Pyrazoles XI. The Synthesis of 1,1′-Dimethylbipyrazolyls (I)

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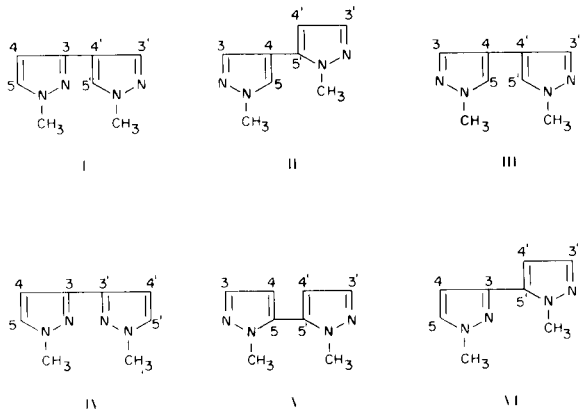
The synthesis of al six isomers of 1,1′-dimethylbipyrazolyl is reported. Their structure assignments were based on nmr data. Nmr spectra were determined in widely different solvents and structure assignments were based on these data, particularly on the found solvent effect. Uv spectral data are also reported.

Introduction.

In connection with our studies of the nitration of pyrazoles (2,3) and particularly of the facile 3-nitration of 1-methyl-4-phenylpyrazole (3) in acetic anhydride solution, the synthesis of the 1,1′-dimethylbipyrazolyl isomers I-VI (see Chart 1) became of interest to us.

CHART 1

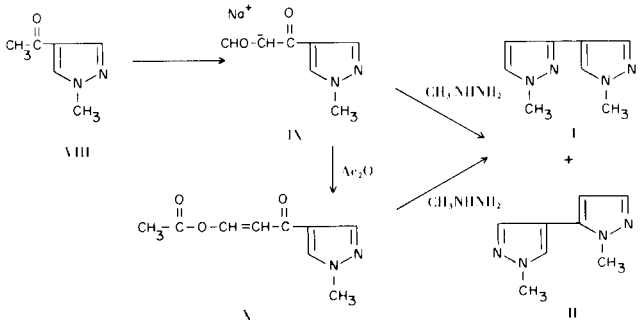


Although many syntheses for bipyrazolyls are reported in literature (4,5,6,7,8), most of them are for polysubstituted bipyrazolyls. Only a few isomers of 1,1′-diphenylbipyrazolyl are known (9,10,11) and two isomers of unsubstituted bipyrazolyl have been described (12,13). To our knowledge no unsubstituted 1,1′-dimethylbipyrazolyls have been reported.

Results.

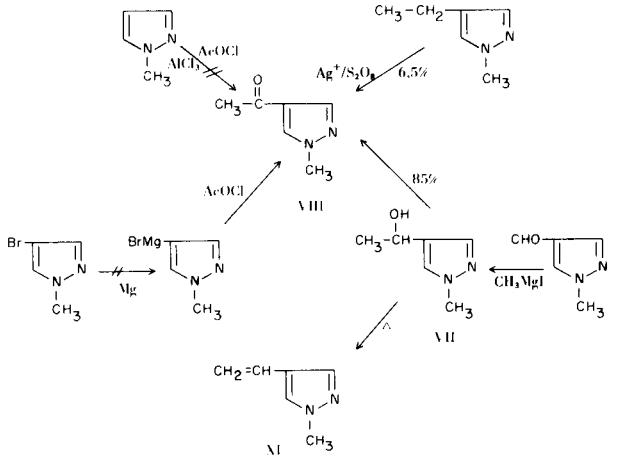
1,1′-Dimethyl-3,4′-bipyrazolyl (I) and 1,1′-dimethyl-4,5′-bipyrazolyl (II) were obtained by ringclosure of 1-(1-methyl-4-pyrazolyl)malonaldehyde (IX) with methylhydrazine (Chart 2). An overall yield of 66% (I/II = 1/9) was obtained when IX was converted to 1-acetoxy-2-(1-methyl-4-pyrazolyl)ethylene (X) before treatment with

