppm (the cis CH_2 proton); $J_{trans} = 15.4$ Hz, $J_{cis} = 8.8$ Hz, and $J_{gem} = 0.8$ Hz. The protons of the pyrrole ring give two doublets at 6.71 (α proton) and 5.92 ppm (β proton), with $J = 3.0$ Hz. Bands of a vinyl group (485, 520, 585, 850, 970, 1180, 1320, 1550, 1600, 1650, 3020, and 3070 cm^{-1}) are observed in the IR spectra, and we also noted the presence of a triplet in the region of $C=C$ stretching vibrations (1550, 1600, and 1650 cm^{-1}), which can evidently be assigned to the different rotational isomers of the 1-vinylpyrroles.

EXPERIMENTAL

Chromatographic analysis was accomplished with a Khrom-4 chromatograph with detection by a catharometer. The column was 2.5-m long and had a diameter of 3 mm, the solid phase was Chromaton N-AW-DMCS, and the liquid phase was 15% DS 550 silicone. The thermostat temperature was 170°, and the carrier gas was helium. The IR spectra of thin layers of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of 10% solutions of the compounds in CCl_4 were obtained with a BS-4878 spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard.

Several typical methods for the synthesis of 1-vinylpyrroles in DMSO are presented below.

1-Vinyl-4,5,6,7-tetrahydroindole (XIV). A) A mixture of 5.5 g (0.04 mole) of 4,5,6,7-tetrahydroindole and 1.6 g of KOH in 100 ml of DMSO was heated in an 1-liter rotating autoclave at 100° in an acetylene atmosphere (the initial pressure was 12 atm) for 3 h, after which the mixture was washed with water. The organic layer was combined with the ether extracts obtained by extraction of the aqueous layer and dried with potassium carbonate. Vacuum distillation yielded 5.8 g (97%) of XIV (Table 1).

B) A 5-liter reaction vessel equipped with a stirrer was charged with 1 liter of DMSO, 150 g (1.24 moles) of 4,5,6,7-tetrahydroindole, and 50 g of KOH, after which the mixture was heated to 400° with stirring, and continuous feeding in of acetylene under a pressure of 1.5 atm was begun. Acetylene absorption ceased after 3.5 h. The mixture was worked up as described above to give 155 g (85%) of XIV.

1-Vinyl-2-phenylpyrrole (IX). A mixture of 1.2 g (8 mmole) of 2-phenylpyrrole, 0.36 g of KOH, and 30 ml of DMSO was heated at 80-90° for 2 h in an 1-liter rotating autoclave under acetylene pressure (the initial pressure was 13 atm), after which the mixture was treated with 150 ml of water, and the ether extracts were washed with water and dried with potassium carbonate. Vacuum fractionation yielded 1.2 g (87%) of vinylpyrrole IX.

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