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Synthesis of 1-Ethylpyrazole-4-carbaldehydes, 1,1'-Methylenebis(3,5-dimethylpyrazole-4-carbaldehyde), and Schiff Bases Derived Therefrom

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Abstract—New pyrazole-containing aldehydes, 1-ethylpyrazole-4-carbaldehyde, 1-ethyl-3,5-dimethylpyrazole-4-carbaldehyde, and 1,1'-methylenebis(3,5-dimethylpyrazole-4-carbaldehyde), were synthesized by the Vilsmeier reaction. Their reactions with primary amines (aniline, hydrazine, ethylenediamine, *p*-phenylenediamine, benzidine) gave the corresponding Schiff bases.

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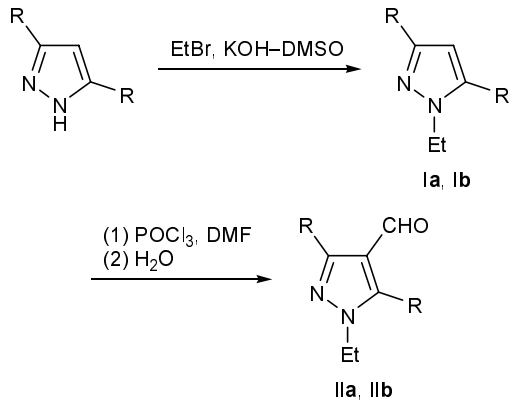
Bis(pyrazol-1-yl)methane derivatives are known to readily form complexes with many transition metal ions [1] and some main group elements [2]. Polymeric compounds possessing chelating fragments in the principal chain and their metal complexes (macromolecular metal chelates) are widely used as selective ion exchangers and polymer-supported catalysts [3]; therefore, they constitute a fairly important class of high-molecular compounds. Taking into account a variety of coordination compounds containing bis(pyrazol-1-yl)methane derivatives as ligands, we believed it reasonable (from both theoretical and practical viewpoints) to insert fragments of such molecules into a polymeric chain with a view to obtain macromolecular chelating ligands.

In the present communication we report on the synthesis of 1-ethylpyrazole-4-carbaldehyde and 1-ethyl-3,5-dimethylpyrazole-4-carbaldehyde as model compounds and of 1,1'-methylenebis(3,5-dimethylpyrazole-4-carbaldehyde) with the goal of estimating the possibility of preparing polyazines and related Schiff bases, polyaldimines, via reaction of bisaldehydes with hydrazine or diamines [4].

The initial *N*-ethylpyrazoles were synthesized by alkylation of pyrazole and 3,5-dimethylpyrazole with ethyl bromide in the superbasic system DMSO–KOH (Scheme 1). This procedure was successfully used previously in the N-alkylation of phenothiazine, phenoxazine [5], imidazole, benzimidazole [6], and benzotriazole [7]. It was also utilized to effect double alkylation of pyrazole derivatives with methylene bromide to obtain bis(pyrazol-1-yl)methanes [7].

The alkylation in superbasic medium readily occurred at room temperature in 2–3 h to give 1-ethylpyrazoles **Ia** and **Ib** in high yield (89–93%). *N*-Ethylpyrazole was also synthesized in 95% yield under conditions of phase-transfer catalysis using the alkylating agent (ethyl iodide) as organic phase; however, the reaction time was 24 h at room temperature [8].

Scheme 1.



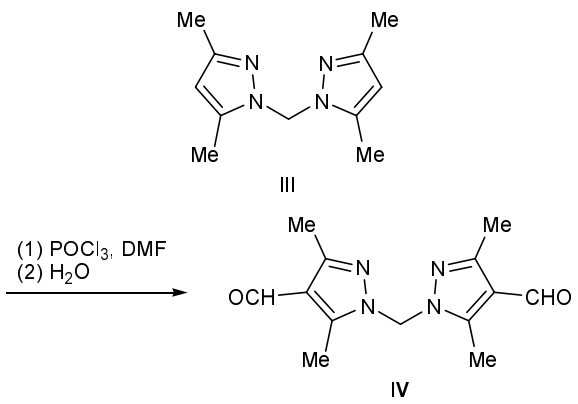
R = H (**a**), Me (**b**).