CHART 2



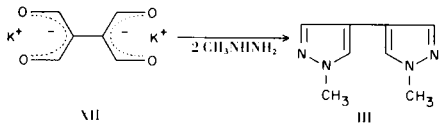
methylhydrazine whereas direct treatment of IX with methylhydrazine only gave a total yield of 33%. Compound IX was the product of formylation of 4-acetyl-1-methylpyrazole (VIII) obtained in excellent yield on oxidation of 1-(1-methyl-4-pyrazolyl)ethanol (VII), which in turn was obtained in good yield from 4-formyl-1-methylpyrazole (14) by action of methylmagnesium iodide. For the preparation of VIII a number of possible synthetic routes were investigated (see Experimental) of which

CHART 3



direct acylation as well as a synthesis *via* 1-methyl-4-pyrazolylmagnesium bromide with acetyl chloride proved to be unsuccessful. Albeit in exceptional low yield (6.5%) VIII could be obtained by oxidation with the silver ion/persulfate couple (15) of 1-methyl-4-ethylpyrazole (16). The method above starting from 4-formyl-1-methylpyrazole (see Chart 3) appeared to be the method of choice. Because of the ratio 1/9 in which the isomers I and II were obtained, the synthesis reported here appears to be primarily a convenient one for the preparation of II.

CHART 4



XII III

1,1′-Dimethyl-4,4′-bipyrazolyl (III), 54%, was prepared from a condensation of methylhydrazine and the potassium salt of 1,1,2,2-ethanetetracarboxaldehyde (XII) (Chart 4), according to the procedure used for the synthesis of 4,4′-bipyrazolyl as described by Trofimenko (13). In general, the utility of this condensation reaction is, however, limited by the rather inaccessibility of XII, which can be prepared by a seven step synthesis starting from diethyl succinate (17,18,19). Efforts to synthesise III from an Ullmann reaction (*cf.* ref. 4) with 4-iodo-1-methylpyrazole failed.

For the synthesis of IV, V and VI the direct condensation of 1,6-diethoxy-1,5-hexadiene-3,4-dione (XIII) with methylhydrazine derived from a method of Effenberger (12) turned out to be the most useful (see Chart 5). Though in low yield (25-34%), in this way all three isomers were obtained and their separation was achieved by

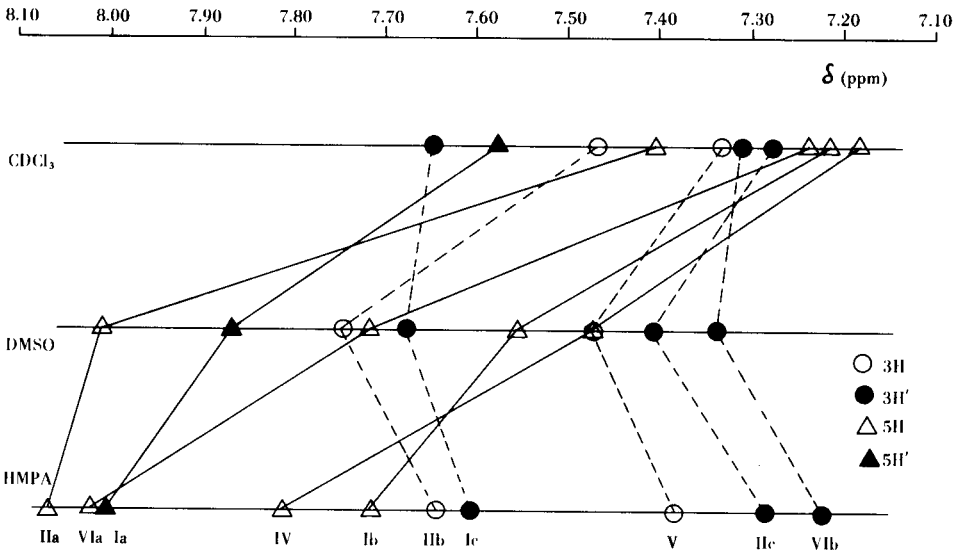


Fig. 1. Solvent effect (deuteriochloroform, DMSO and HMPA) on the chemical shifts of the 3 and 5 protons.

