Pyrazole-3(5)-diazonium salts in the synthesis of novel pyrazolo[5,1-*c*][1,2,4]triazines

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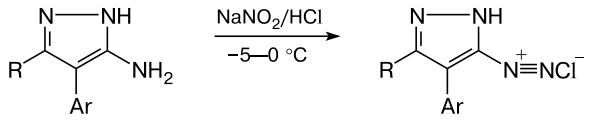
Coupling of pyrazole-3(5)-diazonium salts with cyclic 1,3-dicarbonyl (active methylene) compounds followed by cyclocondensation of the resulting hetarylhydrazones gave novel pyrazolo[5,1-*c*][1,2,4]triazines.

Key words: 3-R-4-aryl-1*H*-5-aminopyrazoles, pyrazolediazonium salts, cyclohexane-1,3-dione, 4-hydroxy-6-methyl-2-pyrone, barbituric acid, hydrazones, pyrazolo[5,1-*c*][1,2,4]-triazines, diazotization, azo coupling, cyclocondensation.

The wide scope of the synthesis of fused nitrogen-containing heterocycles based on α-aminopyrazoles is known to be associated with the binucleophilic nature of the latter. Two- and three-component cyclization reactions in the series of 3(5)-aminopyrazoles **1** involve the endocyclic N atom and the exocyclic amino group.[1,2]

The ability to form diazonium salts **2** (Scheme 1) substantially extends the application area of these compounds.

Scheme 1



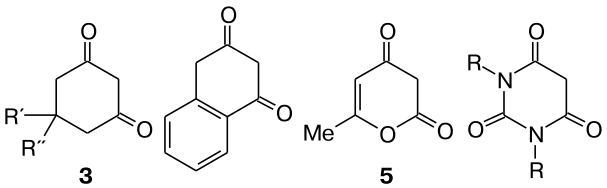
1a—q **2a—q**

1, 2	R	Ar	1, 2	R	Ar
a	Me	Ph	**j**	Me	*m*-ClC_6H_4
b	Et	Ph	**k**	Et	*m*-ClC_6H_4
c	$MeOCH_2$	Ph	**l**	$MeOCH_2$	*m*-ClC_6H_4
d	Me	*p*-FC_6H_4	**m**	Me	*p*-BrC_6H_4
e	Et	*p*-FC_6H_4	**n**	Et	*p*-BrC_6H_4
f	$MeOCH_2$	*p*-FC_6H_4	**o**	Me	*p*-$MeOC_6H_4$
g	Me	*p*-ClC_6H_4	**p**	Et	*p*-$MeOC_6H_4$
h	Et	*p*-ClC_6H_4	**q**	Me	*o*-$MeOC_6H_4$
i	$MeOCH_2$	*p*-ClC_6H_4			

Like aromatic diazonium salts, pyrazole-3(5)-diazonium salts react with active methylene dicarbonyl compounds (*e.g.*, aliphatic β-diketones and β-oxo esters) and active methylene nitriles.[3—5] These coupling reactions have been described in detail and underlie the traditional synthesis of azolo[5,1-*c*][1,2,4]triazines, structural analogs of natural purine bases.

However, the use of cyclic β-diketones and β-oxo esters as azo components has not been documented, although they have considerable synthetic potential.

Proceeding further in our investigations,[6,7] we studied azo coupling reactions of diazonium salts **2a—q** with cyclohexane-1,3-dione and its derivatives **3**, indane-1,3-dione (**4**), 4-hydroxy-6-methyl-2-pyrone (**5**), and barbituric acids **6** (R = H and Me) for design of pyrazolo-[5,1-*c*][1,2,4]triazines containing various cyclic fragments.



3 **4** **5** **6**

3: R´ = R″ = H; R´ = Me, R″ = H; R´ = R″ = Me;
R´ = Ph, *p*-$MeOC_6H_4$, *o*-HOC_6H_4, 2,4-$(MeO)_2C_6H_3$, R″ = H
6: R = H, Me

Freshly prepared diazonium salts were added to a solution of a 1,3-dicarbonyl compound in the presence of a saturated sodium acetate buffer solution.

Reactions of cyclohexane-1,3-dione, dimedone, and its analogs **3** with pyrazolediazonium salts are shown in Scheme 2. The azo coupling gives brightly colored hydrazones **8**. In addition, azo compounds of the types **7** and **7A** are known[4,8,9] to be intermediates in similar reactions.

