SYNTHESIS OF o-AZOBISPYRAZOLE DERIVATIVES

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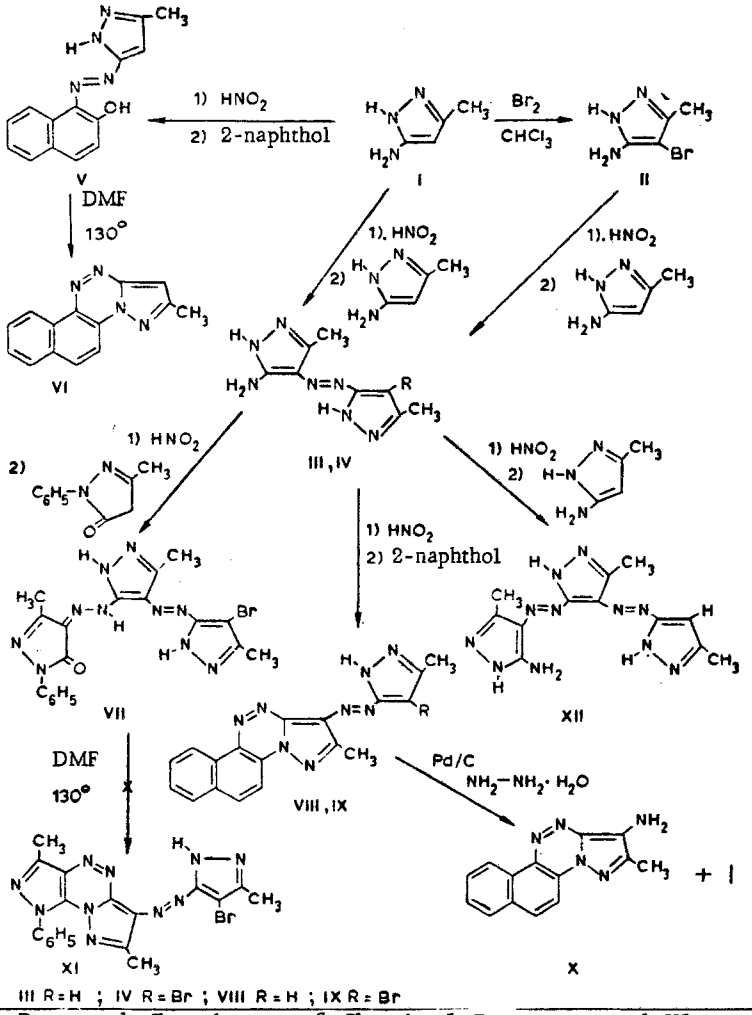
Azobispyrazoles were obtained by diazo coupling of diazotized o-aminoazopyrazoles. The o-azobispyrazole obtained from 3-methyl-1-phenyl-5-pyrazolone exists in the o-azohydrazone form, whereas the o-azobispyrazole obtained from 5-amino-3-methylpyrazole exists in the o-azobis form. A 3-azo derivative of naphtho[2,1-e]-pyrazolo[5,1-c]triazine is formed from 2-naphthol. The structures of the compounds obtained were confirmed by IR, UV, PMR, and mass spectroscopy.

Tetradentate o-azobis compounds, which are of interest as chelating agents, have been synthesized by reaction of the corresponding 1,2-dihydrazine derivatives with 1,2-quinones [1, 2] or by coupling of 1,2-dihydrazinohetarenes [2].

Insofar as diazo coupling of diazotized o-aminoazo compounds is concerned, there are indications [3] that it is difficult to use because of the tendency of o-aminoazo compounds to undergo oxidative closure to a 1,2,3-triazole ring on reaction with nitrous acid [4]. This limitation is evidently associated only with 1,2-derivatives of naphthalene [4], since there are examples of the synthesis of o-azobis compounds in the benzene series [5].