3,4′-isomer.

Ia : 5′-proton.
Ib : 5-proton.
Ic : 3′-proton.

3,3′-isomer.

IV : 5 and 5′-proton.

5,5′-isomer.

V : 3 and 3′-proton.

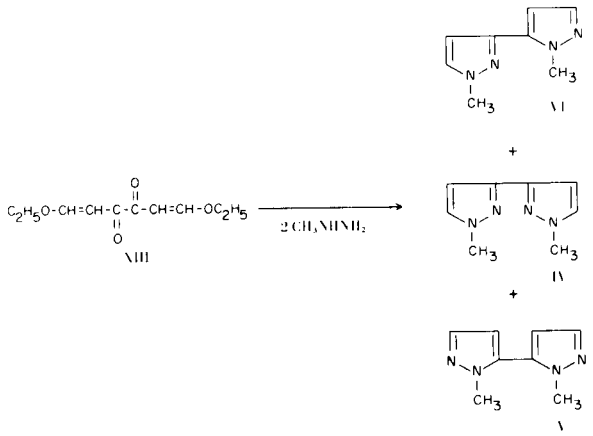
4,5′-isomer.

IIa : 5-proton.
IIb : 3-proton.
IIc : 3′-proton.

3,5′-isomer.

VIa : 5-proton.
VIb : 3′-proton.

CHART 5



fractional sublimation and by short column chromatography (20). The structure of III determined by its method of synthesis is confirmed by its nmr spectrum (see Table I). The structure assignments of I and II and of IV, V and VI were based on the following nmr spectral evidence. From the investigations of Elguero and Jacquier (21) it is known that in the solvents deuteriochloroform and perdeuteriobenzene the 5-proton resonance signal of 1-methyl substituted pyrazoles is distinguished from the signal of the 3-proton by appearing at higher field and with a larger coupling constant ($J_{45} > J_{34}$). In addition a 5-proton resonance signal shows a pronounced solvent effect consisting of a large shift to lower external field in going from nonpolar solvents to polar solvents like DMSO and HMPA. For the 3-proton signal on the contrary, no such shift or only a much smaller one to higher field is observed.

In the case of compounds I and II the nmr spectrum of I showed a pronounced solvent effect (see Fig. 1) for the doublet found at highest external field in deuteriochloroform. In addition this doublet in all three solvents has a larger coupling constant than found for the doublet signals in the spectra of II (J = 1.9-2.0 as compared to J = 1.5-1.7) (see Table I). Consequently I was assigned the structure 1,1′-dimethyl-3,4′-bipyrazolyl with a pyrazole ring with two adjacent protons in the positions 4 and 5. Compound II was assigned the structure 1,1′-dimethyl-4,5′-bipyrazolyl with a pyrazole ring with two adjacent protons in the positions 3 and 4.

In the case of the three isomers IV, V and VI only VI showed two different pairs of adjacent protons with different coupling constants (J = 1.7-1.8 and J = 2.1-2.2) (see Table I) and was therefore assigned the structure with the bond from the 3-position in one pyrazole ring to the 5-position in the other pyrazole ring. Correspondingly, only one proton, that with the largest coupling constant, shows a pronounced solvent effect (see Fig. 1). The nmr spectral difference between IV and V showed a pronounced solvent effect for the doublet found in the spectra of IV (see Fig. 1) in addition to larger coupling constants in all three solvents than found in the spectra of V (J = 2.0 as compared to J = 1.7-1.9) (see Table I). Consequently IV was assigned the structure 1,1′-dimethyl-3,3′-bipyrazolyl with the bond from the 3-position in one ring to the 3-position in the other pyrazole ring, while both rings contain two adjacent protons in the positions 4 and 5. The isomer V was assigned the structure 1,1′-dimethyl-5,5′-bipyrazolyl with the bond from the 5-position in one ring to the 5-position in the other pyrazole

