SYNTHESIS OF o-BISAZO-1H-PYRAZOLES AND STUDY OF THEIR CYCLIZATION TO GIVE COMPOUNDS WITH A 1,2,4-TRIAZINE RING

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The reactivities of o-hydroxyarylazo-1H-pyrazoles in reactions involving the formation of a 1,2,4-triazine ring in alkaline and acidic media as a function of the character of the substituent in the 4 position of the 1H-pyrazole and the temperature were studied. o-Hydroxyarylazo-1H-pyrazoles and o-hydroxyarylbisazo-1H-pyrazoles, as well as condensed 1,2,4-triazines, were synthesized by diazo coupling of diazotized 5-amino-3-methyl-1R-pyrazoles and o-aminoazobipyrazoles with azo components, viz., 2,3-dihydroxynaphthalene, 1-methyl-3-hydroxyindole, 3-methyl-1-phenyl-5-pyrazolone, and 5-amino-3-methyl-1R-pyrazoles. Azo compounds that undergo ring closure to a triazine ring with the liberation of water when solutions are heated are obtained in the case of 2,3-dihydroxynaphthalene; only azo and o-bisazo compounds were synthesized in the case of 5-aminopyrazoles. An o-bisazo compound that is converted to a triazine when the hydroxy group is replaced by chlorine was isolated in the case of 5-pyrazolone; only a triazine was obtained with 1-methyl-3-hydroxyindole. The compounds obtained were characterized by their IR, UV, PMR, and mass spectra.

The ability of o-aminoazopyrazoles to form stable diazonium salts that couple actively with aromatic hydroxy compounds opens up a pathway for the preparation of little-studied tetradentate o-bisazo compounds that are of interest for coordination chemistry. This is particularly true of o-bisazo compounds with nitrogen-unsubstituted pyrazoles, since in this case deprotonation to give chelates with different charge character and pyrazolate chelates is possible.

It has been previously noted that o-hydroxy azo compounds obtained from diazotized 5-aminopyrazoles with an unsubstituted nitrogen atom in the heteroring in some cases undergo cyclization with the formation of a 1,2,4-triazine ring [1-6].

In order to ascertain the possibility of the preparation of o-bisazo compounds that contain a 1H-pyrazole ring we studied the reactivities of o-hydroxyarylazo-1H-pyrazoles in alkaline and acidic media as a function of the character of the substituent in the 4 position of the 1H-pyrazole and the temperature.

2,3-Dihydroxynaphthalene, 1-methyl-3-hydroxyindole, 3-methyl-1-phenyl-5-pyrazolone, and 5-amino-3-methyl-1R-pyrazoles were used as the azo components.

5-Amino-3-methyl-1R-pyrazoles I-V were obtained by the methods in [7-11]. Compound VI was obtained by the method in [6] by bromination of I. Compound VII was obtained by diazo coupling at pH 3-5 of diazotized I with 2,3-dihydroxynaphthalene. The data from the PMR spectrum (Table 2) confirm the structure of VII. The IR spectrum does not contain the characteristic absorption band of a carbonyl group. The cyclization of VII to triazine VIII was

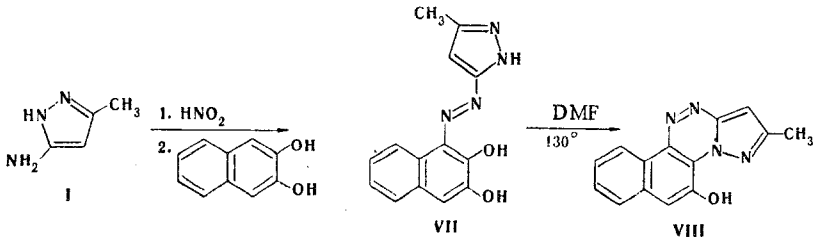

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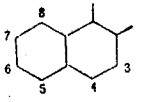
TABLE 1. Physicochemical Constants, Results of Elementary Analysis, and Yields of the Compounds Obtained