III R=H ; IV R=Br ; VIII R=H ; IX R=Br

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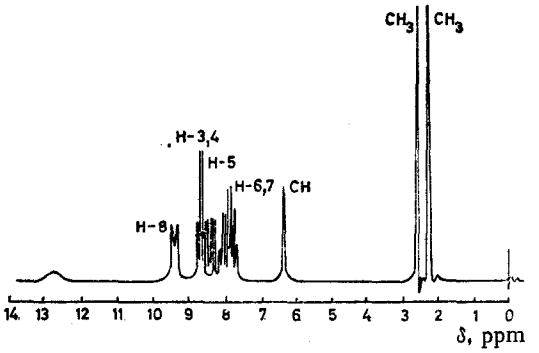

Fig. 1. PMR spectrum of VIII.

It seemed of interest to investigate the possibility of the synthesis of o-azobis compounds from o-aminoazopyrazoles.

Compound II was obtained by bromination of I by the method in [7]. The signal of the pyrazole proton that is observed at 5.48 ppm in the PMR spectrum of I vanishes in the spectrum of II. Compounds III and IV were obtained by diazotization of, respectively, I and II in hydrochloric acid and coupling with I at pH 1.0. Signals of two methyl groups are observed in the PMR spectrum (Table 3). The CH signal of III is observed at 6.40 ppm. Compound V was obtained by coupling of diazotized I with 2-napthol at pH 9-10. A signal of a pyrazole CH proton at 6.60 ppm, a signal of a CH_3 group at 2.40 ppm, a broad NH signal at 13.06 ppm, a narrow OH signal at 14.96 ppm, and signals of six naphthalene protons are observed in the PMR spectrum of V. The IR spectrum does not contain the absorption band of a carbonyl group at 1700 cm^{-1}, but an absorption band at 3460 cm^{-1} corresponding to pyrazole ν_{NH} vibrations and a strong absorption band at 3200 cm^{-1} corresponding to the hydrogen bond of a hydroxyl group are observed in the spectrum. The IR and PMR spectral data indicate that V exists in the azo form rather than in the hydrazone form.

In the case of azo derivatives of 3(or 5)-H- or 3(or 5)-phenylpyrazole closure to a naphtho[2,1-e]pyrazolo[5,1-c]triazine occurred spontaneously or when the compounds were heated in hexane [8].

We were able to effect cyclization of the azo derivative of 3(or 5)-methylpyrazole V only by heating at 130°C in dimethylformamide (DMF) for 10 h.

Signals of six naphthalene protons at 8.30-9.40 ppm and a signal of a pyrazole CH proton at 8.50 ppm are observed in the PMR spectrum of VI.

Closure to a six-membered ring does not occur in the diazotization of IV and coupling at pH 7-8 with 1-phenyl-3-methyl-5-pyrazolone, but o-azobis VII, which exists in the o-azohydrazone form, is formed.

Signals at 10.75 ppm corresponding to two NH groups of pyrazoles and at 11.18 corresponding to a hydrazone NH group are observed in the PMR spectrum of VII. An absorption band at 1730 cm^{-1}, which corresponds to an ν_{CO} absorption band, is noted in the IR spectrum. The UV spectrum has λ_{max} at 329 and 410 nm (349 and 430 nm in alkaline media, 340 and 420 nm at pH 3-5, and 335 and 410 nm at pH 1).

Compounds VIII and IX were obtained instead of the expected o-azobis compounds by diazotization in hydrochloric acid, respectively, of III and IV and coupling at pH 9-10 with 2-naphthol in an alcoholic alkali solution.

Signals of naphthalene protons at 7.44-9.69 ppm and the signal of a pyrazole NH group at 12.88 ppm (VIII) or 10.48 (IX) are observed in the PMR spectra of VIII and IX (Fig. 1). Two maxima at 357 and 455 nm for VIII and at 346 and 453 nm for IX are noted in the UV spectra (in methanol). A shift of the maxima to, respectively, 365 and 490 nm and 370 and 480 nm occurs in alkaline solutions (Fig. 2). A shift to 360 and 470 nm for VIII and to 380 and 475 nm for IX also occurs in acidic media.