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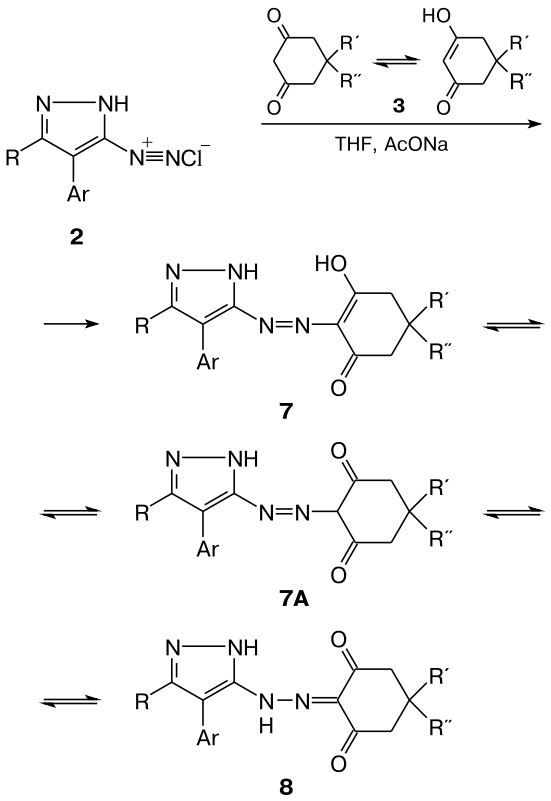
Scheme 2



The resulting pyrazolylhydrazones undergo intramolecular cyclization even in their attempted purification or during measurements of their melting points; in some cases, their intramolecular cyclization occurs spontaneously at 40—50 °C (monitoring by TLC). Because of this, they cannot be identified by spectroscopic methods. We tried several preparative methods of heterocyclocondensation: (1) a room-temperature reaction in 45% H_2SO_4, (2) reflux in glacial acetic acid with anhydrous sodium acetate, (3) reflux in toluene with water removal (in the presence of acetic acid), and (4) heating at 130—140 °C in polyphosphoric acid.

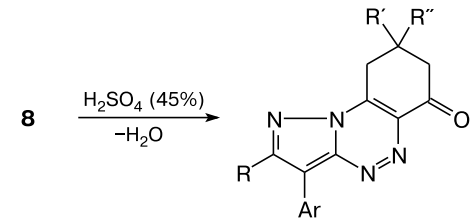
The first approach proved to be most suitable because of high yields and minor resinification.

The reactions gave 8,9-dihydropyrazolo[5,1-*c*][1,2,4]-benzotriazin-6(7*H*)-ones **9a**—**j** (Scheme 3).

The ^{1}H NMR spectra of the compounds obtained show signals for the protons of the cyclohexanone ring at δ 2.70—3.70 but contain no signals for the "acidic" protons (NH and OH).

When refluxed in DMF or DMF—xylene or when heated in DMSO (in some cases, even during recrystallization), pyrazolotriazines **9** obtained from cyclohexane-1,3-dione and some of its 5-monosubstituted derivatives undergo dehydrogenation leading to the fully aromatized tricyclic system pyrazolo[5,1-*c*][1,2,4]benzotriazin-6-ols

