BROMINATION OF 1-VINYLPYRAZOLES

L. A. Es'kova, E. S. Domnina,
G. G. Skvortsova, V. K. Voronov,
N. N. Chipanina, and N. A. Kazakova

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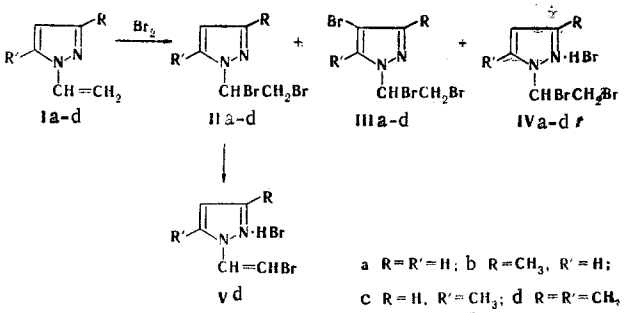
In addition to the principal reaction pathway – addition of bromine to the double bond of the vinyl group – in the bromination of 1-vinylpyrazoles, the hydrogen atom in the 4 position of the pyrazole ring undergoes substitution, and the liberated hydrogen bromide coordinates with the pyrazoles present in the reaction mixture.

1-Vinylazoles behave differently in halogenation reactions. Complexing with halogens predominates in the case of 1-vinylimidazoles, whereas 1-vinyltriazoles primarily add halogens to the double bond of the vinyl group [1, 2]. In the present research our study of the halogenation of 1-vinylazoles was continued in the case of the previously uninvestigated 1-vinylpyrazoles.

It is known that 1,2-dibromo-2-(1-phenyl-4-pyrazolyl)ethane is formed in the bromination of 1-phenyl-4-vinylpyrazole in ether [3]. The addition of bromine to the double bond and bromination in the 4 position of the ring are observed in the reaction of bromine with 1-allylpyrazoles. The bromination product undergoes intramolecular quaternization when it is heated [4].

We have shown that 1-vinylpyrazoles Ia-d are brominated in carbon tetrachloride at −20°C to give a difficult-to-separate mixture of products.

According to the PMR spectroscopic data, the chief reaction products are 1-(1',2'-dibromo)ethylpyrazoles IIIa-d. The liberated hydrogen bromide coordinates with the pyrazoles present in the reaction mixture to give hydrohalides IVa-d.



An increase in the temperature, the addition of the vinylpyrazole to a solution of bromine, and the use of excess bromine increase the percentages of bromo derivatives III. The stabilities of the bromination products differ as a function of the position and number of methyl groups in the ring, and this gives rise to side processes.

Thus a mixture of IIa-IVa is obtained in the reaction of 1-vinylpyrazole with excess bromine at room temperature, regardless of the order of mixing of the reaction components. An increase in the reaction temperature to 60°C leads primarily to the formation of 1-(1',2'-dibromo)ethyl-4-bromopyrazole IIIa with a small amount of 1-(1',2'-dibromo)ethylpyrazole IIa and its hydrobromide IVa. The addition of bromine to the double bond of the vinyl group to give pyrazole IIa (83%) primarily occurs in the reaction of an equivalent amount of bromine with vinylpyrazole Ia. Partial bromination in the 4 position of the ring cannot be avoided even at −20°C; this was confirmed by the results of thin-layer chromatography (TLC). The characteristics of the iso-

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TABLE 1. Characteristics of the Products of Bromination of 1-Vinylpyrazoles