It may be assumed that cyclization of the initially formed o-azobis compound, which exists in the azohydrazone form, occurs through the addition of the pyrazole NH group to the C=O group. The resulting hydroxy derivative of 1H-naphthalen-2-one undergoes dehydration to

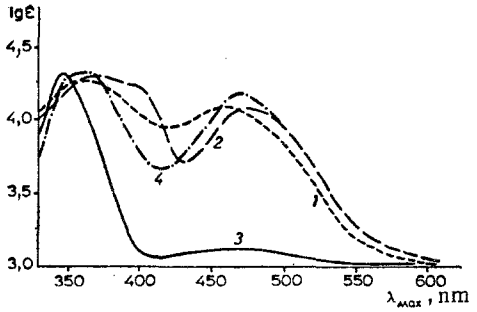

Fig. 2. UV spectra of VIII: 1) in methanol; 2) in 0.1 N solution of $(CH_3)_4N^+OH^-$ in 70% methanol; 3) in acetic acid; 4) in a 0.1 N solution of HCl in 50% acetic acid.

TABLE 1. Physicochemical Constants, Results of Elementary Analysis, and Yields of the Compounds Obtained

Compound	mp, °C	M (by mass spectm.)	Found, %				Empirical formula	Calc., %				Yield, %
			C	H	Br	N		C	H	Br	N	
I*	45—46	97										88
II	118—119	176	27,1	3,4	45,4	23,4	$C_4H_6N_3Br$	27,3	3,4	45,4	23,8	60
III	142—143	205	46,6	5,4		47,5	$C_8H_{11}N_7$	46,8	5,4		47,8	86
IV	225—226	284	33,8	3,5	28,1	34,8	$C_8H_{10}N_7Br$	33,8	3,6	28,1	34,5	80
V	178—179	252	66,8	4,7		21,9	$C_{14}H_{12}N_4O$	66,7	4,8		22,2	90
VI	191—193	234	71,7	4,2		24,4	$C_{14}H_{10}N_4$	71,7	4,3		24,3	40
VII	251—252	469	46,1	3,7	17,0	30,0	$C_{18}H_{17}N_{10}BrO$	46,1	3,7	17,0	29,8	30
VIII	285—286	342	63,0	4,1		32,8	$C_{18}H_{14}N_8$	63,2	4,1		32,7	72
IX	Above 275 (dec.)	421	51,5	3,1	18,6	26,5	$C_{18}H_{13}N_{10}Br$	51,3	3,1	19,0	26,6	53
X	223—224	249	67,5	4,5		28,0	$C_{14}H_{11}N_5$	67,5	4,5		28,1	87
XII	271—272	313	46,1	4,8		49,0	$C_{12}H_{15}N_{11}$	46,0	4,8		49,2	51

*According to the data in [6], this compound has mp 44°C.