Scheme 3

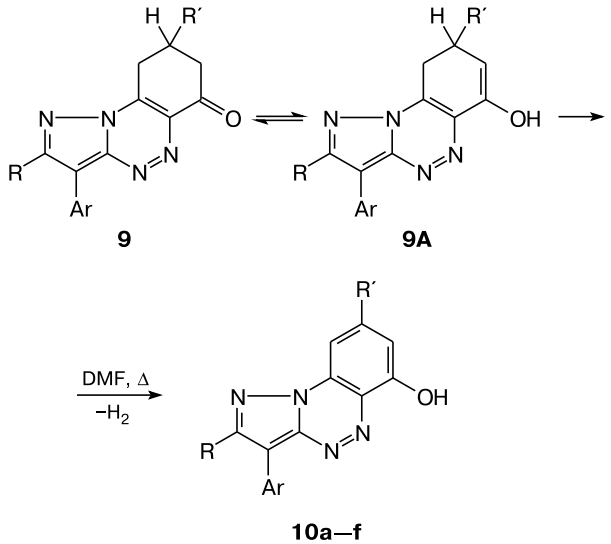


9	R	R′	R″	Ar
a	Et	Me	Me	Ph
b	Me	Me	Me	*p*-Cl-C_6H_4
c	Me	Me	Me	*m*-Cl-C_6H_4
d	Me	Me	Me	*o*-$MeOC_6H_4$
e	Me	Me	Me	*p*-$MeOC_6H_4$
f	Me	Me	H	*p*-$MeOC_6H_4$
g	$MeOCH_2$	Me	H	Ph
h	$MeOCH_2$	Ph	H	Ph
i	Me	Ph	H	*p*-BrC_6H_4
j	Et	*o*-HOC_6H_4	H	Ph

10a—**f**. Obviously, the dehydrogenation passes through the formation of enol **9A** (Scheme 4).

The presumed structures of products **10** were confirmed by mass spectra containing a peak of a characteris-

Scheme 4



10	R	R′	Ar
a	Me	2,4-$(MeO)_2C_6H_3$	Ph
b	$MeOCH_2$	H	Ph
c	Me	2,4-$(MeO)_2C_6H_3$	*p*-ClC_6H_4
d	Me	*o*-HOC_6H_4	Ph
e	Me	*p*-$MeOC_6H_4$	Ph
f	Me	Ph	*p*-FC_6H_4

tic ion with the mass number [M(**9**) – 2], where M(**9**) is the mass number of the corresponding ketone **9**.

The ^{1}H NMR spectra of compounds **10** show a characteristic set of signals: a broadened signal at δ ~11.50 (aromatic OH group) and multiplets at δ 7.20—7.50 due to the aromatic protons of the fused benzene ring.

With indane-1,3-dione (**4**) as an active methylene component for azo coupling, the reaction gives the corresponding hydrazones **11a,b** in a similar way (Scheme 5). High enolization of this reagent, as in the case of dimedone, favors not only its easy coupling with diazonium salts but also cyclocondensation of the reaction intermediates into the target products 6*H*-indeno[1,2-*e*]pyrazolo[5,1-*c*][1,2,4]-triazin-6-ones **12a,b**.

The physicochemical characteristics and mass spectra of compounds **9a—j**, **10a—f**, and **12a,b** are given in Table 1; their ^{1}H NMR spectra are presented in Table 2.

A reaction of pyrazolediazonium salt **2a** with 4-hydroxy-6-methyl-2-pyrone (**5**) occurred somewhat differently. Cyclocondensation of the resulting hydrazone **13** did not yield the expected pyrazolotriazine **14**. The ^{1}H NMR and mass spectra of the product, as well as elemental analysis data, provide evidence for structure **15** (Scheme 6). Obviously, an acidic medium (dilute H_2SO_4 or glacial acetic

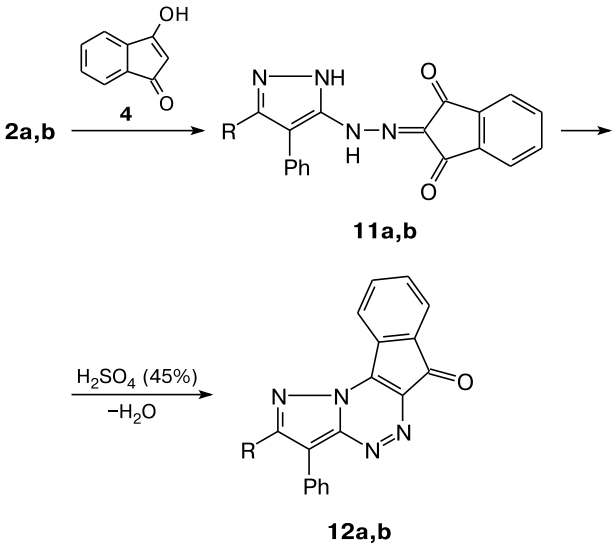
Table 1. Yields, melting points, elemental analysis data, and mass spectra of pyrazolo[5,1-*c*][1,2,4]-triazines **9a—j**, **10a—f**, and **12a,b**