Compound	mp, °C	Found, %			Empirical formula	Calculated, %		
		C	H	Br		C	H	Br
IIa	67—68	23,9	2,5	63,2	$C_5H_6Br_2N_2$	23,6	2,4	62,9
IIIa	42,5—43	18,6	1,7	71,3	$C_5H_5Br_3N_2$	18,1	1,5	72,0
IVa	143—145	18,2	2,1	72,0	$C_5H_7Br_3N_2$	17,9	2,1	71,6
IIb	59—61	27,3	2,9	59,2	$C_6H_8Br_2N_2$	26.9	3,0	59,6
IIIb	55—56	20,6	2,1	69,0	$C_6H_7Br_3N_2$	20,8	2,0	69.1
IVb	175	20,3	2,6	69.3	$C_6H_9Br_3N_2$	20,6	2,6	68,7
IIId	73—74	23,8	2,8	66,0	$C_7H_9Br_3N_2$	23,3	2,5	66,4
Vd	149—150	30,0	3,8	56,3	$C_7H_{10}Br_2N_2$	29,8	3,6	56,7
VI	99—102	29,1	4,2	49,4	$C_4H_7BrN_2$	29,5	4,3	49,0
VII	230	34,3	5,2	45,2	$C_5H_6BrN_2$	33,9	5,1	45,1
VIII	135—136	41,6	5,6	39,7	$C_7H_{11}BrN_2$	41,4	5,5	39,4

TABLE 2. PMR Spectra of Bromo Derivatives of Pyrazoles

Compound	Chemical shifts, δ, ppm							SSCC, Hz				
	3-H	4-H	5-H	3-CH_3	5-CH_3	α-H	β-H	3-H, 4-H	4-H, 5-H	5-H, 3-H	α-H, β-H	β-H, β-H
IIa	7,60 d	6,30 t	7,50 d	—	—	6,35 q	4,64 t; 4,05 q	2,6	1,9	0,8	3,8; 10,8	10,8
IIIa	7,60 s	—	7,60 s	—	—	6,31 q	4,55 t; 4,04 q	—	—	0,8	3,9; 11,0	11,0
IVa	8,50d	6,83 t	8,33 d	—	—	5,99 t	3.88 m	2,6	2,7	0,9	5,4; 6,6	—
IIb	—	6,06d	7,36 d	2,27 s	—	6,26 q	4,62 t; 4,04 q	—	2,4	—	3,7; 10,4	10,4
IIIb	—	—	7,49 s	2,26 s	—	7,19 q	4,55 t; 4,00 q	—	—	—	3,6; 10,8	10,8
IVb	—	6,56 d	8,29 d	2,44 s	—	5,77 q	3,79 m	—	2,7	—	5,4; 6,70	—
IIId	—	—	—	2,21 s	2,30	6,19 q	4,74 t; 4,00 q	—	—	—	3,8; 10,4	10,4
Vd	—	6,39s	—	2,38 s	2,42	7,67 d	— 7,11 d	—	—	—	12,5	—
VI	—	6,51 d	8,06 d	2,41 s*		—	— —	—	2,9	—	— —	—
VII	—	6,30 s	—	2,30 s		—	— —	—	—	—	— —	—
VIII	—	6,41 s	—	2,36 s		7,20 q	5,35 q; 5,67 q	—	—	—	8,7; 15,1	2,5

* The NH signals are superimposed on the signals of the remaining protons of deuteromethanol.

lated bromo derivatives of the pyrazoles are presented in Table 1. Their structures are confirmed by the IR and PMR spectroscopic data (Table 2).

The reaction of 1-vinyl-3-methylpyrazole Ib with an equimolar amount of bromine gives 1-(1',2'-dibromo)ethyl-3-methylpyrazole IIb, which rapidly decomposes to give the hydrobromide of 3-methylpyrazole VI. The lability of the bromine in the α-carbon atom. Because of this, the product of addition of bromine to the vinyl group of pyrazole Id undergoes decomposition in the reaction mixture to give 1-(2'-bromovinyl)-3,5-dimethylpyrazole hydrobromide (Vd). The IR spectrum of Vd contains the absorption bands characteristic for the $\equiv\overset{+}{N}H$ cation (2500-2700 cm^{-1})* and the C=C bond (1640 cm^{-1}). Two "olefin" protons that are trans-oriented (J = 12.5 Hz) are present in the PMR spectrum. From the mixture of products of bromination of pyrazole Id we were able to isolate 1-(1',2'-dibromo)ethyl-4-bromo-3,5-dimethylpyrazole (IIId) and characterize it from its PMR spectrum. In addition to the indicated products, we identified 3,5-dimethylpyrazole hydrobromide (VII) and also isolated the hydrobromide of Id and hydrobromide VIII.