N-Ethylpyrazoles **Ia** and **Ib** were subjected to formylation according to Vilsmeier at 100°C (Scheme 1). This procedure has already been applied to N-substituted pyrazoles, but the product of formylation of 1-methylpyrazole, which is structurally similar to compounds **IIa** and **IIb**, was isolated in only 33% yield [9].

An alternative route to pyrazole-4-carbaldehydes includes reaction of methanetricarbaldehyde with 1 equiv of hydrazine. *N*-Alkylhydrazines could give rise to N-substituted pyrazoles [10]. This method is characterized by higher yields of the target aldehydes, as compared to the Vilsmeier reaction. For example, 1-methylpyrazole-4-carbaldehyde was thus obtained in 95% yield [10]. Reactions of methanetricarbaldehyde with 2 equiv of hydrazine lead to formation of aldehyde azines or (with monosubstituted hydrazine derivatives) the corresponding Schiff bases [10]. However, low accessibility of initial methanetricarbaldehyde restricts the application of this procedure.

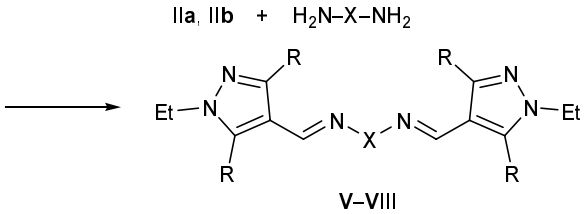
We isolated pyrazolecarbaldehydes **IIa** and **IIb** in 77 and 69% yield, respectively. Presumably, in the early study [9] the conversion of initial *N*-alkylpyrazole was incomplete: the reaction time was as short as 1 h. In the reactions with 1-ethylpyrazoles **Ia** and **Ib**, 6 to 13 h was necessary to attain complete conversion of the substrate (according to the TLC data). Following an analogous procedure but using 2 equiv of phosphoryl chloride, we performed formylation of bis(3,5-dimethylpyrazol-1-yl)methane (**III**) and obtained 87% of the corresponding bisaldehyde **IV** (Scheme 2).

Scheme 2.



Pyrazolecarbaldehydes **IIa** and **IIb** turned out to be fairly reactive compounds, and they readily reacted with hydrazine and diamines even at room temperature to give the corresponding condensation products (azines and Schiff bases) **V**–**VIII** (Scheme 3). We also examined another model of formation of polymeric

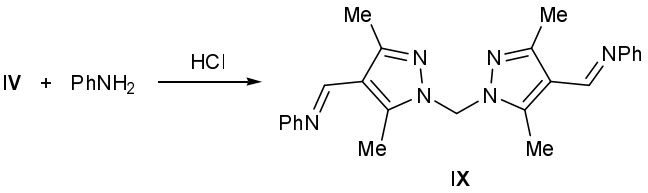
Scheme 3.



R = H (**a**), Me (**b**); **V**, X = bond; **VI**, X = CH_2CH_2; **VII**, X = *p*-C_6H_4; **VIII**, X = *p*-$C_6H_4C_6H_4$-*p*'.

Schiff bases, the condensation of bisaldehyde **IV** with aniline (Scheme 4). It should be noted that this reaction is reversible, and equimolar amounts of the reactants give rise to equilibrium with the condensation product, Schiff base **IX**. Therefore, we used excess aniline and acid catalyst to attain complete conversion of bisaldehyde **IV**. Under these conditions, 61% of **IX** was obtained in several minutes at room temperature.

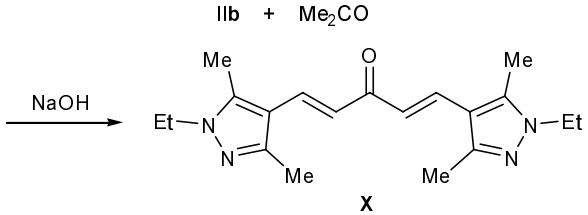
Scheme 4.



The structure of azines **V** and Schiff bases **VI**–**VIII** was confirmed by IR and NMR spectroscopy and elemental analysis.

