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# 1,3,4,6-Tetracarbonyl Compounds: IV.* Reaction of 3,4-Dihydroxy-2,4-hexadiene-1,6-diones with Hydrazine and Arylhydrazines

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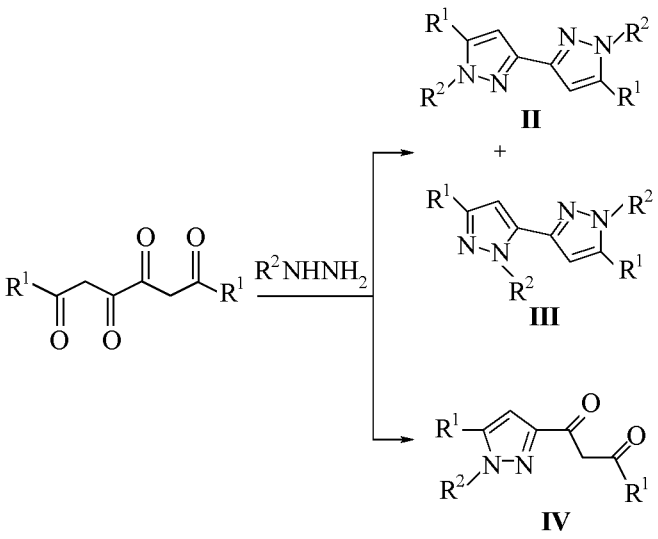
**Abstract**—Reactions of 1,6-disubstituted 3,4-dihydroxy-2,4-hexadiene-1,6-diones with hydrazine hydrate or hydrochloride afforded heterocyclization products, 3,3'-bipyrazoles. The chemoselective reaction of 1,6-diaryl-3,4-dihydroxy-2,4-hexadiene-1,6-diones with arylhydrazines gave rise to 1,1',5,5'-tetraaryl-3,3'-bipyrazoles and 1,5-diaryl-3-aroylacetylpyrazoles. The specific structural features of the pyrazole derivatives obtained are discussed. Some pyrazoles show bacteriostatic and antileukemic activity.

Some terminally substituted 1,3,4,6-tetraketones **I** were established to react with hydrazine, phenylhydrazine, and *p*-nitrophenylhydrazine yielding isomeric symmetrical with respect to the interring bond $C^3$–$C^{3'}$ and nonsymmetrical bipyrazoles **II** and **III** [2–11]. In some cases were also isolated monocyclic products, 3-acylpyrazoles **IV** [4, 11], or mixtures of compounds **I** and **IV** [4] (Scheme 1). It was assumed that the direction of the process depended only on the amount of hydrazine brought into the reaction. The structure of most pyrazoles was established without application of the spectral methods and thus up till now was not very convincing. In all the studies mentioned [2–11] the reaction mechanisms were not considered.

**Scheme 1.**




$R^1$ = Me, Et, Ar, Het; $R^2$ = H, $C_6H_5$, 4-$NO_2C_6H_4$.

The published data suggest that the primary nucleophilic attack of hydrazines is not selective: It is directed both at the external carbonyl group $C^{1,6}$=O of the β-diketo fragment and at the internal carbonyl $C^{3,4}$=O of the α-oxounit in the initial tetraketones **I** [4, 8, 11]. As evidence of the chemoselectivity in reaction of 1,3,4,6-tetraketones with hydrazines is considered formation in some cases of isomer mixtures of pyrazoles (see, e.g., [4]). This fact may be understood in a way as participation in the reaction of one among the tautomeric forms of 1,3,4,6-tetraketones A–C (Scheme 2) that are present in the solutions of the compounds [1, 12] (as unambiguously shows X-ray diffraction analysis in the solid state exists only chelate structure B [1, 13–17]).

Some bipyrazoles **II** found application as additives to scintillators [6] and in synthesis of heat-resistant polymers [10]. Also short communications appeared on biological activity of pyrazoles **II** and **IV** [11, 18]. The practical applications of these products generated by reactions of 1,3,4,6-tetraketones, and requirement of new isomeric pyrazoles with new structures stimulated further studies of reactions between tetracarbonyl synthons **I** and hydrazines. We investigated reactions of 1,6-disubstituted 3,4-dihydroxy-2,4-hexadiene-1,6-diones (**Ia–f**) with hydrazine hydrate or hydrochloride in

* For communication III see [1].

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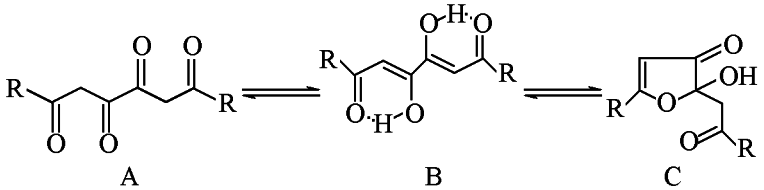
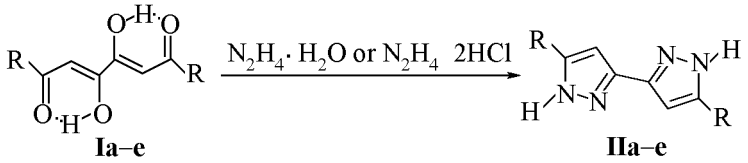
**Scheme 2.**



A B C

R = Alk R = Alk, Ar R = Ar

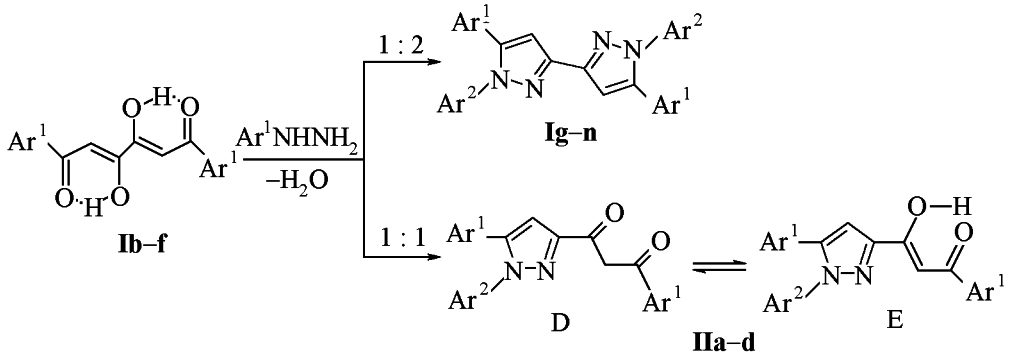
**Scheme 3.**




**Ia–e** **IIa–e**

R = $CH_3$ (**a**), $C_6H_5$ (**b**), 4-$CH_3C_6H_4$ (**c**), 2,4-$(CH_3)_2C_6H_3$ (**d**), 4-$ClC_6H_4$ (**e**), 4-$FC_6H_4$ (**f**).