TABLE 2. Electronic Spectra of II-XII

Compound	Solvent	λ_{max}, nm (lg ε)					
		1	2	3	4	5	6
II	Methanol		235 (4,52)				
III	Same		236 (4,23)		360 (4,20)		
III	DMF[a]						416 (3,29)
IV	Methanol		234 (4,15)	326 (4,11)	340 (4,09)		
V	Same		254 (4,49)	300 (4,88)	355 (3,71)		410 (3,78)
VI	Ethanol[b]						410 (3,96)
VII	Methanol	225 (4,12)	245 (4,46)		329 (4,30)	360 (3,81)	410 (4,21)
VII	0.1 N solution of $(CH_3)_4N^+OH^-$ in 70% methanol[b]				349 (4,15)		480 (3,83)
VII	CH_3COOH[b]				340 (3,97)		420 (3,93)
VII	0.1 N solution of HCl in 50% CH_3COOH[b]				335 (4,05)		410 (3,96)
VIII	Methanol	222 (4,25)	257 (4,48) 250 (4,26)		357 (4,26)		455 (4,08)
VIII	0.1 N solution of $(CH_3)_4N^+OH^-$ in 70% methanol[b]				365 (4,28)	400 (4,23)	490 (4,04)
VIII	CH_3COOH[b]				345 (4,33)		460 (3,11)
VIII	0.1 N solution of HCl in 50% CH_3COOH[b]				360 (4,30)		4,70 (4,17)
IX	Methanol	224 (4,04)	256 (4,19)		346 (4,04)		453 (3,86)
IX	0.1 N solution of $(CH_3)_4N^+OH^-$ in 70% methanol[b]				370 (4,16)		480 (3,90)
IX	CH_3COOH[b]				365 (4,19)	385 (4,15)	460 (4,11)
IX	0.1 N solution of HCl in 50% CH_3COOH[b]				380 (4,07)		475 (4,16)
X	Ethanol						500 (4,29)
XII	DMF[a]						471 (3,73)

[a]The spectra were recorded from 400 nm. [b]The spectra were recorded from 330 nm.

TABLE 3. PMR Spectra of II-XII

Compound	Solvent (concentration)	Temp., °C	δ*, ppm				(J, Hz)					
							naphthalene ring protons					other groups
			CH_3	NH_2	NH	CH	3†	4†	5	6, 7	8	
II	$CDCl_3$ (0,1 M)	20	2,18 s	4,60 brs								
III	d_6-Acetone(0,1 M)	30	2,47 s, 2,58 s	3,94 brs	6,33 (2H) brs	6,40 s						
IV	d_6-DMSO(0,05 M)	30	2,27 s, 2,42 s	8,20 brs	8,20 (2H) brs							
V	$CDCl_3$ (0,05 M)	30	2,40 s			6,53 s			6,76—7,79 m		8,66 dd (8)	
V	H_6-DMSO (0,1 M)	30			13,06 brs	6,60 s	7,99 d (9)	7,13 d (9)	7,87 dd (8)	7,46, 7,64 mm	8,64 dd (8)	14,96 s (OH)
VI	H_6-DMSO(0,05 M)	25				8,50 s			8,20—7,68 m		9,32 dd (8)	
VII	H_6-DMSO(0,01 M)	20			10,75 brs (2H), 11,18 brs (1H)							3,5-H d (8), 7,92, 4-H s, 7,47, 2,6-H, t_j 7,47, t_j 7,20 (8), C_6H_5
VIII	d_6-DMSO(0,1 M)	100	2,45 s, 2,56 s		12,88 brs	6,40 s	8,57 d (9)	8,42 d (9)	8,20 dd (8)	7,82; 7,99 mm	9,42 dd (8)	
IX	H_6-DMSO(0,08 M)	140			10,48 brs							
X	H_6-DMSO(0,05 M)	20		5,33 brs			8,83 d (9)	8,43 d (9)	8,20 dd (8)	7,74—8,07 m	9,69 dd (8)	
XII	H_6-DMSO(0,1 M)	30		7,24 brs	11,94 brs (1H) 12,80 brs (2H)	6,20 s	7,43 d (9)	7,43 d (9)	8,24 dd (8)	8,04 d (8)	9,20 dd (8)	
XII	H_6-DMSO(0,1 M)	100		6,79 brs	12,30 brs (3H)	6,20 s						
XII	d_6-Acetone(0,1 M)	30	2,49 s, 2,55 s 2,68 s	7,32 brs	10,80 brs	6,48 s						

*Abbreviations: s is singlet, d is doublet, t is triplet, m is multiplet, and br s is broad singlet.
†The chemical shifts of the naphthalene protons attached to 3-C and 4-C were calculated with respect to an AB system, and the remaining shifts were found as the centers of the corresponding multiplets.

VIII and IX [9].