Aldehyde **IIb** readily reacted with acetone in the presence of sodium hydroxide (Claisen–Schmidt reaction) to give unsaturated ketone **X** (Scheme 5). Theoretically, this condensation could lead to formation of three isomers with respect to the double C=C bonds, *E*,*E*, *Z*,*Z*, and *E*,*Z*. The ^{1}H NMR spectrum of the condensation product contained only one signal from each olefinic proton; analogous pattern was observed in the ^{13}C NMR spectrum for the double-bonded carbon atoms. These data indicate that only one symmetric isomer is formed. The vicinal coupling constant for the olefinic protons is equal to 15.9 Hz; this value corre-

Scheme 5.



sponds to *E* configuration at the double bond. Therefore, compound **X** was assigned *E*,*E* configuration. Presumably, high stereoselectivity of the condensation is determined by greater thermodynamic stability of the *E*,*E* isomer as compared to *Z*,*Z*, and *E*,*Z*. The latter are expected to involve considerable steric hindrances due to approach of the pyrazole rings to each other. In fact, the results of PM3 quantum-chemical calculations of the enthalpies of formation of possible isomers (HyperChem™ 7.0 [11]) showed that the *E*,*E* isomer is by 32.6 kJ/mol more stable than the *E*,*Z* isomer which follows next in stability.

EXPERIMENTAL

The NMR spectra were recorded on Bruker DRX-500 (compound **Ia**) and Bruker AV-300 instruments. The IR spectra were measured on a Specord spectrometer from samples prepared as KBr pellets (solid substances) or thin films (0.1 mm, liquids). The progress of reactions and the purity of products were monitored by TLC on Silufol plates using hexane–acetone (1 : 1) as eluent; chromatograms were developed by treatment with iodine vapor or a solution of 2,4-dinitrophenylhydrazine.

1-Ethyl-1*H*-pyrazole (Ia). Powdered potassium hydroxide, 5.04 g (90 mmol), was added to a solution of 4.08 g (60 mmol) of pyrazole in 30 ml of DMSO. The resulting suspension was stirred for 1 h at 80°C and cooled to room temperature, and 6.54 g (60 mmol) of ethyl bromide in 10 ml of DMSO was added over a period of 1 h at 20°C. The mixture was then stirred for 3 h (TLC), poured into 150 ml of water, and treated with chloroform (5 × 20 ml). The extract was washed with 30 ml of water, dried over sodium sulfate, and distilled under atmospheric pressure. Yield 5.33 g (93%), colorless liquid, bp 123–126°C, n_D^{20} = 1.4700. IR spectrum, ν, cm^{-1}: 1510, 1440, 1400 (pyrazole [12]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.37 t (3H, C**H**$_3$CH$_2$, *J* = 7.5 Hz), 4.74 q (2H, C**H**$_2$CH$_3$, *J* = 7.5 Hz), 6.12 t (1H, 4-H, *J* = 2 Hz), 7.29 d (1H, 3-H, *J* = 2 Hz), 7.37 d (1H, 5-H, *J* = 2 Hz).

1-Ethyl-3,5-dimethyl-1*H*-pyrazole (Ib) was synthesized in a similar way from 12.0 g (125.2 mmol) of 3,5-dimethyl-1*H*-pyrazole, 13.64 g (125.2 mmol) of ethyl bromide, and 10.52 g (187.8 mmol) of KOH. Yield 13.88 g (89%), colorless liquid, bp 140–142°C, n_D^{20} = 1.4702. IR spectrum, ν, cm^{-1}: 1545, 1465, 1375 (pyrazole). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.34 t (3H, C**H**$_3$CH$_2$, *J* = 7.2 Hz), 2.15 s (3H, 3-CH$_3$), 2.24 s (3H, 5-CH$_3$), 3.99 q (2H, C**H**$_2$CH$_3$, *J* = 7.2 Hz), 5.77 s (1H, 4-H).

1-Ethyl-1*H*-pyrazole-4-carbaldehyde (IIa). Phosphoryl chloride, 5.05 g (33 mmol), was added dropwise over a period of 5 min to a mixture of 2.88 g (30 mmol) of compound **Ia** in 5 ml of DMF on cooling with an ice–water mixture. The mixture was heated to 100°C, kept for 13 h at that temperature, cooled to room temperature, and poured into 50 ml of cold water. Aqueous sodium hydroxide was added to pH 4, and the mixture was treated with chloroform (5 × 20 ml). The extract was dried over sodium sulfate, and the solvent was removed on a rotary evaporator at a residual pressure of 100 mm. Yield 2.87 g (77%), oily substance, bp 46–48°C (5 mm), n_D^{20} = 1.5183. IR spectrum, ν, cm^{-1}: 1680 (C=O); 1540, 1460, 1390 (pyrazole). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.47 t (3H, C**H**$_3$CH$_2$, *J* 7.2 Hz), 4.27 q (2H, C**H**$_2$CH$_3$, *J* = 7.2 Hz), 7.95 s (1H, 3-H), 8.32 s (1H, 5-H), 9.86 s (1H, CHO). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 15.7 (CH$_3$), 48.1 (CH$_2$), 125.3 (C^4), 134.1 (C^5), 140.6 (C^3), 184.9 (CHO). Found, %: C 57.78; H 6.63; N 22.11. $C_6H_8N_2O$. Calculated, %: C.05; H 6.50; N 22.57.