**Scheme 4.**




**Ib–f** **Ig–n** D **IIa–d** E

**II**, $Ar^2$ = $C_6H_5$, $Ar^1$ = $C_6H_5$ (**g**), 4-$CH_3C_6H_4$ (**h**), 2,4-$(CH_3)_2C_6H_3$ (**i**), 4-$ClC_6H_4$ (**j**), 4-$FC_6H_4$ (**k**); $Ar^2$ = 2-$CH_3C_6H_4$, $Ar^1$ = $C_6H_5$ (**l**), 4-$ClC_6H_4$ (**m**); $Ar^1$ = $C_6H_5$, $Ar^2$ = 4-$HOOCC_6H_4$ (**n**); **IV**, $Ar^1$ = $C_6H_5$, $Ar^2$ = $C_6H_5$ (**a**), 2-$CH_3C_6H_4$ (**b**); $Ar^1$ = 4-$ClC_6H_4$, $Ar^2$ = 2-$CH_3C_6H_4$ (**c**); $Ar^1$ = $C_6H_5$, $Ar^2$ = 4-$HOOCC_6H_4$ (**d**).

ethanol, dioxane, or acetic acid. The reaction proceeds at short boiling of reagents mixture and disregarding the ratio of the latter provides 5,5'-disubstituted 3,3'-bipyrazoles **IIa–f** [18–21] (Scheme 3).

5,5'-Diaryl-substituted bipyrazoles **IIb–f** form in high yields, from 80 to 91%, but the yield of compound **IIa** with methyl groups in *5* and *5′* positions is considerably lower, only 48%, due to notable tarring in the reaction mixture characteristic of nucleophilic reactions with 2,5-dihydroxy-3,5-octadiene-2,7-dione (**Ia**). Unlike the reaction with hydrazine the treating of 1,6-diaryl-3,4-dihydroxy-2,4-hexadiene-1,6-diones (**Ib–f**) with equimolar amount or with double excess of phenyl-, o-tolyl- or p-carboxyphenylhydrazine after short boiling of the reagent mixture in acetic acid depending on the reagents ratio afforded two reaction products that basing on spectral data were assigned structures 1,1',5,5'-tetraaryl-3,3'-bipyrazoles (**IIg–n**) and 3-aroyl-1,5-diarylpyrazoles (**IVa–d**) [18–21] (Scheme 4).

Yields, melting points, and elemental analyses of compounds **IIa–n** and **IVa–d** are given in Table 1, and their spectral characteristics are listed in Table 2. The constants of the known compounds **IIa, g, IVa** are consistent with the published data [2–4, 6] (Table 1).

In the IR spectra of compounds **II** are observed the bands at 1617–1590 and 1580–1543 $cm^{-1}$ corresponding to vibrations of C=C and C=N bonds in the pyrazole and benzene rings. These bands are in good agreement with the published data for the known bipyrazoles [8, 11].

**Table 1.** Yields, melting points, and elemental analyses of pyrazoles **IIa**–**n**, **IVa**–**d**

| Compd. no. | Yield,[a] % | mp, °C (decomp.) | Found, % | | | Formula | Calculated, % | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | C | H | N (Hlg) | | C | H | N (Hlg) |
| **IIa**[b] | 48 | 278–279 | 59.69 | 6.52 | 33.80 | $C_8H_{10}N_4$ | 59.24 | 6.21 | 34.54 |
| **IIb** | 91 | 320–321 | 75.14 | 5.37 | 18.94 | $C_{18}H_{14}N_4$ | 75.50 | 4.93 | 19.57 |
| **IIc** | 80 | >320 | 76.13 | 6.29 | 18.17 | $C_{20}H_{18}N_4$ | 76.41 | 5.77 | 17.82 |
| **IId** | 85 | 255–256 | 76.86 | 6.31 | 16.75 | $C_{22}H_{22}N_4$ | 77.16 | 6.48 | 16.36 |
| **IIe** | 85 | >320 | 61.20 | 3.85 | 15.36 (20.27) | $C_{18}H_{12}Cl_2N_4$ | 60.86 | 3.41 | 15.77 (19.96) |
| **IIf** | 80 | >320 | 66.47 | 4.23 | 16.92 | $C_{18}H_{12}F_2N_4$ | 67.08 | 3.75 | 17.38 (11.79) |
| **IIg**[c] | 68 | 233–234 | 81.84 | 4.77 | 13.12 | $C_{30}H_{22}N_4$ | 82.17 | 5.06 | 12.78 |
| **IIh** | 50 | 217–218 | 82.51 | 6.12 | 11.78 | $C_{32}H_{26}N_4$ | 82.38 | 5.62 | 12.01 |
| **IIi** | 61 | 283–284 | 83.07 | 5.75 | 11.64 | $C_{34}H_{30}N_4$ | 82.56 | 6.11 | 11.33 |
| **IIj** | 50 | 234–235 | 71.39 | 4.41 | 10.68 (14.25) | $C_{30}H_{20}Cl_2N_4$ | 71.01 | 3.97 | 11.04 (13.97) |
| **IIk** | 42 | 204–205 | 75.22 | 4.86 | 11.32 | $C_{30}H_{20}F_2N_4$ | 75.94 | 4.25 | 11.81 (8.01) |
| **IIl** | 44 | 233–234 | 82.77 | 5.90 | 12.34 | $C_{32}H_{26}N_4$ | 82.38 | 5.62 | 12.01 |
| **IIm** | 48 | 271–272 | 72.13 | 4.66 | 10.71 (13.59) | $C_{32}H_{24}Cl_2N_4$ | 71.78 | 4.52 | 10.46 (13.24) |
| **IIn** | 35 | >300 | 72.68 | 4.49 | 11.05 | $C_{32}H_{22}N_4O_4$ | 72.99 | 4.21 | 10.64 |
| **IVa**[d] | 53 | 162–163 | 79.34 | 4.70 | 8.31 | $C_{24}H_{18}N_2O_2$ | 78.67 | 4.95 | 7.65 |
| **IVb** | 47 | 169–170 | 79.36 | 5.71 | 7.12 | $C_{25}H_{20}N_2O_2$ | 78.93 | 5.30 | 7.36 |
| **IVc** | 40 | 175–176 | 66.46 | 3.78 | 5.84 (15.49) | $C_{25}H_{18}Cl_2N_2O_2$ | 66.83 | 4.04 | 6.23 (15.78) |
| **IVd** | 61 | 183–184 | 73.27 | 4.63 | 7.25 | $C_{25}H_{18}N_2O_4$ | 73.16 | 4.42 | 6.83 |