Compound	mp, °C	Found, %			Empirical	Calc., %			M	M+a	Yield, %
		C	H	N		C	H	N			
VII	206—207	62,6	4,5	20,8	$C_{14}H_{12}N_4O_2$	62,7	4,5	20,9	268,28	268	85
VIII	221—222	67,2	4,0	22,5	$C_{14}H_{10}N_4O$	67,2	4,0	22,4	250,26	250	15
X	227—228	36,3	4,1	33,0	$C_9H_{12}N_7Br$ [b]	36,3	4,1	32,9	298,15	297	84
XII	108—109	58,0	8,0	33,9	$C_{14}H_{22}N_7$	58,1	8,0	33,9	289,39	289	25
XIII	173—174	64,0	8,1	27,5	$C_{20}H_{19}N_7$	64,4	8,1	27,4	357,42	357	35
XIV	Above 353	36,7	3,6	39,4	$C_{12}H_{14}N_{11}Br$ [c]	36,7	3,6	39,3	392,22	—	45
XV	216—217 (with dec.)	40,1	4,3	36,8	$C_{14}H_{18}N_{11}Br$ [d]	40,0	4,3	36,7	420,28	—	30
XVI	224—225 (with dec.)	50,2	3,8	24,8	$C_{19}H_{17}N_8OBr$ [e]	50,3	3,8	24,7	453,30	—	65
XVII	292—293 (with dec.)	57,4	4,2	29,7	$C_{18}H_{16}N_8O_2$	57,5	4,3	29,8	376,38	376	50
XVIII	Above 350 resinified	60,3	4,0	31,2	$C_{18}H_{14}N_8O$	60,3	3,9	31,3	358,36	358	40 [f]
XIX	297—298 (with dec.)	59,2	4,4	36,6	$C_{17}H_{15}N_9$	59,1	4,4	36,5	345,37	345	70
XXII	285—286 (with dec.)	47,9	3,4	31,1	$C_{18}H_{15}N_{10}Br$ [g]	47,9	3,3	31,0	451,29	450	60

[a]The molecular weights (M) were determined by mass spectrometry. [b]Found: Br 26.5%. Calculated: Br 26.8%. [c]Found: Br 20.3%. Calculated: Br 20.4%. [d]Found: Br 18.9%. Calculated: Br 19.0%. [e]Found: Br 17.7%. Calculated: Br 17.6%. [f]In the cyclization of XVII to XVIII the yield was 95%. [g]Found: Br 17.6%. Calculated: Br 17.7%.

TABLE 2. UV and PMR Spectra of VII, VIII, and XVI-XVIII

Compound	Solvent (concn., mole/liter)	T., °C	δ, ppm, J, Hz					δ, ppm, J, Hz				Solvent	λ_{max}, nm (lg ε)
			CH_3	NH	CH	OH[a]	OH[b]	naphthalene ring protons[c] 4	5	6,7	8		
VII	d_6-DMSO (0,1)	110		9,20 br s	6,48 s	15,60 s	12,50 s	7,17 s	7,28—7,58		8,34 d, J=7,0	DMF	305 (3,85) 450 (4,06)
VII	d_6-DMSO (0,2)	22		9,73 br s	6,53 s	15,83 s	12,85 s	7,18 s	7,48 dd, J=7,0; 2,0	7,34 e[d]	8,30 dd, J=7,0; 2,0		
VIII	d_6-DMSO (0,1)	22	2,61 s		7,41 s		10,69 s	7,64—7,86 m	7,94 d, J=8,0	7,64—7,86 m	9,19 d, J=8,0	Ac-OH	295 (4,06) 316 sh (4,02)
VIII	$CDCl_3$ (0,05)	22	2,60 s		7,16 s		10,69 s		7,59—7,81 m		9,39 d, J=8,0	Methanol	306 (4,08) 442 (3,87) 410 (3,62)
XVI[e]	d_6-DMSO (0,15)	22	2,16 s 2,24 s				12,89 s		Above 7,15 m		7,69 d, J=8,7	Methanol	345 i (4,05) 380 (4,20) 405 (4,14)
XVII	d_6-DMSO (0,1)	22	2,31 s (6H)	13,13 br s	6,45 s	15,93 s	9,70 s	7,05 s	7,25—7,35 m		8,20 d, J=8,0	DMF	294 (3,84) 355 (3,85) 495 (3,85)
XVIII	d_6-DMSO (0,1)	30		10,70 br s	6,42 s		13,10 s	7,97 s	8,06 dd, J=8,0; 1,5	7,64—7,90 m	9,30 dd, J=8,0; 1,5	DMF	330 (4,00) 345 (4,02) 450 (3,86)