1-Ethyl-3,5-dimethyl-1*H*-pyrazole-4-carbaldehyde (IIb) was synthesized in a similar way from 6.20 g (50 mmol) of compound **Ib** and 8.42 g (55 mmol) of $POCl_3$ (reaction time 6.5 h). Yield 69%, bp 142°C (30 mm), n_D^{20} = 1.5120. IR spectrum, ν, cm^{-1}: 1660 (C=O); 1540, 1485, 1370 (pyrazole). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.32 t (3H, C**H**$_3$CH$_2$, *J* = 7.2 Hz), 2.31 s (3H, 3-CH$_3$), 2.49 s (3H, 5-CH$_3$), 4.03 q (2H, C**H**$_2$CH$_3$, *J* = 7.2 Hz), 9.85 s (1H, CHO). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 9.7 (3-CH$_3$), 12.9 (5-CH$_3$), 15.3 (CH$_3$), 44.0 (CH$_2$), 118.7 (C^4), 144.6 (C^5), 150.5 (C^3), 184.3 (C=O). Found, %: C 62.58; H 7.50; N 18.12. $C_8H_{12}N_2O$. Calculated, %: C 63.13; H 7.95; N 18.41.

1,1'-Methylenebis(3,5-dimethyl-1*H*-pyrazole-4-carbaldehyde) (IV) was synthesized in a similar way from 5.10 g (25 mmol) of compound **III** [7] and 8.41 g (55 mmol) of $POCl_3$ (reaction time 6 h). Yield 87%, colorless crystals, mp 285°C (decomp., from benzene). IR spectrum, ν, cm^{-1}: 1680 (C=O); 1550, 1480, 1390 (pyrazole). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 2.34 s (6H, 3-CH$_3$), 2.81 s (6H, 5-CH$_3$), 6.32 s (2H, CH$_2$), 9.94 s (2H, CHO). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 10.2 (3-CH$_3$), 13.1 (5-CH$_3$), 60.0 (CH$_2$), 119.3 (C^4), 147.5 (C^5), 151.6 (C^3), 185.8 (C=O). Found, %: C 60.00; H 6.24; N 21.60. $C_{13}H_{16}N_4O_2$. Calculated, %: C.99; H 6.20; N 21.52.

1-Ethyl-1*H*-pyrazole-4-carbaldehyde azine (Va). Hydrazine sulfate, 0.130 g (1 mmol), was added to

a solution of 0.248 g (2 mmol) of compound **IIa** in 1 ml of 25% aqueous ammonia. The mixture was left to stand for 12 h at room temperature, and the precipitate was filtered off and washed with water. Yield 0.210 g (86%), colorless crystals, mp 108–109°C (from benzene–hexane, 1:1). IR spectrum, ν, cm^{-1}: 1625 (C=N); 1530, 1440, 1375 (pyrazole). ^1H NMR spectrum (acetone-d_6), δ, ppm: 1.48 t (6H, C**H**$_3$CH$_2$, J = 7.2 Hz), 4.25 q (4H, C**H**$_2$CH$_3$, J = 7.2 Hz), 7.84 s (2H, 3-H), 8.08 s (2H, 5-H), 8.52 s (2H, CH=N). Found, %: C 58.68; H 6.72; N 34.88. $C_{12}H_{16}N_6$. Calculated, %: C 59.00; H 6.60; N.40.