Compound	Yield* (%) (method of synthesis)	M.p./°C	Found / Calculated (%)			Molecular formula	MS**, *m/z*
			C	H	N		
9a	82 (*A*), 80 (*B*), 65 (*D*)	122—124	71.02 71.23	6.44 6.29	17.57 17.49	$C_{19}H_{20}N_4O$	321/320.4
9b	80 (*A*), 71 (*B*)	229—231	63.69 63.44	4.80 5.03	16.28 16.44	$C_{18}H_{17}ClN_4O$	341/340.8
9c	75 (*A*)	197—199	63.70 63.44	4.86 5.03	16.29 16.44	$C_{18}H_{17}ClN_4O$	341/340.8
9d	68.5 (*A*), 63(*B*)	207—209	68.09 67.84	5.70 5.99	16.58 16.66	$C_{19}H_{20}N_4O_2$	336/336.4
9e	72.5 (*A*)	185—187	68.12 67.84	5.72 5.99	16.58 16.66	$C_{19}H_{20}N_4O_2$	336/336.4
9f	69 (*A*), 48 (*B*)	238—240	67.33 67.07	5.40 5.63	17.28 17.38	$C_{18}H_{18}N_4O_2$	323/322.4
9g	63.5 (*B*)	157—159	67.30 67.07	5.38 5.63	17.27 17.38	$C_{18}H_{18}N_4O_2$	323/322.4
9h	76 (*B*)	182—184	72.12 71.86	5.03 5.24	14.40 14.57	$C_{23}H_{20}N_4O_2$	384/384.4
9i	71 (*A*)	248—250	60.76 60.98	4.14 3.95	13.03 12.93	$C_{22}H_{17}BrN_4O$	433/433.3
9j	58 (*A*), 45.5 (*C*)	165—167	72.09 71.86	5.01 5.24	14.49 14.57	$C_{23}H_{20}N_4O_2$	384/384.4
10a	70.5	188—190	69.52 69.89	5.00 4.89	13.70 13.58	$C_{24}H_{20}N_4O_3$	412/412.4
10b	63	170—172	66.91 66.66	4.30 4.61	18.16 18.29	$C_{17}H_{14}N_4O_2$	306/306.3
10c	55	201—203	64.27 64.50	4.58 4.29	12.70 12.54	$C_{24}H_{19}ClN_4O_3$	447/446.9
10d	62	255—257	72.00 71.73	4.16 4.38	15.08 15.21	$C_{22}H_{16}N_4O_2$	369/368.4
10e	73	207—209	72.53 72.24	4.40 4.74	14.59 14.65	$C_{23}H_{18}N_4O_2$	382/382.4
10f	60	205—207	71.56 71.34	3.90 4.08	15.01 15.13	$C_{22}H_{15}FN_4O$	370/370.4
12a	73 (*A*), 65 (*B*)	290—292	73.36 73.07	3.60 3.87	17.80 17.94	$C_{19}H_{12}N_4O$	312/312.3
12b	79 (*A*), 75 (*B*)	>300	73.80 73.61	3.15 4.32	17.07 17.17	$C_{20}H_{14}N_4O$	326/326.4

* For the recrystallized product.

** Found/calculated.

Scheme 5



11, **12:** R = Me (**a**), Et (**b**)

acid with anhydrous sodium acetate) promotes recyclization of the lactone ring. Subsequent addition of a water molecule gives poorly soluble 7-methyl-4-(2-oxopropyl)-8-phenylpyrazolo[5,1-*c*][1,2,4]triazine-3-carboxylic acid (**15**).

The ^{1}H NMR spectrum of compound **15** shows doublets at δ 3.05 and 3.24 for two methylene protons and an unusual high-field signal (δ 8.28) for the carboxyl proton. Apparently, this upfield shift can be associated with the magnetic anisotropy effect of the keto group.