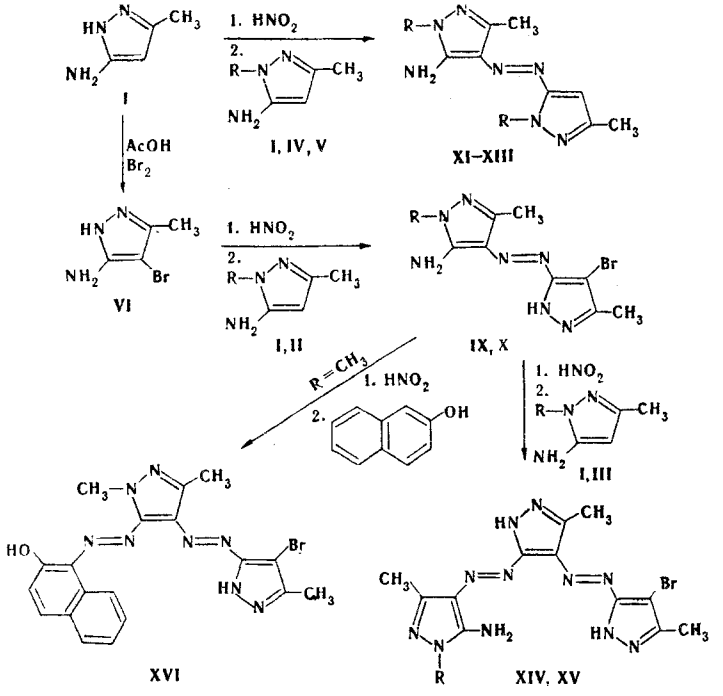
[a]This is the OH group attached to C_2. [b]Attached to C_3. [c]The numbering of the protons in the naphthalene ring is 

[d]The chemical shifts were calculated in accordance with an AB system. [e]3.31 (3H, s, $CH_3-N<$); center at 7.15 ppm (1H, m, 3-H).

carried out by heating it in dimethylformamide (DMF) at 130°C. A marked shift of the signals of the naphthalene protons to weak field is observed in the PMR spectrum of VIII; this is characteristic for condensed triazine systems [4].

Compounds IX-XIII were obtained by the method in [6] by diazotization, respectively, of VI, I, IV, and V in a hydrochloric acid medium and coupling at pH 1 with 5-aminopyrazoles I, II, IV, and V. The PMR spectra of o-amino azo compounds IX-XIII contain a broad singlet of an NH_2 group at 5.60-6.30 ppm (in $CDCl_3$), the corresponding signals of methyl groups, and signals of the substituents attached to the pyrazole nitrogen atom. Bands of symmetrical and asymmetrical stretching vibrations of the NH_2 group are observed in the IR spectra at 3480 and 3380 cm^{-1} (in $CHCl_3$). The data from the IR and PMR spectra indicate that IX-XIII exist in the azo form.

Bisazo compounds XIV and XV were obtained by diazotization of IX and X and coupling at pH 3-5 with I and II, respectively. Signals of three methyl groups and signals of NH_2 and NH groups are observed in the PMR spectra of XIV and XV, while a doublet and a triplet of signals of an ethyl group are observed in the PMR spectrum of XV. o-Bisazo compound XVI was obtained by coupling diazotized (in hydrochloric acid) X with 2-naphthol at pH 9-10. The PMR spectrum (Table 2) confirms its structure.