1-Ethyl-3,5-dimethyl-1*H*-pyrazole-4-carbaldehyde azine (Vb) was synthesized in a similar way from 0.152 g (1 mmol) of aldehyde **IIb** and 0.065 g (0.5 mmol) of hydrazine sulfate. Yield 95%, colorless crystals, mp 175–176°C (from benzene). IR spectrum, ν, cm^{-1}: 1620 (C=N); 1530, 1490, 1360 (pyrazole). ^1H NMR spectrum (acetone-d_6), δ, ppm: 1.47 t (6H, C**H**$_3$CH$_2$, J = 6.9 Hz), 2.48 s (6H, 3-CH$_3$), 2.63 s (6H, 5-CH$_3$), 4.19 q (4H, C**H**$_2$CH$_3$, J = 6.9 Hz), 8.69 s (2H, CH=N). Found, %: C 64.39; H 8.38; N 27.74. $C_{16}H_{24}N_6$. Calculated, %: C.97; H 8.05; N 27.97.

***N*,*N*′-Bis[(1-ethyl-1*H*-pyrazol-4-yl)methylidene]-ethane-1,2-diamine (VIa).** A solution of 0.248 g (2 mmol) of compound **IIa** and 0.078 g (1 mmol) of ethylenediamine monohydrate in 1 ml of benzene was kept for 24 h at room temperature. The solvent was removed, and the solid residue was recrystallized from hexane–toluene, 1:1. Yield 0.169 g (62%), colorless crystals, mp 78–79°C. IR spectrum, ν, cm^{-1}: 1645 (C=N); 1550, 1440, 1380 (pyrazole). ^1H NMR spectrum (acetone-d_6), δ, ppm: 1.44 t (6H, C**H**$_3$CH$_2$, J = 7.2 Hz), 3.72 s (4H, CH$_2$CH$_2$), 4.18 q (4H, C**H**$_2$CH$_3$, J = 7.2 Hz), 7.71 s (2H, 3-H), 7.92 (2H, 5-H), 8.20 s (2H, CH=N). Found, %: C.49; H 7.37; N 31.03. $C_{14}H_{20}N_6$. Calculated, %: C 61.74; H 7.40; N 30.86.

***N*,*N*′-Bis[(1-ethyl-3,5-dimethyl-1*H*-pyrazol-4-yl)-methylidene]ethane-1,2-diamine (VIb)** was synthesized in a similar way from 0.456 g (3 mmol) of aldehyde **IIb** and 0.117 g (1.5 mmol) of ethylenediamine monohydrate. Yield 77%, mp 101.5–102.5°C (from hexane–toluene, 3:1). IR spectrum, ν, cm^{-1}: 1640 (C=N); 1550, 1440, 1365 (pyrazole). ^1H NMR spectrum (acetone-d_6), δ, ppm: 1.32 t (6H, C**H**$_3$CH$_2$, J = 7.2 Hz), 2.26 s (6H, 3-CH$_3$), 2.41 s (6H, 5-CH$_3$), 3.73 s (4H, CH$_2$CH$_2$), 4.01 q (4H, C**H**$_2$CH$_3$, J = 7.2 Hz), 8.24 s (2H, CH=N). Found, %: C.09; H 8.37; N 25.41. $C_{18}H_{28}N_6$. Calculated, %: C 65.82; H 8.59; N 25.59.

***N*,*N*′-Bis[(1-ethyl-1*H*-pyrazol-4-yl)methylidene]-benzene-1,4-diamine (VIIa).** A solution of 0.248 g (2 mmol) of compound **IIa** and 0.108 g (1mmol) of *p*-phenylenediamine in 1 ml of dioxane was kept for 3 h at room temperature. The mixture was poured into 15 ml of water and treated with chloroform (3×10 ml), the extract was dried over sodium sulfate, and the solvent was removed to obtain 0.306 g (96%) of a solid material which was recrystallized from isopropyl alcohol. Yield 0.228 g (71%), light yellow crystals, mp 166–167°C. IR spectrum, ν, cm^{-1}: 1620 (C=N); 1550, 1360 (pyrazole). ^1H NMR spectrum (acetone-d_6), δ, ppm: 1.49 t (6H, C**H**$_3$CH$_2$, J = 7.2 Hz), 4.25 q (4H, C**H**$_2$CH$_3$, J = 7.2 Hz), 7.21 s (4H, H$_{arom}$), 7.91 s (2H, 3-H), 8.16 s (2H, 5-H), 8.51 s (2H, CH=N). Found, %: C 67.54; H 6.03; N.91. $C_{18}H_{20}N_6$. Calculated, %: C 67.48; H 6.29; N 26.23.