Compound X was obtained by reduction of VIII in alcohol with hydrazine hydrate in the presence of palladium on carbon.

Signals of six naphthalene protons at 7.43-9.20 ppm and the signal of an NH_2 group at 5.33 ppm are observed in the PMR spectrum.

Azobis compound XII was obtained by diazotization of III and coupling with I at pH 3-5.

Signals of three methyl groups at 2.49, 2.55, and 2.68 ppm, a signal of a pyrazole CH proton, and signals of an NH_2 group and three NH groups are observed in the PMR spectrum of XII.

A shift of the maximum at 416 nm in the UV spectrum of III to the long-wave region at 471 nm in the spectrum of XII is noted along with an increase in ε: This is the result of the inclusion of a second azo group in the conjugation system.

EXPERIMENTAL

The IR spectra of $CHCl_3$ solutions and mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The UV spectra of methanol solutions of the compounds were recorded with a Varian XL-100 spectrometer with tetramethylsilane as the internal standard. The mass spectra were obtained with an MS-702 mass spectrometer equipped with an electron impact source with direct introduction of the samples into the ionization region. Thin-layer chromatography was accomplished on Silufol UV-254 plates.

5-Amino-3-methylpyrazole (I). This compound was obtained by the method [6]; its physical constants were in agreement with the literature data (Table 1).

5-Amino-4-bromo-3-methylpyrazole (II). A 240.1-g (1.5 moles) sample of bromine was added dropwise with stirring and cooling to a solution of 145.65 g (1.5 moles) of I in 150 ml of chloroform, and the mixture was maintained at room temperature for 2 h. It was then neutralized to pH 9-10 with 40% sodium hydroxide solution, and the precipitate was removed by filtration, washed with water, dried, and recrystallized from benzene. The product was subjected to TLC in an acetone–hexane system (5:1), and the chromatogram was developed with iodine.

5-(or 3)-Amino-3(or 5),3'(or 5')-dimethyl-4,5'(or 3')-azobis-1H-pyrazole (III). A diazonium solution, prepared from a solution of 9.71 g (0.1 mole) of I in 100 ml of water and 22 ml of concentrated HCl and a solution of 7 g (0.1 mole) of sodium nitrite in 10 ml of water, was added dropwise with stirring to a solution of 9.71 g (0.1 mole) of I in 200 ml of water and 20 ml of acetic acid, and the resulting precipitate was removed by filtration, washed with water, dried, and recrystallized from glacial acetic acid. The product was subjected to TLC in an acetone–hexane system (5:1).

5-(or 3)-Amino-4'-bromo-3(or 5),3'-(or 5')-dimethyl-4,5'(or 3')azobis-1H-pyrazole (IV). This compound was similarly obtained and recrystallized from glacial acetic acid. The product was subjected to TLC in an acetone–hexane system (5:1).

5(or 3)-(2-Hydroxy-1-naphthylazo)-3(or 5)-methyl-1H-pyrazole (V). This compound was similarly obtained at pH 9-10 and was recrystallized from chloroform. The product was subjected to TLC in an alcohol–hexane system (1:1).

4-Methyl-naphtho[2,1-e]pyrazolo[5,1-c]triazine (VI). A solution of 2.52 g (0.01 mole) of V in 20 ml of DMF was heated at 130°C for 10 h, and the resulting yellow needles were removed by filtration, washed with DMF and water, and dried. The product was subjected to TLC in chloroform–carbon tetrachloride–acetone system (5:2:2).

3-Methyl-1-phenyl-1H-pyrazole-4,5-dione 4-[4-(4-bromo-3(or 5)-methyl-1H-pyrazol-5(or 3)-yl)azo]-3(or 5)-methyl-1H-pyrazol-5(or 3)-ylhydrazone (VII). This compound was obtained at pH 7-8 by the procedure used to prepare VIII and was purified by chromatography with a column filled with L 40/100 silica gel and was recrystallized from DMF. The product was subjected to TLC in a DMF–carbon tetrachloride system (1:4).