[a] Yield of compounds **IIa**–**f** is given for preparation by reaction of tetraketones **I** with hydrazine hydrate.
[b] mp 286°C [3].
[c] Yield 73% [6], mp 232 [2], 233 [4], 231°C [6].
[d] mp 164–166.5°C [4].

In the $^1$H NMR spectra of bipyrazoles **II** recorded in DMSO-$d_6$ alongside the signals from the protons of substituents in *5* and *5'* positions (Table 2) appeared in a weak field at 6.58–7.05 ppm a resonance from the methine proton located in *4* position of the pyrazole ring.

The signal at 6.29 ppm from $C^{4,4'}H$ in the $^1$H NMR spectrum of compound **IIa** lacking conjugated benzene rings is an exception. In the spectra of compounds **IIb–f** appears also a broadened signal of the proton attached to the nitrogen atom of pyrazole ring (13.10–13.45 ppm); the signal disappears on addition of deutereted acetic acid $CD_3COOD$. In the spectrum of bipyrazole **IIa** this signal is observed in a stronger field, at 12.68 ppm. The other signals save that of NH group of the ring are not affected with addition of deuteroacetic acid. The spectral characteristics of bipyrazoles **IIa** and IId are in a satisfactory agreement with $^1$H NMR prediction spectra calculated along the software of ACD/Labs (see EXPERIMENTAL). Certain discrepancies between the experimental and prediction $^1$H NMR spectra (in the experimental spectrum the signal of methine proton is shifted upfield as compared with the predicted spectrum, and the peak of the proton at the pyrrole nitrogen of the ring is on the contrary shifted more downfield than in the predicted spectrum) may be due to solvation in DMSO solution.

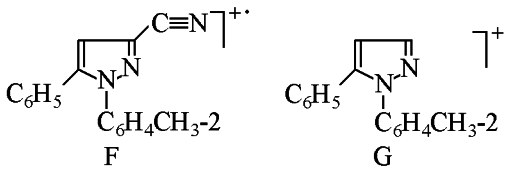
In the mass spectrum of bipyrazole **IIl** are present a molecular ion peak of maximum intensity, fragment ion peaks, for instance, that of nitrile F (*m/z* 259), that of 3-pyrazole G (*m/z* 233), and also peaks of ions derived from these fragment ions, e.g., of nitrile

**Table 2.** [1]H NMR spectra of pyrazoles **IIa–e, g–i, k–m, IVa–d** in solutions in DMSO-$d_6$

| Compd. no. | Chemical shift, δ, ppm |
|---|---|
| **IIa** | 2.23 s (6H, $CH_3$), 6.29 s (2H, CH), 12.68 br.s (2H, NH) |
| **IIb** | 6.59 s (2H, CH), 6.92–7.80 m (10H arom), 13.10, 13.37 br.s (2H, NH) |
| **IIc** | 2.30 s (6H, $CH_3$), 6.58 s (2H, CH), 7.00–7.75 m (8H arom), 13.30, 13.45 br.s (2H, NH) |
| **IId** | 2.32 s (6H, *o*-$CH_3$), 2.42 s (6H, *p*-$CH_3$), 6.76 s (2H, CH), 7.11, 7.42 m (6H arom), 13.12, 13.25 br.s (2H, NH) |
| **IId**[a] | 2.32 s (6H, *o*-$CH_3$), 2.43 s (6H, *p*-$CH_3$), 6.77 s (2H, CH), 7.08, 7.11, 7.13, 7.42, 7.45 (6H arom) |
| **IIe** | 6.65 s (2H, CH), 7.05–7.85 m (8H arom), 13.30, 13.42 br.s (2H, NH) |
| **IIg** | 7.01 s (2H, CH), 7.19–7.50 m (20H arom) |
| **IIh** | 2.32 s (6H, $CH_3$), 7.06 s (2H, CH), 7.17–7.41 m (18H arom) |
| **IIi** | 2.28 s (6H, $CH_3$), 2.50 s (6H, $CH_3$), 6.95 s (2H, CH), 7.03–7.28 m (16H arom) |
| **IIk** | 7.03 s (2H, CH), 7.20–7.42 m (18H arom) |
| **IIl** | 2.03 s (6H, $CH_3$), 7.01 s (2H, CH), 7.15–7.58 m (18H arom) |
| **IIm** | 1.96 s (6H, $CH_3$), 7.05 s (2H, CH), 7.28–7.51 m (16H arom) |
| **IVa** | 4.80 s (2H, $CH_2$, form D[b], 40%), 7.02 s (1H, CH of pyrazole), 7.15 c (1H, CH, form E[b], 60%), 7.25–7.68, 8.02–8.08 (15H arom), 16.45 br.s (1H, OH, form E[b]) |
| **IVb** | 1.96 s (3H, $CH_3$), 7.01 s (1H, CH), 7.10–7.95 m (14H arom) |
| **IVc** | 1.93 s (3H, $CH_3$), 6.95 s (1H, CH), 7.22–8.14 m (12H arom) |
| **IVd** | 6.93 s (1H, CH), 7.25–7.96 m (14H arom), 12.73 s (1H, OH) |