***N*,*N*′-Bis[(1-ethyl-3,5-dimethyl-1*H*-pyrazol-4-yl)-methylidene]benzene-1,4-diamine (VIIb)** was synthesized in a similar way from 0.608 g (4 mmol) of aldehyde **IIb** and 0.216 g (2 mmol) of *p*-phenylenediamine. Yield 86%, mp 178–179°C (from *i*-PrOH–H$_2$O, 1:1). IR spectrum, ν, cm^{-1}: 1620 (C=N); 1550, 1445, 1355 (pyrazole). ^1H NMR spectrum (acetone-d_6), δ, ppm: 1.37 t (6H, C**H**$_3$CH$_2$, J = 6.9 Hz), 2.42 s (6H, 3-CH$_3$), 2.58 s (6H, 5-CH$_3$), 4.09 q (4H, C**H**$_2$CH$_3$, J = 6.9 Hz), 7.20 s (4H, H$_{arom}$), 8.52 s (2H, CH=N). Found, %: C 69.83; H 7.64; N 22.59. $C_{22}H_{28}N_6$. Calculated, %: C.18; H 7.50; N 22.32.

***N*,*N*′-Bis[(1-ethyl-1*H*-pyrazol-4-yl)methylidene]-biphenyl-4,4'-diamine (VIIIa).** A solution of 0.248 g (2 mmol) of compound **IIa** and 0.184 g (1 mmol) of benzidine in 12 ml of dioxane was kept for 24 h at room temperature. The mixture was poured into 80 ml of water, and the precipitate was filtered off and dried. Yield 0.315 g (80%), mp 215–216°C (from hexane–toluene, 1:1). IR spectrum, ν, cm^{-1}: 1620 (C=N); 1585 (C=C$_{arom}$); 1545, 1445, 1380 (pyrazole). ^1H NMR spectrum (acetone-d_6), δ, ppm: 1.51 t (6H, C**H**$_3$CH$_2$, J = 7.2 Hz), 4.28 q (4H, C**H**$_2$CH$_3$, J = 7.2 Hz), 7.28 d (4H, 3-H$_{arom}$, J = 8.1 Hz), 7.71 d (4H, 2-H$_{arom}$, J = 8.1 Hz), 7.94 s (2H, 3-H), 8.19 (2H, 5-H), 8.55 s (2H, CH=N). Found, %: C 72.99; H 6.24; N 21.37. $C_{24}H_{24}N_6$. Calculated, %: C 72.70; H 6.10; N 21.20.

***N*,*N*′-Bis[(1-ethyl-3,5-dimethyl-1*H*-pyrazol-4-yl)-methylidene]biphenyl-4,4'-diamine (VIIIb)** was synthesized in a similar way from 0.608 g (4 mmol) of aldehyde **IIb** and 0.368 g (2 mmol) of benzidine. Yield 80%, mp 184.5–185°C (from *i*-PrOH). IR spectrum, ν, cm^{-1}: 1625 (C=N); 1600 (C=C$_{arom}$); 1545, 1355 (pyra-

zole). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.38 t (6H, C**H**$_3$CH$_2$, J = 7.2 Hz), 2.44 s (6H, 3-CH$_3$), 2.59 s (6H, 5-CH$_3$), 4.11 q (4H, C**H**$_2$CH$_3$, J = 7.2 Hz), 7.27 d (4H, 3-H$_{arom}$, J = 6.9 Hz), 7.67 d (4H, 2-H$_{arom}$, J = 6.9 Hz), 8.54 s (2H, CH=N). Found, %: C.78; H 7.47; N.15. $C_{28}H_{32}N_6$. Calculated, %: C 74.30; H 7.13; N.56.

Bis[3,5-dimethyl-4-(phenyliminomethyl)-1*H*-pyrazol-1-yl]methane (IX). Aniline, 2 ml (20 mmol), and concentrated hydrochloric acid, 0.2 ml, were added to a solution of 0.300 g (1.15 mmol) of compound **IV** in 20 ml of ethanol. After 5 min, the colorless precipitate was filtered off. Yield 0.283 g (61%), mp 157–158°C (from hexane–toluene, 1:1). The filtrate was poured into 200 ml of water and extracted with chloroform (4×15 ml), and the extract was evaporated to isolate an additional portion (0.110 g) of compound **IX**. Overall yield 84%. IR spectrum, ν, cm^{-1}: 1620 (C=N); 1580 (C=C$_{arom}$); 1545, 1420, 1345 (pyrazole). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 2.42 s (6H, 3-CH$_3$), 2.85 s (6H, 5-CH$_3$), 6.32 s (2H, CH$_2$), 7.16–7.37 m (10H, H$_{arom}$), 8.48 s (2H, CH=N). Found, %: C 73.31; H 6.12; N 20.08. $C_{25}H_{26}N_6$. Calculated, %: C 73.14; H 6.38; N 20.47.