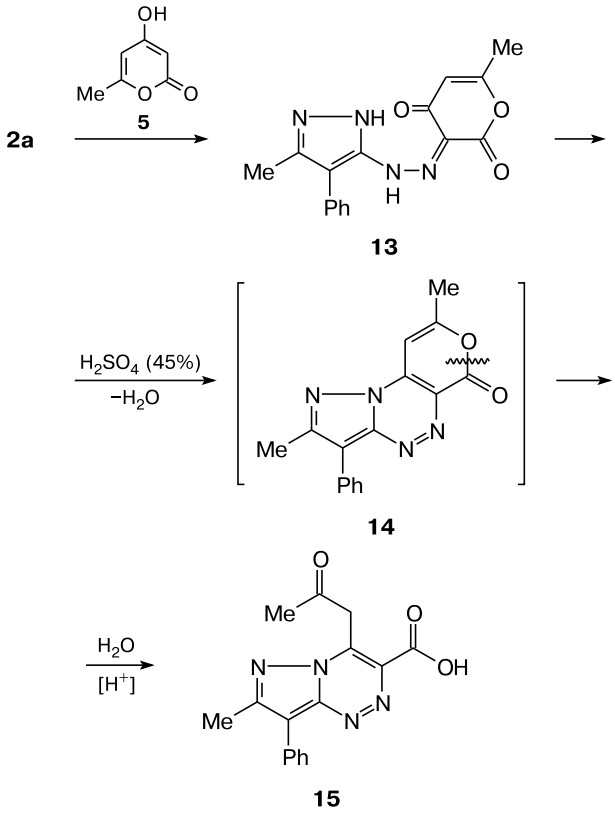
Coupling of diazonium salt **2a** with barbituric acids **6** gave brightly colored linear products in high yields (Scheme 7). According to their ^{1}H NMR spectra, they exist as azo enols **17a,b** rather than hydrazones **16a,b**. A single low-field signal at δ 14.40—14.60 was assigned[8,10] to the NH proton of the pyrazole ring. A signal for the OH group at δ 3.50—4.00 is greatly broadened because of proton exchange.

In an attempted synthesis of pyrazolotriazines **18**, we obtained the following results. Heterocyclization of 1,3-dimethyl-5-[(3-methyl-4-phenyl-1*H*-pyrazol-5-yl)diazenyl]pyrimidine-2,4,6-trione (**17b**) failed under various conditions. Such a behavior is due to the inertness of amide carbonyl in cyclocondensation reactions. However, heating of azo compound **17a** in polyphosphoric acid (PPA) at 130—140 °C for many hours afforded the

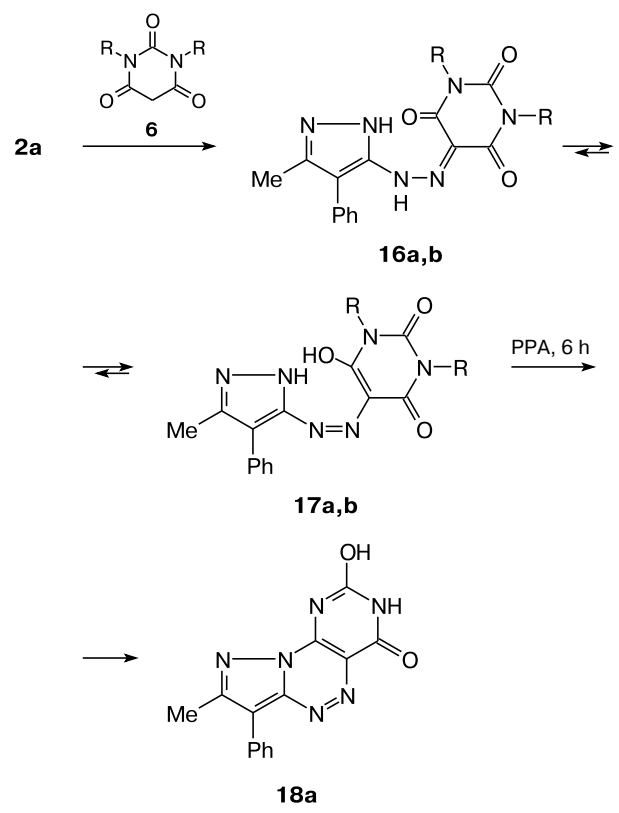
Table 2. ^{1}H NMR spectra of pyrazolo[5,1-*c*][1,2,4]triazines **9a**—**j**, **10a**—**f**, and **12a,b**