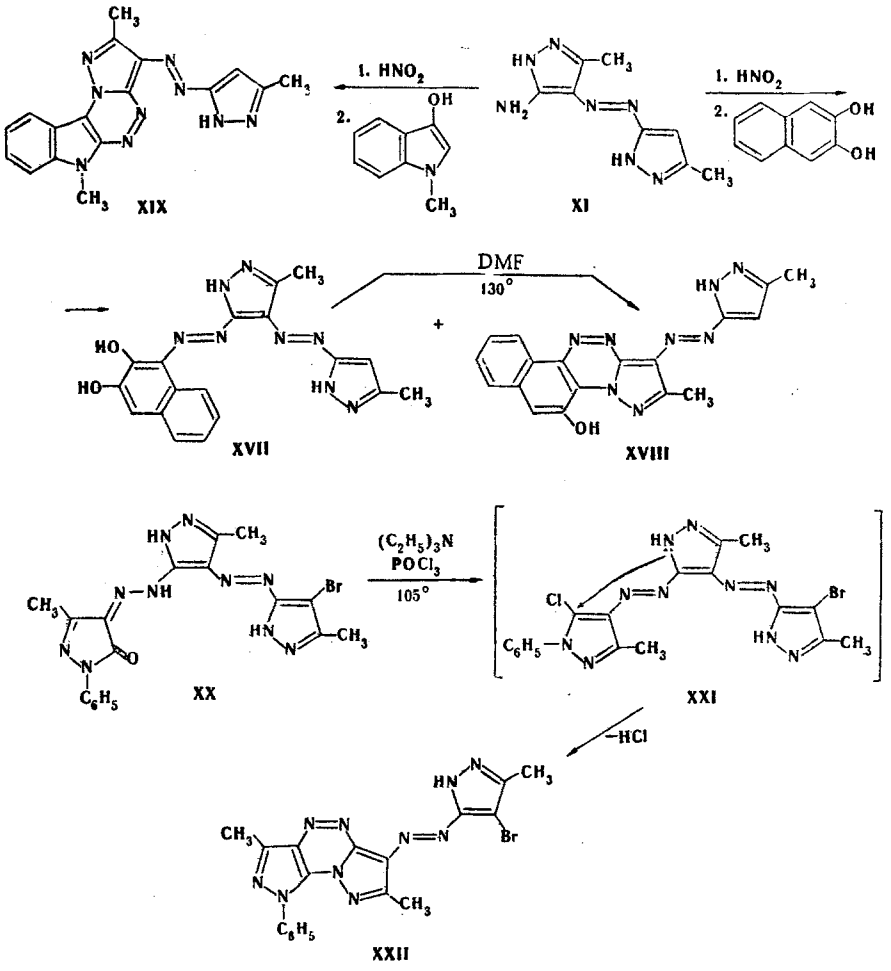


I, VI, IX, XI, XIV R=H; II, X R=CH_3; III, XV R=C_2H_5; IV, XII R=i-C_3H_7; V, XIII R=C_6H_5

In contrast to the reaction with 2-naphthol [6], in the case of coupling of diazaazopyrazole, obtained in hydrochloric acid from XI, with 2,3-dihydroxynaphthalene (pH 3-5) we isolated triazine XVIII and o-bisazo compound XVII, which is converted to triazine XVIII when the solutions are heated gently. The corresponding signals of aromatic and aliphatic protons and of two NH and two OH groups are observed in the PMR spectrum of XVII. The IR spectrum does not contain the characteristic absorption band of a carbonyl group.

The condensation of XVII to give XVIII went to completion at 130°C in DMF after 10 min. The signals of the aromatic protons in the PMR spectrum of XVIII were shifted 0.8 ppm, on the average, to low field. The weak-field shifts of the protons located near the triazine ring can be explained by the considerable redistribution of the electron density because of the formation of a triazine system [4].

Triazine XIX was obtained by diazotization of XI in a hydrochloric acid medium and coupling with 1-methyl-3-hydroxyindole at pH 10. The pronounced (>1.5 ppm) shift of the aromatic protons to weak field in the PMR spectrum confirms triazine structure XIX. Azohydrazone XX did not undergo cyclization to triazine system XXII when it was heated in hydrochloric acid, DMF, DMSO, trichloromethane, and propanol [6].