(1*E*,4*E*)-1,5-Bis(1-ethyl-3,5-dimethyl-1*H*-pyrazol-4-yl)penta-1,4-dien-3-one (X). A solution of 0.912 g (6.0 mmol) of compound **IIb**, 0.22 ml (3.0 mmol) of acetone, and 0.360 g (9.0 mmol) of sodium hydroxide in a mixture of 5 ml of ethanol and 5 ml of water was left to stand for 12 h at room temperature. The mixture was diluted with 20 ml of water and treated with chloroform (4×15 ml). The solvent was removed from the extract to isolate 0.747 g (76%) of compound **X**, mp 137–137.5°C (from *i*-PrOH–H$_2$O, 1:1). IR spectrum, ν, cm^{-1}: 1650 (C=C); 1620 (C=O): 1580, 1435, 1345 (pyrazole). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.38 t (6H, C**H**$_3$CH$_2$, J = 6.9 Hz), 2.38 s (6H, 3-CH$_3$), 2.45 s (6H, 5-CH$_3$), 4.12 q (4H, C**H**$_2$CH$_3$, J = 6.9 Hz), 6.79 d [2H, **H**C=CHC(O), J = 15.9 Hz], 7.68 d [2H, HC=C**H**C(O), J = 15.9 Hz]. Found, %: C 70.07; H 7.95; N.22. $C_{19}H_{26}N_4O$. Calculated, %: C 69.91; H.03; N 17.16.

REFERENCES

1. Pettinari, C., Marchetti, F., Cingolani, A., Leonesi, D., Colapietro, M., and Margadonna, S., *Polyhedron*, 1998, vol. 17, p. 4145; Pettinari, C., Cingolani, A., Lobbia, G., Marchetti, F., Martini, D., Pellei, M., Pettinari, R., and Santini, C., *Polyhedron*, 2004, vol. 23, p. 451.
2. Pettinari, C., Lorenzotti, A., Sclavi, G., Cingolani, A., Rivarola, E., Colapietro, M., and Cassetta, A., *J. Organomet. Chem*., 1995, vol. 496, p. 69; Chai, J.F., Tang, L.F., Jia, W.L., Wang, Z.H., Wang, J.T., Leng, X.B., and Wang, H.G., *Polyhedron*, 2001, vol. 20, p. 3249.
3. Pomogailo, A.D. and Uflyand, I.E., *Ros. Khim. Zh*., 1996, vol. 40, nos. 4–5, p. 55.
4. Khuhawar, M.Y., Mughal, M.A., and Channar, A.H., *Eur. Polym. J*., 2004, vol. 40, p. 805.
5. Khlebnikov, A.I., Anfinogenov, V.A., Rybal'chenko, T.A., and Filimonov, V.D., *Izv. Vyssh. Uchebn. Zaved., Ser. Khim. Khim. Tekhnol*., 1996, nos. 1–2, p. 31.
6. Starikova, O.V., Dolgushin, G.V., Larina, L.I., Komarova, T.N., and Lopyrev, V.A., *Arkivoc*, 2003, part 13, p. 119.
7. Potapov, A.S. and Khlebnikov, A.I., *Izv. Vyssh. Uchebn. Zaved., Ser. Khim. Khim. Tekhnol*., 2003, no. 7, p. 66.
8. Diez-Barra, E., de la Hoz, A., Sánchez-Migallón, and Tejeda, J., *Synth. Commun*., 1990, vol. 20, p. 2849.
9. Finar, I.L. and Lord, G.H., *J. Chem. Soc*., 1957, p. 3314.
10. Takagi, K., Bajnati, A., and Hubert-Habart, M., *Bull. Soc. Chim. Fr*., 1990, p. 660.
11. *HyperChem Computational Chemistry: Molecular Visualization and Simulation (Release 7 for Windows)*, Hypercube, Canada, 2002.
12. *Physical Methods in Heterocyclic Chemistry*, Katritzky, A.R., Ed., New York: Academic, 1963.