Thus our studies showed that, in contrast to the vinyl derivatives of imidazoles and triazoles, 1-vinylpyrazoles do not form complexes with bromine. The addition of bromine to the vinyl group and subsequent elimination of hydrogen bromide to give hydrobromides and electrophilic substitution in the 4 position of the ring are characteristic for them.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in CCl_4 or CD_3OD were recorded with a BS487B spectrometer at room temperature with tetramethylsilane as the internal standard.

* The spectroscopic manifestation of donor-acceptor interactions of 1-vinylpyrazoles with hydrogen chloride have been examined in greater detail [5].

Bromination of Vinylpyrazoles Ia-d. These compounds were brominated in the cold or at room temperature in CCl_4. The precipitated hydrobromides were removed from the reaction mixtures by filtration. The CCl_4 was removed from the mother liquors, and the residual bromination products were recrystallized from hexane or petroleum ether. In the case of vinylpyrazole Id the products were isolated by fractional precipitation with ether and purified by recrystallization or sublimation.

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RESEARCH IN THE CHEMISTRY OF PYRAZOLIDINE

XXIII.* STUDY OF THE REACTION OF 3,5-DIOXOPYRAZOLIDINES WITH β-NITROSTYRENE

K. A. Sapozhnikova, A. S. Sopova, and B. L. Moldaver

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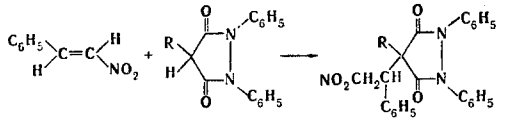
Products of Michael condensation containing a 1-phenyl-2-nitroethyl residue in the 4 position of the heteroring are formed in high yields in the reaction of equimolar amounts of 4-methyl-, 4-ethyl-, 4-isopropyl-, 4-butyl-, 4-isoamyl-, and 4-phenyl-1,2-diphenyl-3,5-dioxopyrazolidines and 1,2-diphenyl-3,5-dioxopyrazolidine with β-nitrostyrene under basic catalysis conditions. 1,2-Diphenyl-3,5-dioxopyrazolidine adds two equivalents of β-nitrostyrene when a twofold excess of the latter is present.

4-Monosubstituted and 4-unsubstituted 3,5-dioxopyrazolidines (DOP) are capable of adding compounds with an activated double bond – phenyl vinyl ketone [2] and azomethines [3] – to the 4-C atom of the heteroring. It is also known that arylnitroethylenes readily react with β-dicarbonyl compounds under the conditions of the Michael reaction [4-7]. The reaction of arylnitroethylenes with 1,2-diphenyl-DOP (DDP) and its 4-monosubstituted derivatives has not been studied.

We have studied the electrophilic addition of β-nitrostyrene (I) to 4-substituted DDP (IIa-g), as a result of which we obtained adducts of Michael condensation (IIIa-g) in 70-90% yields:



I IIa-g IIIa-g IV

II, III a R = H; b R = CH_3; c R = C_2H_5; d R = iso-C_3H_7; e R = C_4H_9; f R = iso-C_5H_{11}; g R = C_6H_5; IV R = $C_6H_5CHCH_2NO_2$

Compound IIa also reacts with two equivalents of styrene I to give 4,4-bis(1-phenyl-2-nitroethyl)-DDP

* See [1] for communication XXII.

Leningrad Pharmaceutical-Chemistry Institute, Leningrad 197022.

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