STUDIES ON PYRAZOLES

LX. Synthesis of N-Vinylpyrazoles*

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A new method has been developed for the synthesis of N-vinylpyrazoles from pyrazoles not substituted at the nitrogen atom. This synthesis is accomplished by the action of vinyl acetate and is catalyzed by mercuric sulfate.

In continuation of our research on the synthesis of vinylpyrazoles [2], we applied the vinyl interchange (Umvinylierung) method using vinyl acetate to prepare N-vinylpyrazoles. This procedure had given excellent results with some heterocycles having a free NH group [3].

To synthesize N-vinylpyrazoles by this method, we selected a series of pyrazoles with a free NH group and with various substituents in position 4 of the nucleus. Mercuric sulfate (II), prepared directly within the reaction mixture was employed as catalyst. At the temperature of boiling vinyl acetate, the reaction continued for 1–7 hr, depending on the structure of the pyrazole. Electron-acceptor groups in position 4 of the pyrazole nucleus increase the acidity of the NH group and accelerate the reaction, while electron-donor groups retard it. The end of the reaction was determined by means of thin-layer chromatography on alumina. The table summarizes the data on the duration of the reactions, the yields, and the constants of the vinylpyrazoles obtained. The UV spectra of the vinylpyrazoles indicate that introduction of the vinyl group in position 1 gives rise to a bathochromic shift of approximately 40 nm.

EXPERIMENTAL

N-Vinylpyrazoles. To 56 ml of vinyl acetate, 1 g of mercuric acetate (II) was added, followed by 0.12 ml of anydrous H_2SO_4 added carefully, drop by drop. Next 0.03 mole of the corresponding pyrazole was added, and the mixture was heated under reflux on a boiling water bath until the spot of the initial pyrazole disappeared from the thin-layer chromatogram (1–7 hr). After the reaction was completed, the excess of vinyl acetate was distilled off under vacuum, and 100 ml of absolute ether and 2 g of anhydrous sodium acetate were added to the residue in order to decompose the catalyst. The precipitate of mercuric acetate was filtered off, and the filtrate was washed first with 2 N Na_2CO_3, next with H_2O until neutral in reaction, and finally dried over magnesium sulfate. After stripping off the solvent, the residue was distilled in vacuo or recrystallized. Chromatography of the vinylpyrazoles was carried out on a nonactivated thin layer of alumina, (activity II) on the Brockmann scale. The UV spectra of the N-vinylpyrazoles in methanol solutions were recorded in an SF-4 apparatus.

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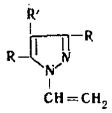
*For part LIX, see [1].

N-Vinylpyrazoles 

R	R′	Duration of the reaction, in hr	Bp (pressure in mm) or mp., °C	n_D^{20}	d_4^{20}	UV spectra		Empirical formula	Found, %		Calc., %		R_f (in CCl_3)	Yield, %
						λ_{max}, nm	lg ε		C	H	C	H		
H	H	1	61 (50)	1.5145	1.0030	247	4.08	$C_5H_6N_2$	63.49 63.30	6.72 6.67	63.80	6.42	0.71	70
CH_3	H	4	80 (20)	1.5151	0.9618	253	4.06	$C_7H_{10}N_2$	68.41 68.36	8.18 8.17	68.82	8.25	0.70	78
CH_3	CH_3	7	79—81 (6)	1.5070	0.9970	257	4.04	$C_8H_{12}N_2$	70.46 70.31	8.76 8.74	70.49	8.87	0.66	76
CH_3	Cl	1.5	103—104 (22)	1.5180	1.1180	225 260	3.73 4.03	$C_7H_9ClN_2$	53.56 53.49	6.14 5.95	53.68	5.79	0.81	80.5
CH_3	Br	1.5	92 (8)	1.5510	1.4060	262	3.90	$C_7H_9BrN_2$	41.91 41.78	4.89 4.68	41.50	4.51	0.81	85
CH_3	I	1.5	107 (4)	1.5838	1.6470	228 262	3.68 3.96	$C_7H_9IN_2$	34.16 34.09	3.97 3.77	33.89	3.66	0.81	80
CH_3	$COCH_3$	1	62—63*	—	—	270	4.17	$C_9H_{12}N_2O$	66,00 65.95	7.50 7.30	65.89	7.36	0.53	80
CH_3	NO_2	1.5	131—132 (6) 46—47*	—	—	294	4.06	$C_7H_9N_3O_2$	50.38 50.31	5.67 5.50	50.29	5.42	0.77	85
C_6H_5	Br	2	69—70**	—	—	280	4.29	$C_{17}H_{13}BrN_2$	62.73 62.57	4.11 4.05	62.72	4.02	0.88	86

*From heptane.
**From petroleum ether.

REFERENCES

1. I. I. Grandberg, A. N. Kost, and L. F. Morozova, KhGS [Chemistry of Heterocyclic Compounds], 887, 1968.

2. I. I. Grandberg and G. I. Sharova, KhGS [Chemistry of Heterocyclic Compounds], 325, 1968.

3. H. Hopff, U. Wyss, and H. Lüssi, Helv. Chim. Acta, 43, 135, 1960.

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