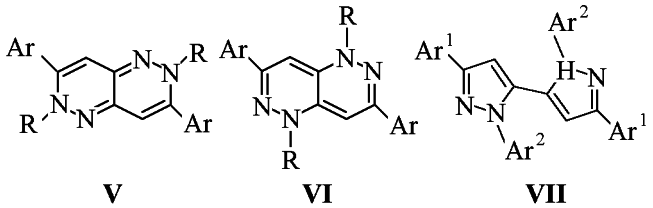
[a] Spectrum registered in a mixture DMSO-$d_6$–$CD_3COOD$, internal reference TMS. [b] See Scheme 4.

fragments $[C_6H_5C{\equiv}N{-}C_6H_4CH_3\text{-}2]^+$ (*m/z* 194) and $[C_6H_5C{\equiv}N]_0$ (*m/z* 103). These data fully confirm the structure of compounds **II** obtained and are well consistent with the known data on fragmentation of pyrazole derivatives at electron impact [22].




This set of fragment ions, first of all ions $[1/2M]_0$ formed from bipyrazoles **II**, permits to exclude the alternative structures pyridazino[4,3-*c*]pyridazines **V** and **VI** (Scheme 5) although their formation could not have been considered improbable basing on the published data [23].

**Scheme 5.**




R = H, Ar.

Since in the mass spectrum of compound **IIl** are present peaks of fragment ions F and G with *m/z* 259 and 233, and also a peak of *N*-*o*-tolylbenzonitrile ion (*m/z* 194) the possible isomeric structures with axial symmetry along the $C^3$–$C^3$ bond of 2,2',5,5'-tetraaryl-3,3'-bipyrazoles **VII** and nonsymmetrical bipyrazoles **III** ($R^1$ = $R^2$ = Ar, Scheme 1) should be rejected.

Analysis of spectra of mass-ion series [24] of bipyrazoles **II** shows that as a rule the most abundant are the ions of the first and second homologous groups including pyrazole and nitile ions. The high selectivity of fragmentation (*N* = 1 or 2), high or maximum intensity of the molecular ion peak alongside with low intensity of the fragment ions of pyrazole, the selective rupture of the N–N bond in the ring, the stability of the corresponding pyrazole ions, all these data are in conformity with published data on pyrazole derivatives decomposition under electron impact [22, 25] and also evidence the correct assignment of the structure to compounds **II**.

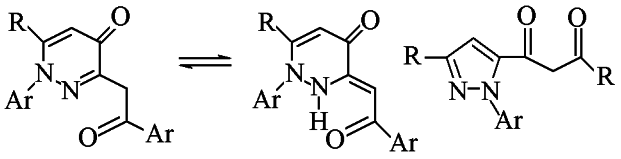
In the IR spectra of pyrazoles **IV** is present a broad absorption band at low frequencies corresponding to stretching vibrations of carbonyl groups in the β-diketone moiety in the 1610–1565 $cm^{-1}$ region evidencing that in the solid state in the molecule exists an OH-chelate cycle with an intramolecular hydrogen bond of –O–H···O=C< type (form E) [26]. Yet in the [1]H NMR spectrum of compound **IVa** recorded in

DMSO-$d_6$ solution alongside the methine proton signal of the enolized benzoylacetyl fragment at 7.15 ppm and the broadened signal of the hydroxy proton from enol at 16.45 ppm appears also the $CH_2$ group signal at 4.80 ppm (Table 2) indicating that both keto-enol form E and β-diketone tautomer D are present in the solution; the fraction of the latter amounts to 40%.

The spectral data indicate that compounds **IV** cannot have a structure of 3-aroylmethyl-1,6-diaryl-1*H*-4-pyridazinones (**VIII**); their formation could not be excluded a priori (Scheme 6). Thus in the IR spectra of compounds **IV** no carbonyl group bands appear at higher frequencies than 1610 $cm^{-1}$; however according to published data the absorption band of carbonyl $C^4=O$ stretching vibrations in the IR spectra of 1*H*-4-pyridazinones *VIII* is observed at the frequency no less than 1616 $cm^{-1}$ [27] and most often at 1639–1630 $cm^{-1}$ [27–29].

In the mass spectrum of compound **IVc** are present the peaks of the fragment ion $[4\text{-}ClC_6H_4\text{–}C{\equiv}N\text{–}C_6H_4CH_3\text{-}2]^+$ (*m/z* 228, 230), that are not consistent with a structure of the corresponding 5- aroylacetyl-1,3-diarylpyrazole (**IX**) (Scheme 6).

**Scheme 6.**



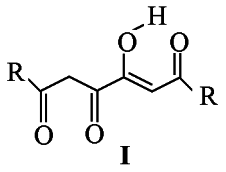

**VIII** **IX**

R = Ar.

Besides in the spectrum were lacking peaks of ions $[4\text{-}ClC_6H_4CO\text{–}CH_2CO\text{–}C{\equiv}N\text{–}C_6H_4CH_3\text{-}2]^+$ (*m/z* 298, 300) and $[4\text{-}ClC_6H_4\text{–}C{\equiv}N\text{–}NHC_6H_4CH_3\text{-}2]^+$ (*m/z* 243, 245) that would form at fragmentation of the corresponding derivative **IX**.