When we refluxed XX in $POCl_3$ with an equimolar amount of triethylamine, we obtained triazine XXII instead of the expected chloro derivative XXI. The formation of triazine XXII probably proceeds through XXI.

By analyzing the results and the literature data one can make the following correlations with respect to the reactivities of o-hydroxyarylazo-1H-pyrazoles.

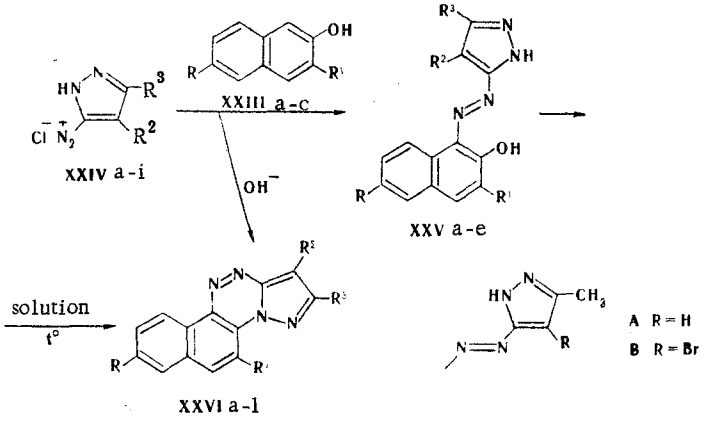
Azo compounds that are converted to triazines XXVIa-f when the solutions (except for alkaline solutions) are heated are obtained by coupling hydroxynaphthols XXIIIa-c with 1H-diazopyrazoles that have an electron-donor substituent in the 4 position of the pyrazole in an alkaline medium. Only triazines XXVIg-l are formed in alkaline media when there is an electron-acceptor substituent present, and only triazine XIX is also obtained with 1-methyl-

TABLE 3. UV and PMR Spectra of X and XII-XV

Compound	Solvent (concn., mole/liter	δ, ppm, J, Hz, 22°C					λ_{max}, nm (log ε) in methanol
		CH_3	HN	NH_2	CH	other groups	
X	d_6-DMSO (0,4)	2,21 s 2,29 s	10,30 br s	7,32br s		3,59 (3H, s, CH_3—N<)	380 (4,70), 410 (4,71)
XII	$CDCl_3$ (0,2)	2,40 s 2,56 s		5,75 br s	6,12 s	1,44 [6H, d, J=7,0 $(CH_3)_2$]; 1,51 [6H, d, J=7,0 $(CH_3)_2$]; 4,14 (1H, m, CH); 4,93 (1H, m, CH)	410 (4,48)
XIII	$CDCl_3$ (0,2)	2,38 s 2,48 s		6,00br s	6,25 s	7,10—7,65 (10H, m, 2Ph)	420 (4,49)
XIV	d_6-DMSO (0,2)	2,38 s 2,48 s 2,50 s	8,19 br s	(5H)			340 (4,14), 465 (4,04)
XV	d_6-DMSO (0,1)	2,25 s 2,33 s 2,49 s		7,73 br s		1,25 (3H, t, J=6,5, CH_3); 3,93 (2H, q, J=6,5, CH_2—N<)	340 (4,09), 470 (4,06)

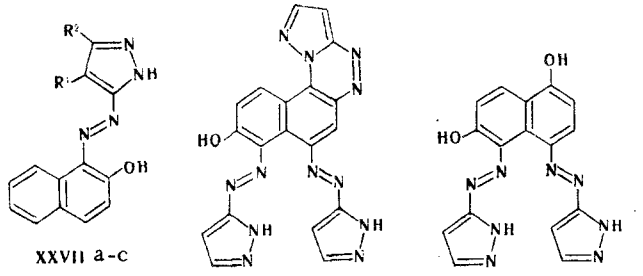
3-hydroxyindole under similar conditions. Azo and o-bisazo compounds XVII and XXVIIa-c are formed in acidic media (pH 3-5); triazines XVIII can be obtained when solutions of these compounds are heated.