3-[3(or 5)-Methyl-5(or 3)-pyrazolylazo]-4-methylnaphtho[2,1-e]pyrazolo[5,1-c]triazine (VIII). A diazonium solution prepared from a solution of 3.08 g (0.015 mole) of III in 100

ml of isopropyl alcohol, 50 ml of water, and 4 ml of concentrated HCl, and a solution of 1.05 g (0.015 mole) of sodium nitrite in 20 ml of water, was added dropwise with cooling and stirring to a solution of 2.16 g (0.015 mole) of 2-naphthol and 1.5 g of sodium hydroxide in 30 ml of water, and the precipitate that formed at pH 7-8 was removed by filtration, washed with water, dried, and recrystallized from DMF. The product was subjected to TLC in a chloroform–carbon tetrachloride–acetone system (5:2:2).

3-[4-Bromo-3(or 5)-methyl-5(or 3)-pyrazolylazo]-4-methylnaphtho[2,1-e]pyrazolo[5,1-c]-triazine (IX). This compound was obtained at pH 8-9 as in the preceding experiment and was recrystallized from acetone–DMF (1:4). The product was subjected to TLC in a chloroform–carbon tetrachloride–acetone system (5:2:3).

3-Amino-4-methylnaphtho[2,1-e]pyrazolo[5,1-c]triazine (X). A 0.125-g (2.5 mmole) sample of hydrazine hydrate was added to a mixture of 0.858 g (2.5 mmole) of VIII, 15 g of palladium on activated charcoal, and 300 ml of alcohol, and the mixture was heated for 4 h. The alcohol was then evaporated, and the residue was recrystallized from alcohol. The product was subjected to TLC in a chloroform–carbon tetrachloride–acetone system (5:2:2). The mother liquor was evaporated, and I was leached out from the residue with water. The water was removed by distillation to give I.

3(or 5)-[3(or 5)-Amino-5(or 3)-methyl-4-pyrazolylazo]-4-[3(or 5)-methyl-5(or 3)-pyrazolylazo]-3(or 5)-methylpyrazole (XII). A diazonium solution prepared from 3.075 g (0.015 mole) of III in 100 ml of isopropyl alcohol, 50 ml of water, 6 ml (0.060 mole) of HCl, and a solution of 1.05 g (0.015 mole) of sodium nitrite in 20 ml of water was added to a solution of 1.45 g (0.015 mole) of I and 3.0 g of sodium acetate in 30 ml of water, 30 ml of isopropyl alcohol, and 30 ml of acetic acid, and the mixture was cooled and treated with a 10% solution of sodium hydroxide to pH 3-5. The resulting precipitate was removed by filtration, washed with water, dried, and recrystallized from alcohol. The product was subjected to TLC in a chloroform–carbon tetrachloride–acetone system (5:2:4).

LITERATURE CITED

1. V. M. Dziomko and K. A. Dunaevskaya, Trudy IREA, No. 30, 33 (1967).
2. V. M. Dziomko, K. A. Dunaevskaya, and K. E. Kalinina, Zh. Org. Khim., 8, 161 (1972).
3. I. M. Kogan, The Chemistry of Dyes [in Russian], Goskhimizdat, Moscow (1956), p. 109.
4. M. A. Chekalin, B. V. Passet, and B. A. Ioffe, The Technology of Organic Dyes and Intermediates [in Russian], Khimiya (1972), p. 307.
5. T. Zincke, Ber., 20, 1180 (1890).
6. E. Alcalde, J. Heterocycl. Chem., 11, 423 (1974).
7. D. E. Worrall and E. Lawin, J. Am. Chem. Soc., 61, 104 (1939).
8. J. Vilarrasa and R. Granados, J. Heterocycl. Chem., 11, 867 (1974).
9. H. Reimlinger and A. Van Overstraeten, Ber., 99, 3350 (1966).