Apparently the reaction of 1,6-disubstituted 3,4-dihydroxy-2,4-hexadiene-1,6-diones **I** with hydrazine and arylhydrazines occurs regioselectively with primary addition of the latter to enolized carbonyl group $=C^3\text{–}O\text{–}H$ or $=C^4\text{–}O\text{–}H$ with equal probability when in positions *1* and *6* of bichelate B are the same substituents R. Further the arising monoenhydrazinocarbonyl intermediate undergoes heterocyclization into the corresponding 3-acyl derivatives of pyrazole **IV** or in the presence of excess hydrazine into bipyrazoles **II**. This scheme is fully consistent with the current views on involving the dienol chain form of 1,3,4,6-tetraketones B into reaction with nucleophiles [18, 21, 30]. In reaction with hydrazine takes part just the dienol tautomer B of 1,3,4,,6-tetraketones and not the ring form C present in the solution. In the latter case the nucleophilic attack of hydrazine should be directed at the $C^5$ atom of the ring that according to the quantum-chemical calculations is the most probable site for attack in the nucleophilic reactions with charge and orbital control where the substrates are 2-hydroxy-2,3-dihydro-3-furans [31]. The formation of monopyrazole **IV** and not the alternative compounds **III**, **VII**, or **IX** unambiguously proves the proposed reaction scheme.

It should be mentioned that in the $^1H$ NMR spectra of a number of initial 1,3,4,6-tetraketones **I** whose spectra were measured for the first time we revealed several tautomeric forms in equilibrium. For instance, in the spectrum of solution of 4,5-dihydroxy-3,5-octadiene-2,7-dione (**Ia**) in DMSO-$d_6$ are present 4 forms (Scheme 2): a dienol chain form B (R = $CH_3$), 36%, ring form 2-hydroxy-2,3-dihydro-3-furanone C (R = $CH_3$), 59%, and two minor chain tautomers: detected for the first time ketoenol H (R = $CH_3$), 4%, and traces of keto form A (R = $CH_3$), about 0.6%. However in deuterochloroform the spectrum of compound Ia is significantly less complicated: the predominant form is dienol B (R = $CH_3$), 96%, and a minor isomer A (R = $CH_3$), 4% (see EXPERIMENTAL).




**I**

R = $CH_3$, 2,4-$(CH_3)_2C_6H_3$.

$^1H$ NMR spectrum in DMSO-$d_6$ of 1,3,4,6-tetraketone **Id** containing two o,p-dimethylphenyl substituents at both ends of the chain showed the presence of only two tautomers: dienol form B [R = 2,4-$(CH_3)_2C_6H_3$)], 10%, and prevailing cyclic semiacetal C [R = 2,4-$(CH_3)_2C_6H_3$], 90% (Scheme 2). The spectrum of compound **Id** demonstrated the absence of the chain ketone form A [R = 2,4-$(CH_3)_2C_6H_3$] and monoenol H [R = 2,4$(CH_3)_2C_6H_3$]. The spectra are consistent with the known data on the presence in DMSO solutions of 1,6-disubstituted 1,3,4,6-tetraketones of open-chain and cyclic tautomers with prevalence of the latter [1, 12, 32]. However in contrast to the above mentioned example in deuterochloroform

the $^1$H NMR spectrum showed the presence of the sole dienol tautomer B (see EXPERIMENTAL) also in agreement with the published data on the spectra of 1,6-diaryl-1,3,4,6-tetraketones [32].

Preliminary studies indicate that bipyrazoles **II** possess bacteriostatic activity with respect to *Staphylococcus aurous* and *Escherichia coli* [18, 30]. Bipyrazoles *IIb, d, e, g* were tested for antitumor and anti-AIDS activity. A pronounced antileukemic activity was revealed in compound **IId**.

## EXPERIMENTAL

IR spectra of compounds **II** and **IV** were recorded on spectrophotometers UR-20, Specord M-80, and Phillips Analytical PU9716 IR from mulls in mineral oil. $^1$H NMR spectra of compounds **I**, **II**, and **IV** were registered on spectrometers RYa-2310 (60 MHz), Bruker AM-300 and Varian VXP-300 (300 MHz) from solutions in deuterochloroform, DMSO-$d_6$ or a mixture of DMSO-$d_6$ with $CDCl_3$. Internal reference TMS or HMDS. $^{13}$C NMR spectra of compounds **II** were measured on JEOL EX90A FT-NMR instrument at operating frequency 22, 30 MHz from solutions in DMSO. Mass spectra of compounds **I, II**, and **IV** were obtained on Kratos MS-30 instrument (Great Britain) in direct input mode, emission current 1000 mA, ionizing electrons energy 70 eV, evaporator temperature 120–150°C. The prediction NMR spectra were constructed with the use of a routine from ACD/Labs Software Co (Toronto, Canada, http://www.acdlabs.com). The calculations did not take into account the solvation effects. The homogeneity of compounds was proved by TLC on Silufol UV-254 plates, eluent benzene–ether–acetone, 10 : 9 : 1, development in iodine vapor. The known initial 1,3,4,6-tetraketones Ia–e were prepared by Claisen condensation of methyl ketones with diethyl oxalate in the presence of sodium ethylate [1, 2, 6, 33–36].