The formation of triazine systems from azo compounds for which 5-amino-3-methylpyrazole [6] and p-cresol [1] were used as azo compounds was not observed. In the case of 3-methyl-1-phenyl-5-pyrazolone [1, 6] cyclization to triazine XXII took place when the hydroxy group was replaced by chlorine by heating XX in phosphorus oxychloride in the presence of triethylamine.

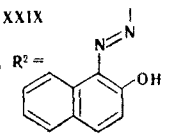


XXIVa, XXIIIa, XXVa, XXVIa, e $R=R^1=R^2=R^3=H$; XXIV b $R^2=Ph$, $R^3=H$; c $R^2=H$, $R^3=CH_3$; d $R^2=NO_2$, $R^3=H$; e $R^2=NO_2$, $R^3=CH_3$; f $R^2=CO_2Et$, $R^3=H$; g $R^2=A$, $R^3=CH_3$; h $R^2=B$, $R^3=CH_3$; XXIII b $R=OH$, $R^1=H$; c $R=H$, $R^1=OH$; XXV b $R=R^2=R^3=H$, $R^1=OH$; c $R=R^1=R^3=H$, $R^2=Ph$; d $R=R^1=R^2=H$, $R^3=CH_3$; e = VII $R=OH$, $R^1=R^2=H$, $R^3=CH_3$; XXVI b $R=OH$, $R^1=R^2=R^3=H$; d $R=R^1=R^3=H$, $R^2=Ph$; d $R=R^1=R^2=H$, $R^3=CH_3$; f = VIII $R=R^2=H$, $R^1=OH$, $R^3=CH_3$; g $R=R^1=R^3=H$, $R^2=NO_2$; h $R=R^1=H$, $R^2=NO_2$, $R^3=CH_3$; i $R=R^1=R^3=H$, $R^2=CO_2Et$; j $R=R^1=H$, $R^2=A$, $R^3=CH_3$; k $R=R^1=H$, $R^2=B$, $R^3=CH_3$; l = XVIII $R=H$, $R^1=OH$, $R^2=A$, $R^3=CH_3$; XXV a-c, XXVI a-c lit. [1]; XXVIg-i lit. [3]; XXVIe lit.[4]; XXVd, XXVId, j, m [6].

Substituents attached to the azo compounds affect the cyclization, and cyclization of the azo compound to triazine XXVIc takes place even at room temperature [1] on passing from a hydroxy group (in the ortho position relative to the azo group) to a methoxy group. The condensation of the triazo compound obtained in an alkaline medium to triazine XXVIII also proceeds readily. As in the case of XXIX, a second triazine ring is not formed.



XXVII[12] a $R^1=NO_2$, $R^2=H$; b $R^1=NO_2$, $R^2=NH_2$; c $R^1=OH$, $R^2=$



EXPERIMENTAL

The IR spectra were obtained with a UR-20 spectrometer. The UV spectra were obtained with SF-4a and UNICAM-100 spectrophotometers. The PMR spectra were recorded with Varian XL-100-12 (100 MHz) and Tesla-80 BS-487C (80 MHz) spectrometers with tetramethylsilane as the internal standard. The mass spectra were obtained with an AEI MS-702 spectrometer with direct introduction of the samples into the ionization region; the ionizing-electron energy was 70 eV, and the temperature of the block for vaporization of the samples was 120-180°C. Thin-layer chromatography (TLC) was carried out on Silufol UV-254 plates in the following systems: acetone—hexane (5:1) for I-VI (development with iodine), the same system (5:1)

for IX-XI, the same system (1:1) for XVI, the same system for XII (1:4), the same system for XIII (1:5), and the same system (2:5) for XXII; ethanol—tetrachloromethane (1:5) for XVIII; trichloromethane—tetrachloromethane—acetone (5:2:2) for VIII, the same system (5:2:3) for VII and XVII, the same system (5:2:5) for XIV-XV, and the same system (5:2:8) for XIX.