Compound	δ (*J*/Hz)
9a	1.18 (s, 6 H, 2 Me); 2.40 (t, 3 H, C<u>H</u>$_3$CH$_2$, *J* = 7.4); 2.75 (s, 2 H, CH$_2$); 3.05 (q, 2 H, CH$_3$C<u>H</u>$_2$, *J* = 7.7); 3.47 (s, 2 H, CH$_2$); 7.44 (t, 1 H, H arom., *J* = 7.1); 7.58 (t, 2 H, H arom., *J* = 7.8); 7.88 (d, 2 H, H arom., *J* = 7.8)
9b	1.25 (s, 6 H, 2 Me); 2.72 (s, 3 H, Me); 2.78, 3.44 (both s, 2 H each, CH$_2$); 7.51, 7.87 (both d, 2 H each, H arom., *J* = 8.3)
9c	1.25 (s, 6 H, 2 Me); 2.71 (s, 3 H, Me); 2.80, 3.39 (both s, 2 H each, CH$_2$); 7.08 (d, 1 H, H arom., *J* = 8.1); 7.26 (s, 1 H, H arom.); 7.45 (d, 1 H, H arom., *J* = 8.0); 8.00 (t, 1 H, H arom., *J* = 7.8)
9d	1.24 (s, 6 H, 2 Me); 2.71 (s, 3 H, Me); 2.84, 3.70 (both s, 2 H each, CH$_2$); 3.80 (s, 3 H, MeO); 7.02—7.17, 7.35—7.52 (both m, 2 H each, H arom.)
9e	1.22 (s, 6 H, 2 Me); 2.70 (s, 3 H, Me); 2.72, 3.77 (both s, 2 H each, CH$_2$); 3.85 (s, 3 H, MeO); 7.09, 7.76 (both d, 2 H each, H arom., *J* = 8.5)
9f	1.25 (d, 3 H, Me, *J* = 6.2); 2.58 (d, 2 H, CH$_2$, *J* = 6.9); 2.69 (s, 3 H, Me); 2.77 (s, 1 H, CH); 3.15, 3.79 (both q, 1 H each, CH, *J* = 6.7); 3.85 (s, 3 H, MeO); 7.10, 7.77 (both d, 2 H each, H arom., *J* = 8.5)
9g	1.24 (d, 3 H, Me, *J* = 6.2); 2.63 (d, 2 H, CH$_2$, *J* = 6.7); 2.82 (s, 1 H, CH); 3.16 (q, 1 H, CH, *J* = 6.7); 3.49 (s, 3 H, <u>Me</u>OCH$_2$); 3.79 (q, 1 H, CH, *J* = 6.7); 4.76 (s, 2 H, MeOC<u>H</u>$_2$); 7.39—7.58 (m, 3 H, H arom.); 7.95 (d, 2 H, H arom., *J* = 7.8)
9h	2.83 (m, 1 H, CH); 2.89 (s, 3 H, <u>Me</u>OCH$_2$); 3.34, 4.45 (both d, 2 H each, CH, *J* = 6.8); 4.73 (s, 2 H, MeOC<u>H</u>$_2$); 7.40—8.00 (m, 10 H, H arom.)
9i	2.69 (s, 3 H, Me); 2.73 (d, 2 H, CH$_2$, *J* = 6.7); 2.82 (d, 1 H, CH, *J* = 6.8); 3.15 (q, 1 H, CH, *J* = 18.0); 3.70 (q, 1 H, CH, *J* = 18.1); 7.45—7.56 (m, 7 H, H arom.); 7.89 (d, 2 H, H arom., *J* = 7.3)
9j	1.40 (t, 3 H, C<u>H</u>$_3$CH$_2$, *J* = 6.5); 2.90 (m, 1 H, CH); 3.09 (q, 2 H, CH$_3$C<u>H</u>$_2$, *J* = 7.8); 3.66—4.00 (m, 4 H, CH$_2$); 6.80—7.80 (m, 9 H, H arom.); 9.55 (s, 1 H, OH)
10a	2.68 (s, 3 H, Me); 3.75, 3.83 (both s, 3 H each, MeO); 6.89—7.82 (m, 10 H, H arom.); 11.60 (br.s, 1 H, OH)
10b	3.50 (s, 3 H, MeO); 4.75 (s, 2 H, CH$_2$); 7.12—8.01 (m, 8 H, H arom.); 11.49 (br.s, 1 H, OH)
10c	2.69 (s, 3 H, Me); 3.77, 3.85 (both s, 3 H each, MeO); 6.78—7.93 (m, 9 H, H arom.); 11.45 (s, 1 H, OH)
10d	2.71 (s, 3 H, Me); 6.76—7.82 (m, 11 H, H arom.); 9.52 (s, 1 H, C$_6$H$_4$O<u>H</u>); 11.40 (br.s, 1 H, OH)
10e	2.40 (s, 3 H, Me); 3.81 (s, 3 H, MeO); 6.98—7.90 (m, 11 H, H arom.); 11.55 (br.s, 1 H, OH)
10f	2.70 (s, 3 H, Me); 7.40–7.85 (m, H arom.); 11.69 (br.s, 1 H, OH)
12a	2.80 (s, 3 H, Me); 7.48—8.36 (m, 9 H, H arom.)
12b	1.34 (t, 3 H, C<u>H</u>$_3$CH$_2$, *J* = 7.5); 2.81 (q, 2 H, CH$_3$C<u>H</u>$_2$, *J* = 7.8); 7.45—8.49 (m, 9 H, H arom.)