**4,5-Dihydroxy-3,5-octadiene-2,7-dione (Ia).** To 100 ml of methanol preliminary distilled from sodium metal was added by portions 4.6 g (0.2 mmol) of sodium, then methanol was distilled off till dryness, and to sodium methylate thus obtained was added 150 ml of anhydrous ethyl ether. Then at cooling and stirring was added dropwise a mixture of 14.6 g (0.1 mol) of diethyl oxalate and 11.6 g (0.2 mol) of acetone. On the next day the solid residue was dissolved in 40 ml of water, and by portions while stirring was added 10% aqueous hydrochloric acid till pH 3–4. The reaction product was extracted into ether (3 × 50 ml), the extracts were combined, and washed with a saturated water solution of sodium carbonate till neutral. The solvent was evaporated till dryness, the residue was recrystallized from ethanol. We obtained colorless crystals of compound **Ia**. Yield 5 g (29%). mp 119–120°C (publ.: 120–121°C [3, 4, 34], 123°C [37]). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.25 s (6H, $CH_3$), 3.93 s [4H, $CH_2$, keto form A, 4% (Scheme 2)], 6.38 s (2H, CH, enol form B, 96%), 13.85 br.s (2H, OH, form B). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.17 s [3H, $C^5CH_3$, form C (Scheme 2)], 2.22 s (6H, $CH_3$, form B), 2.28 s (3H, $C\underline{H}_3COCH_2$, form C), 2.78 d, 2.90 d (2H, $C\underline{H}_2COCH_3$, $^2J$ 14.0 Hz, form C, 59%), 3.88 s (1H, $C\underline{H}_2$, form A, ~0.6%), 3.97 s [1H, $CH_2$, form H, 4% (Scheme 6)], 5.39 s (1H, $C^4H$, form C), 6.23 s (1H, CH, form H), 6.37 s (1H, CH, form B, 36%), 7.63 s (1H, $C^2OH$), form C). Mass spectrum, *m/z* ($I_{rel}$, %) (peaks presented have $I_{rel} > 2\%$): 170 (3) $M_0$, 142 (2) $[M–CO]_0$, 127 (17) $[M–CH_3CO]^+$, 109 (2) $[M–CH_3CO–H_2O]_0$, 86 (3), 85 (100) $[CH_3COCH_2C{\equiv}O]^+$, 71 (2), 69 (8) $[O{=}C{=}CH–C{\equiv}O]^+$, 55 (6), 53 (3), 45 (2), 43 $[CH_3CO]^+$, 41 (10), 40 (29), 33 (28). The fragmentation character of compound **Ia** under the electron impact is well consistent with the known scheme of degradation of 1,6-diaryl-1,3,4,6-tetraketones under such conditions [38]. Found, %: C 56.47; H 5.92. $C_8H_{10}O_4$. Calculated, %: C 56.79; H 6.23.

**1,6-Bis(2,4-dimethylphenyl)-3,4-dihydroxy-2,4-hexadiene-1,6-dione (Id).** To 100 ml of methanol was added by small portions 4.6 (0.2 mmol) of sodium, then methanol was distilled off till dryness, the sodium methylate was ground into powder and charged into a flat-bottom flask, and 150 ml of ether was added thereto. Then at cooling and stirring was added dropwise a mixture of 14.6 g (0.1 mol) of diethyl oxalate and 29.6 g (0.2 mol) of 2',4'-dimethylacetophenone. On the next day the dry residue was thoroughly mixed with 100 ml of hot water and at stirring concn. HCl was added till pH 3–4. The precipitate was washed with water and ethanol and recrystallized from dioxane. Yield 19.6 g (56%). mp 160–161°C (publ.: 169–170°C [35]). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 2.37 s (6H, *o*-$CH_3$), 2.58 s (6H, *p*-$CH_3$), 6.88 s (2H, CH), 7.12 s, 7.27 s, 7.62 s, 7.66 s (6H arom), 15.43 s (2H, OH); 100% of dienol form B (Scheme 2). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.22 s, 2.30 s, 2.33 s, 2.39 s, 2.50 s (12H, $4CH_3$), 3.47 d, 3.69 d [2H, $C\underline{H}_2COAr$, $^2J$ 17.5 Hz, form C (Scheme 2)], 5.97 s (1H, $C^4H$, form C, 90%), 6.91 s (1H, CH, form B, 10%), 7.06 s, 7.11 s, 7.13 s, 7.17 s, 7.45 s, 7.48 s, 7.69 s, 7.72 s (6H arom), 7.85 br.s (1H, $C^2OH$, form C). $C_{22}H_{22}O_4$.

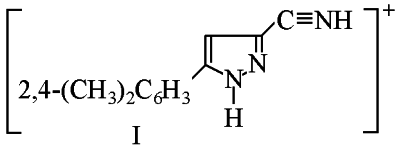
**1,6-Bis(*p*-fluorophenyl)-3,4-dihydroxy-2,4-hexadiene-1,6-dione (If)** was prepared as compound **Id**. Yield 16.2 g (49%). mp 204–205°C. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 3.52 d, 3.85 d [2H, C$\underline{H}_2$COAr, $^2J$ 16.0 Hz, form C (Scheme 2)], 6.37 s (1H, C$^4$H, form C, 77%), 7.26–7.40 s, 7.86–8.03 s (9H, CH, 8H arom). $C_{18}H_{12}F_2O_4$.

**5,5′-Disubstituted 3,3′-bipyrazoles IIa–f.** General procedure. To a solution of 0.004 mol of an appropriate 1,3,4,6-tetraketone **Ia–f** in 30–70 ml of dioxane, ethanol, or acetic acid was added at stirring 0.2 ml (nearly 1 equiv) or 0.5 ml (excess) of 70% water solution of hydrazine or 0.84 g (0.008 mmol) of hydrazine hydrochloride, and the mixture was boiled for 10–20 min. The precipitate was filtered off and recrystallized from dioxane, acetic acid, or benzene; or the solvent was evaporated, and the residue was recrystallized from dioxane or benzene.

**5,5′-Dimethyl-3,3′-bipyrazole (IIa).** Yield 0.3 g (48%). mp 278–279°C (decomp.) (publ.: 286°C [3]). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.23 s (6H, $CH_3$), 6.29 s (2H, CH), 12.68 br.s (2H, NH). Further are given for comparison the data of prediction $^1$H NMR spectrum, δ, ppm: 2.33 s (6H, $CH_3$), 6.11 s (2H, CH), 11.88 br.s (2H, NH). $^{13}$C prediction spectrum, $\delta_C$, ppm: 11.82±1.7 ($CH_3$), 11.99±2.1 ($CH_3$), 103.72±3.3 (C$^4$), 103.83±3.3 (C$^{4'}$), 140.13±4.5 (C$^3$), 140.50±1.0 (C$^5$), 145.98±12.7 (C$^{3'}$), 147.01± ±6.1 (C$^{5'}$).