5-Amino-3-methyl-1-R-pyrazoles (I-V). These compounds were obtained by the methods in [7-11], and their constants were in agreement with the literature data: I had mp 44-45°C (mp 44°C [7]), II had mp 79-80°C (mp 80-81°C [8]), III had mp 99-101°C (mp 100-101°C [9]), IV had mp 110-112°C (mp 111-112°C [10]), and V had mp 114-115°C (mp 116°C [11]). 5-Amino-4-bromo-3-methylpyrazole (VI) was obtained by bromination of I in acetic acid by the method in [6] and had mp 118-119°C. 5(or 3)-Amino-(3 or 5, 3' or 5') dimethyl-4,5'(or 3')-azobis-1H-pyrazole (XI) and 5(or 3)-amino-4'-bromo-(3 or 5, 3' or 5') dimethyl-4,5'(or 3')-azobis-1H-pyrazole (IX) were obtained by the method in [6] and had mp 142-143 and 225-226°C, respectively.

4-(3-Methyl-4-bromo-5-pyrazolylazo)-5-amino-1,3-dimethyl pyrazole (X). A diazonium solution prepared from 8.8 g (0.05 mole) of I, 12 ml (0.12 mole) of concentrated HCl, 3.5 g (0.05 mole) of sodium nitrite, and 150 ml of water was added with stirring to a solution of 5.56 g (0.05 mole) of II, 3 g of sodium acetate hydrate in 200 ml of water, and 20 ml of acetic acid, after which the mixture was brought up to pH 3-5 by the addition of a 10% solution of sodium hydroxide with cooling and stirring. The resulting precipitate was removed by filtration, washed with water, dried, and recrystallized from DMF to give 12.5 g of product X, which was quite soluble in trichloromethane and DMSO but only slightly soluble in isopropyl alcohol and acetone.

Azo compounds XII and XIII were similarly obtained; they were quite soluble in trichloromethane, DMSO, and DMF but only slightly soluble in acetone.

5-(5-Amino-3-methyl-4-pyrazolylazo)-4-(4-bromo-3-methyl-5-pyrazolylazo)-3-methyl pyrazole (XIV). A solution of a diazonium compound prepared from 4.47 g (0.015 mole) of IX in 100 ml of isopropyl alcohol, 60 ml of water, 50 ml of acetic acid, 5 ml of concentrated HCl, and 1.05 g (0.015 mole) of sodium nitrite in 10 ml of water was added to a solution of 1.45 g (0.015 mole) of pyrazole I in 50 ml of isopropyl alcohol, 50 ml of water, and 50 ml of acetic acid (the pH of the solution was two). Water (300 ml) and a 10% solution of sodium hydroxide (to pH 5) were added, and the precipitate was removed by filtration, washed with water, purified by column chromatography on 100/160 silica gel [elution with acetone—tetrachloromethane (3:1)], and recrystallized from ethanol to give 2.65 g of XIV as a dark-red finely crystalline powder that was quite soluble in DMF, DMSO, and acetic acid and satisfactorily soluble in acetone.

5-(5-Amino-1-ethyl-4-pyrazolylazo)-4-(4-bromo-3-methyl-5-pyrazolylazo)-3-methyl pyrazole (XV). A solution of a diazonium compound prepared from 0.28 g (0.001 mole) of X, 2 ml of concentrated HCl, 3 ml of concentrated H_2SO_4, 3 ml of acetic acid, and 0.07 g (0.001 mole) of sodium nitrite in 2 ml of water (pH 1) was added with cooling and stirring to a solution of 0.125 g (0.001 mole) of III and 1 g of sodium acetate in 10 ml of acetic acid, after which the pH of the reaction mixture was brought up to three to five with 10% sodium hydroxide solution, and the resulting precipitate was removed by filtration, washed with water, dried, purified by column chromatography on 100/160 silica gel [elution with acetone—tetrachloromethane (2:1)], and recrystallized from acetone to give 0.11 g of XV as a red finely crystalline powder that was quite soluble in DMF and DMSO, only slightly soluble in ethanol and acetone, and insoluble in benzene and trichloromethane.