Scheme 6



Scheme 7



target product 2-hydroxy-8-methyl-7-phenyl-3,4-dihydropyrazolo[5,1-*c*]pyrimido[4,5-*e*][1,2,4]triazin-4-one (**18a**).

The ^{1}H NMR spectrum of pyrazolotriazine **18a** contains no signal for the pyrazole NH fragment but shows a higher-field signal for an analogous proton in the pyrimidine ring (δ 11.80). A strongly broadened signal for water at δ 3.30—3.80 suggests the presence of a hydroxy group.

PPA stands for polyphosphoric acid
16, 17: R = H (**a**), Me (**b**)

The formation of compound **18a** is also evident from mass spectra and elemental analysis data.

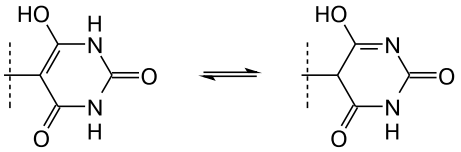
Apparently, the cyclization of azo compound **17a** is possible because of the formation of additional lactim

Table 3. Yields, melting points, elemental analysis data, and mass and ^{1}H NMR spectra of compounds **15**, **17a,b**, and **18a**

Compound	Yield (%) (method of synthesis)	M.p. /°C	Found / Calculated (%) C	H	N	Molecular formula	MS*, *m/z*	δ (*J*/Hz)
15	49 (*A*), 43 (*B*)**	187 (decomp.)	62.20 / 61.93	4.45 / 4.55	17.92 / 18.06	$C_{16}H_{14}N_4O_3$	310 /310.3	1.92, 2.59 (both s, 3 H each, Me); 3.05 (d, 1 H, CH_2, J = 8.9); 3.24 (d, 1 H, CH_2, J = 8.5); 7.43 (t, 1 H, H arom., J = 7.0); 7.55 (t, 2 H, H arom., J = 7.8); 7.78 (d, 2 H, H arom., J = 7.7); 8.28 (s, 1 H, COOH)
17a	93	>300	54.09 / 53.85	3.60 / 3.87	26.80 / 26.91	$C_{14}H_{12}N_6O_3$	312 /312.3	2.28 (s, 3 H, Me); 7.33 (m, 3 H, H arom.); 7.45 (m, 2 H, H arom.); 12.38, 12.55 (both s, 1 H each, NH); 14.49 (s, 1 H, NH)
17b	90	>300	56.19 / 56.47	4.90 / 4.74	24.81 / 24.69	$C_{16}H_{16}N_6O_3$	340 /340.3	2.28, 3.12, 3.20 (all s, 3 H each, Me); 7.37 (m, 3 H, H arom.); 7.47 (m, 2 H, H arom.); 14.45 (s, 1 H, NH)
18a	67	>300	57.39 / 57.14	3.29 / 3.43	28.42 / 28.56	$C_{14}H_{10}N_6O_2$	294 /294.3	2.70 (s, 3 H, Me); 7.50 (s, 3 H, H arom.); 7.88 (s, 2 H, H arom.); 11.79 (s, 1 H, NH)

* Found/calculated.
** For the product recrystallized from AcOH.

Scheme 8



17a **19**

tautomer **19**, which is precluded for compound **17b** (Scheme 8).

The physicochemical characteristics and ^{1}H NMR spectra of products **15**, **17a,b**, and **18a** are given in Table 3.

To sum up, our efficient syntheses of novel pyrazolo[5,1-*c*][1,2,4]triazines **9a—j**, **10a—f**, **12a,b**, **15**, and **18a** demonstrated that cyclic 1,3-dicarbonyl compounds are promising azo components in reactions with pyrazolediazonium salts. These reactions under optimized conditions provide a convenient route to pyrazolotriazines fused with alicyclic, aromatic, and heterocyclic fragments.