**5,5′-Bis(*p*-tolyl)-3,3′-bipyrazole (IIc).** Yield 1 g (80%). mp >320°C (decomp.). $^{13}$C NMR spectrum (DMSO-$d_6$), $\delta_C$, ppm: 20.65 ($CH_3$), 99.24 (C$^4$, C$^{4'}$), 125.00, 126.80, 127.86, 128.47, 129.47, 136.08 (C arom), 137.10 (C$^3$, C$^{3'}$), 141.20 (C$^5$, C$^{5'}$).

**5,5′-Bis(2,4-dimethylphenyl)-3,3′-bipyrazole (IId).** Yield 1.15 g (85%). mp 255–256°C (decomp). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.32 s (6H, *o*-$CH_3$), 2.42 s (6H, *p*-$CH_3$), 6.76 s (2H, CH), 7.11 m, 7.42 m (6H arom), 13.12 br.s, 13.25 br.s (2H, NH). Further are given for comparison the data of prediction $^1$H NMR spectrum, δ, ppm: 2.32 s (6H, *o*-$CH_3$), 2.36 s (6H, *p*-$CH_3$), 6.97 s, 7.06 s, 7.09 s, 7.41 s, 7.52 s (6H arom), 7.95 s (2H, C$^4$H), 8.68 br.s (2H, NH). $^{13}$C NMR spectrum (DMSO-$d_6$), $\delta_C$, ppm: 20.52 ($CH_3$), 102.50 (C$^4$, C$^{4'}$), 126.12, 128.07, 131.86 (C arom), 134.93 (C$^3$, C$^{3'}$), 137.22 (C$^5$, C$^{5'}$). Further are given for comparison the data of prediction $^{13}$C NMR spectrum, $\delta_C$, ppm: 19.43±0.6, 20.90±0.1, 20.93±0.3 (C$\underline{H}_3$), 101.03±3.2, 107.92±3.0 (C$^4$, C$^{4'}$), 125.06±0.4, 127.45±0.3, 129.20±0.5, 130.16±0.6, 130.58±1.2, 132.18±1.6, 133.38±4.7, 134.23±0.2, 135.09±2.5, 135.28±5.8, 137.07±0.6, 141.44±1.5 (C arom), 139.10±4.9 (C$^3$), 145.55±2.4 (C$^5$), 146.18±12.7 (C$^{3'}$), 148.03±2.5 (C$^5$). Mass spectrum, *m/z* ($I_{rel}$, %) (peaks presented have $I_{rel}$ > 5%): 343 (23) $[M+1]^+$, 342 (97) $M_0$, 341 (21), 226 (5), 198 (15) [I], 171 (25) $[1/2M]^+$ [J], 170 (6), 163 (9), 156 (12), 154 (6), 151 (5), 148 (8), 146 (16), 145 (100) $[1/2M–C{\equiv}N]^+$, 144 (43) $[1/2M–HCN]_0$, 143 (10), 142 (7), 141 (11), 131 (23), 130 (70) $[1/2M–C{\equiv}N–CH_3]^+$, 129 (10) $[1/2M–HCN–CH_3]^+$, 128 (14), 127 (7), 117 (8), 116 (9), 114 (16), 105 (8) $[2,4\text{-}(CH_3)_2C_6H_3]^+$, 103 (6), 91 (8), 88 (13), 79 (6), 77 (12).

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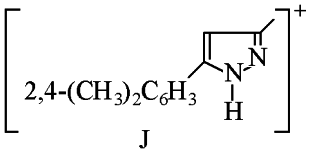


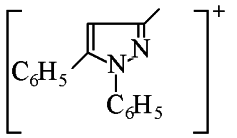

J

**5,5′-Bis(*p*-chlorophenyl)-3,3′-bipyrazole (IIf).** Yield 1.2 g (85%). mp >320°C (decomp.). IR spectrum, ν, cm$^{-1}$: 3220 (NH), 1617, 1565, 1533, 1495, 1465, 1382, 1351, 1168, 1102, 1057, 978, 834, 793. $^{13}$C NMR spectrum (DMSO-$d_6$): 100.08 (C$^4$, C$^{4'}$), 126.92, 127.88, 128.85, 129.24, 132.15, 135.90 (C arom), 141.45 (C$^3$, C$^{3'}$), 143.16 (C$^5$, C$^{5'}$). Further are given for comparison the data of prediction $^{13}$C NMR spectrum, $\delta_C$, ppm: 100.68 (C$^4$), 107.22 (C$^{4'}$), 125.55, 128.14, 128.18, 129.64, 130.50, 131.52, 132.55, 136.01 (C arom), 143.48 (C$^{3'}$), 145.38 (C$^3$), 145.66 (C$^5$), 146.87 (C$^{5'}$). Mass spectrum, *m/z* ($I_{rel}$, %): 359 (4) $[M+4]_0$, 358 (15) $[(M+4)–H]^+$, 357 (14) $[M+2]^+$, 356 (72) $[(M+2)–H]^+$, 355 (31) $M_0$, 354 (100) $[M–H]^+$, 345 (2), 343 (5), 341 (6), 325 (6), 322 (2), 320 (7), 293 (3), 291 (13), 230 (1), 228 (3), 226 (9), 224 (6), 181 (4), 179 (3) $[1/2(M+2)]^+$, 177 (6) $[1/2M]^+$, 164 (3), 162 (6), 153 (6), 150 (3), 148 (6), 146 (9), 139 (6), 138 (12), 131(9), 127 (9), 119 (7), 113 (8), 111 (9) $[p\text{-}ClC_6H_4]^+$, 106 (6), 105 (12), 102 (9), 101 (6), 91 (11), 89 (7), 77 (6), 76 (11) $[C_6H_5]^+$, 74 (8), 69 (18), 57 (16), 56 (11), 55 (9), 51 (11), 50 (6).