5-(2,3-Dihydroxy-1-naphthylazo)-3-methyl-pyrazole (VII). A 0.97-g (0.01 mole) sample of I in 10 ml of water, 5 ml of concentrated HCl, and a solution of 0.7 g (0.01 mole) of sodium nitrite in 5 ml of water were added dropwise with stirring and cooling to a solution of 1.6 g (0.01 mole) of 2,3-dihydroxynaphthalene and 1 g of sodium acetate in 20 ml of water and 10 ml of ethanol, and the precipitate that formed at pH 3-5 was removed by filtration, washed with water, dried, and recrystallized from DMF—acetone (1:1).

Compounds XVII-XIX were obtained in the same way as VII. Compounds XVII was recrystallized from trichloromethane—tetrachloromethane—acetone (5:1:2) and was then reprecipitated three times (in order to remove triazine XVIII) from solution in DMF by the addition of tetrachloromethane; XVIII was obtained from the mother liquor from the recrystallization of XVII. The mother liquor was evaporated, and the residue was recrystallized from DMSO; when XVII was heated in DMF at 130°C it was converted completely to XVIII after 10 min. The con-

densation proceeds in any solvent, but the solubility of XVII is lower in other solvents. Compound XIX was recrystallized from DMF. UV spectrum (in DMF), λ_{max} (log ε): 375 (4.00); i 390 (3.98); 480 nm (3.86). PMR spectrum (0.2 mole in d_6-DMSO, 30°C): 6.36 (1H, s, pyrazole CH), 7.52 (1H, dd, J = 8.0, 2.5 Hz, 10-H), 7.78-8.04 (2H, m, 8,9-H), 8.49 (1H, d, J = 8.0 Hz, 7-H), and 12.96 ppm (1H, broad s, NH).

4-Methyl-6-hydroxynaphtho[2,1-e]pyrazolo[5,1-c][1,2,4]triazine (VIII). A 2.68-g (0.01 mole) sample of VII was heated in 50 ml of DMF at 130°C for 6 h, after which the DMF was removed by vacuum evaporation, and triazine VIII was purified with a column filled with neutral Brockmann activity II Al_2O_3 (elution with trichloromethane). The second fraction was evaporated, and the residue was recrystallized from DMSO to give 0.375 g (15%) of VIII.

4-(4-Bromo-3-methylpyrazolylazo)-5-(2-hydroxy-1-naphthylazo)-1,3-dimethylpyrazole (XVI). A solution prepared from 0.149 g (0.5 mmole) of X in 15 ml of concentrated HCl and 0.035 g (0.5 mmole) of dry sodium nitrite was added to a solution of 0.072 g (0.5 mmole) of 2-naphthol in 100 ml of a 10% solution of potassium hydroxide and 15 ml of ethanol, after which the pH of the solution was brought up to three to five, and the resulting precipitate was removed by filtration, washed with water, dried, and reprecipitated from ethanol by the addition of water to give 0.12 g of XVI, which was soluble in ethanol, DMF, and DMSO.

6-(4-Bromo-3-methyl-5-pyrazolylazo)-3,7-dimethyl-1-phenylpyrazolo[2,3-c:3,4-e][1,2,4]-triazine (XXII). A mixture of 4.7 g (0.01 mole) of XX, 1.01 g (0.01 mole) of triethylamine, and 50 ml of phosphorus oxychloride was refluxed at 105°C for 4 h, after which the phosphorus oxychloride was removed by distillation, and the residue was treated with water. The precipitate was removed by filtration, washed with water, dried, and chromatographed with a column filled with neutral Brockmann activity II Al_2O_3 (elution with trichloromethane). The second fraction was collected and evaporated, and the residue was recrystallized from trichloromethane or DMSO to give 2.71 g of XXII as a bright-orange finely crystalline powder that was soluble in DMF but only slightly soluble in DMSO. UV spectrum (in methanol), λ_{max} (log ε): 420 nm (3.78). PMR spectrum (0.1 mole in d_6-DMSO): 2.26 (3H, s, CH_3), 2.67 (3H, s, CH_3), 2.81 (3H, s, CH_3), 7.54-7.68 (3H, m, m- and p-H), 7.73-7.90 (2H, m, o-H), and 13.54 ppm (1H, broad s, NH).

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