Experimental

The reagents and products were identified, and the reaction mixtures were qualitatively analyzed during the reactions, by TLC on Silufol UV-254 plates (Merck). Individual solvents (light petroleum, chloroform, ethyl acetate, and isopropyl alcohol) and their mixtures in various ratios were used as eluents; spots were visualized under UV light or in the iodine vapor. ^{1}H NMR spectra were recorded on a Bruker AC-300 instrument (300 MHz) in DMSO-d_6 with Me_4Si as the internal standard. Mass spectra were recorded on an LKB-9000 spectrometer (direct inlet probe, ionizing energy 70 eV). Elemental analysis was carried out on a Carlo Erba NA 1500 instrument.

3-R-4-Aryl-1*H*-5-aminopyrazoles were prepared according to a known procedure.[11] 5-Monosubstituted cyclohexane-1,3-diones[12] and 4-hydroxy-6-methyl-2-pyrone[13] were prepared as described earlier. The other chemicals and solvents (ACROS Organics, Aldrich, Lancaster, and VEKTON) were used without additional purification.

Pyrazolylhydrazones 8, 11a,b, and 13 and azo compounds 17a,b (general procedure). A mixture of 3(5)-aminopyrazole **1** (0.03 mol), water (10 mL), and HCl (d = 1.19 g mL^{-1}; 0.09 mol) was cooled to 0 °C. Aqueous $NaNO_2$ (0.03 mol) was added with stirring at such a rate as to prevent a temperature rise. The mixture was kept at 0 °C for 10 min and added in portions to a solution of azo components **3**, **4**, **5**, or **6** (0.03 mol), THF (20 mL), and acetic acid or their mixture with a saturated aqueous solution of sodium acetate (10 g per every 0.01 mol of compound **1**). The reaction mixture was continuously stirred for several hours. The precipitate of hydrazone that formed was filtered off, washed with water and cold isopropyl alcohol, and dried at 20—30 °C. The yields were 75—92%.

2-R-3-Aryl-8,9-dihydropyrazolo[5,1-*c*][1,2,4]benzotriazin-6(7*H*)-ones 9a—j (general procedure *A*). A mixture of a hydrazone (0.01 mol) and 45% H_2SO_4 (20—30 mL) was stirred at room temperature for 15—30 min. After the reaction was completed, the mixture was poured into water (300 mL). The precipitates of products that formed were filtered off, washed with water to pH 7, and recrystallized from AcOH—toluene (1 : 2).

General procedure *B*. A mixture of a hydrazone (0.01 mol) with an equal mass amount of anhydrous sodium acetate was refluxed in acetic acid (20—30 mL) for 10—15 min. The product was isolated as described under general procedure *A*.

General procedure *C*. A solution of a hydrazone (0.01 mol) was refluxed with a Dean—Stark trap in a mixture of toluene (20 mL) and acetic acid (5 mL) until liberation of water ceased. The mixture was cooled and the product was filtered off and recrystallized.

General procedure *D*. A mixture of equal mass amounts of a hydrazone and polyphosphoric acid was heated at 130—140 °C for 5—6 h. The product was isolated as described under general procedure *A*.

2-R-3-Phenyl-6*H*-indeno[1,2-*e*]pyrazolo[5,1-*c*][1,2,4]triazin-6-ones 12a,b and 7-methyl-4-(2-oxopropyl)-8-phenylpyrazolo-[5,1-*c*][1,2,4]triazine-3-carboxylic acid (15) were obtained according to procedures *A* and *B*.

2-Hydroxy-8-methyl-7-phenyl-3,4-dihydropyrazolo[5,1-*c*]-pyrimido[4,5-*e*][1,2,4]triazin-4-one (18a) was obtained as described under general procedure *D*.

2-R-8-R´-3-Arylpyrazolo[5,1-*c*][1,2,4]benzotriazin-6-ols 10a—f (general procedure). A solution of ketone **9** in a small amount of DMF, DMF—xylene, or DMSO was refluxed for 5—15 min. The reaction mixture was cooled and the crystals that formed were filtered off, washed with isopropyl alcohol, and recrystallized from DMF—xylene (1 : 3).

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