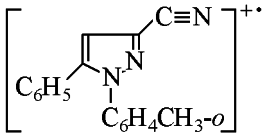
**1,1′-5,5′-Tetraaryl-3,3′-bipyrasoles IIg–n).** General procedure. To a solution of 0.002 mol of an appropriate 1,3,4,6-tetraketone **Ib–f** in 20 ml of acetic acid was added 0.004 mol of phenylhydrazine, *o*-tolylhydrazine, or p-carboxyphenylhydrazine, and

the mixture was boiled for 5–10 min. The precipitate was filtered off and recrystallized from benzene or a mixture dioxane–hexane, 1 : 1.

**1,1′,5,5′-Tetraphenyl-3,3′-bipyrazole (IIg).** Yield 0.6 g (68%). mp 233–234°C (decomp.). IR spectrum, $\nu$, $cm^{-1}$: 1592, 1543, 1497, 1445. Mass spectrum, *m/z* ($I_{rel}$, %) (peaks presented have $I_{rel}$ > 5%): 439 (27) $[M+1]^+$, 438 (77) $M_0$, 437 (29) $[M-1]^+$, 334 (18) $[M-C_6H_5-HCN]^+$, 219 (18) $[1/2M]^+$ [J], 204 (5), 192 (7), 190 (7), 180 (30)



K



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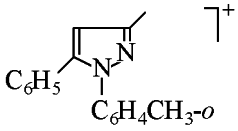
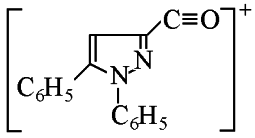


M



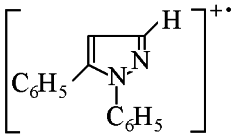
N

$[C_6H_5C{\equiv}N-C_6H_5]^+$, 165 (11), 152 (5), 116 (5), 105 (6) $[C_6H_5CH{=}NH]_0$, 102 (6), 91 (9), 89 (11), 78 (9), 77 (100) $[C_6H_5]^+$, 65 (5), 51 (38).

**1,1′-Bis(*o*-tolyl)-5,5′-diphenyl-3,3′-bipyrazole (III).** Yield 0.4 g (44%). mp 233–234°C (decomp.). Mass spectrum, *m/z* ($I_{rel}$, %) (peaks presented have $I_{rel}$ > 5%): 466 (100) $M_0$, 259 (10) [L], 233 (17) $[1/2M]^+$ [M], 194 (11) $[C_6H_5C{\equiv}N-C_6H_4CH_3\text{-}o]^+$, 128 (10) $[C_6H_5C{\equiv}C-C{\equiv}NH]^+$, 105 (24) $[o\text{-}CH_3C_6H_4N]^+$, 103 (6) $[C_6H_5C{\equiv}N]_0$, 91 (20) $[o\text{-}CH_3C_6H_4]^+$.

**3-Aroylacetyl-1,5-diarylpyrazoles IVa–d.** General procedure. To a solution of 0.002 mol of 1,3,4,6-triketone **Ib** or **Ie** in 20 ml of acetic acid was added 0.002 mol of phenylhydrazine, o-tolylhydrazine, or *p*-carboxyphenylhydrazine, and the mixture was boiled for 5–10 min. The precipitate was filtered off and recrystallized from benzene or a mixture dioxane–hexane, 1 : 1.

**3-Benzoylacetyl-1,5-diphenylpyrazole (IVa).** Yield 0.38 g (53%). mp 162–163°C (publ.: 164–166.5°C [4]). Mass spectrum, *m/z* ($I_{rel}$, %) (peaks presented have $I_{rel}$ > 5%): 439 (5), 438 (21), 437 (8), pyrazole IIg impurity that we failed to separate from the main product; 367 (17) $[M+1]^+$, 366 (65) $M_0$, 365 (10) $[M-1]^+$, 338 (19) $[M-CO]^+$, 337 (17) $[M-CO-H]^+$, 297 (6) $[M-O{=}C{=}CH-C{\equiv}O]^+$, 289 (5) $[M-C_6H_5]^+$, 248 (26), 247 (100) $[M-C_6H_5COCH_2]^+$ [N], 237 (6), 236 (13), 220 (6) [O], 219 (12) [P], 218 (5), 193 (6), 180 (16) $[C_6H_5C{\equiv}N-C_6H_5]^+$, 165 (7), 131 (6), 116 (14), 106 (11), 105 (94) $[C_6H_5C{\equiv}O]^+$, 104 (8), 89 (8), 78 (7), 77 (74) $[C_6H_5]^+$.



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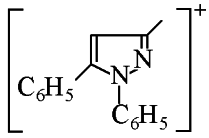

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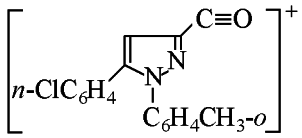

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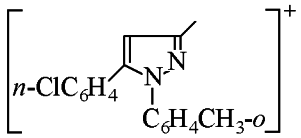

S

**1-*o*-Tolyl-3-(*p*-chlorobenzoylacetyl)-5-*p*-chlorophenylpyrazole (IVc).** Yield 0.35 g (40%). mp 175–176°C. Mass spectrum, *m/z* ($I_{rel}$, %) (peaks presented have $I_{rel}$ > 5%): 452 (10), 450 (51), 448 (73) (peaks ratio 14 : 70 : 100) $[M]_0$, 311 (17), 309 (45) $[M-p\text{-}ClC_6H_4CO]^+$, 297 (16), 295 (50) $[M-p\text{-}ClC_6H_4COCH_2]^+$ [C], 269 (6), 267 (15) [R], 230 (7), 228 (11) $[p\text{-}ClC_6H_4-C{\equiv}N-C_6H_4CH_3\text{-}o]^+$, 183 (36), 181 (100) $[p\text{-}ClC_6H_4-COCH_2C{\equiv}O]^+$, 141 (21), 139 (63) $[p\text{-}ClC_6H_4-C{\equiv}O]^+$, 113 (8), 111 (21) $[p\text{-}ClC_6H_4]^+$, 69 (57) $[O{=}C{=}CH-C{\equiv}O]^+$.

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