TABLE I

Chemical Shift in Ppm

Bipyrazolyl	Solvent	5H	5H′	3H	3H′	4H	4H′	J in Hz
I	$CDCl_3$	7.22	7.58	-----	7.65	6.14	-----	J_{45} = 1,9
	DMSO	7.56	7.87	-----	7.68	6.32	-----	J_{45} = 2,0
	HMPA	7.72	8.02	-----	7.61	6.27	-----	J_{45} = 2.0
II	$CDCl_3$	7.41	-----	7.47	7.28	-----	6.10	$J_{3'4'}$ = 1.5
	DMSO	8.01	-----	7.75	7.41	-----	6.34	$J_{3'4'}$ = 1.7
	HMPA	8.07	-----	7.65	7.29	-----	6.24	$J_{3'4'}$ = 1.7
III	$CDCl_3$	7.23	7.23	7.35	7.35	-----	-----	-----
IV	$CDCl_3$	7.18	7.18	-----	-----	6.39	6.39	J_{45} = 2.0
	DMSO	7.48	7.48	-----	-----	6.31	6.31	J_{45} = 2.0
	HMPA	7.82	7.82	-----	-----	6.32	6.32	J_{45} = 2.0
V	$CDCl_3$	-----	-----	7.33	7.33	6.12	6.12	J_{34} = 1.9
	DMSO	-----	-----	7.48	7.48	6.48	6.48	J_{34} = 1.6
	HMPA	-----	-----	7.39	7.39	6.57	6.57	J_{34} = 1.7
VI	$CDCl_3$	7.24	-----	-----	7.32	6.27	6.31	$J_{3'4'}$ = 1.8; J_{45} = 2.1
	DMSO	7.72	-----	-----	7.34	6.42	6.50	$J_{3'4'}$ = 1.8; J_{45} = 2.1
	HMPA	8.02	-----	-----	7.23	6.52	6.47	$J_{3'4'}$ = 1.7; J_{45} = 2.2

ring, while both rings contain two adjacent protons in the positions 3 and 4.

The uv spectra of the six isomeric 1,1′-dimethylbipyrazolyls, determined in methanol at room temperature, are tabulated in Table II. The magnitudes of their maximum wavelength of the longest π-π^* absorption band appear to be much larger than found for alkylpyrazoles but only somewhat smaller than found for the monophenylpyrazoles (22,23,24). This indicates that the conjugation between two pyrazole moieties is of the same order of magnitude as found for a pyrazole ring and a phenyl group. The fact that the lowest value is found for V may indicate a hypsochromic shift due to two methyl groups in the ortho position.

TABLE II

Uv Spectral Data of 1,1′-Dimethylbipyrazolyls in Methanol at Room Temperature (in nm).

No.	Isomer	λ max	log ε
I	3,4′	240	4.43
II	4,5′	236	4.44
III	4,4′	233	4.55
IV	3,3′	243	4.50
V	5,5′	227	4.46
VI	3,5′	244	4.48

EXPERIMENTAL

All melting and boiling points are uncorrected. Elemental analyses were performed by Mr. W. J. Buis in the Micro Analytic Department of TNO, Utrecht, The Netherlands. Nmr spectra were recorded on a Jeol Minimar 60 MHz; chemical shifts are given relative to tetramethylsilane. All glc data were obtained on a Varian Aerograph Series 1400 instrument, using a 2% O.V.17 column (temp. 180°). Uv spectra were measured at room temperature in methanol on a Bausch and Lomb Spectronic 505 and a Carry 1115 spectrophotometer. The results (see Table II) are the average values of a number of measurements. The accuracy of the given data is within 2%. Mass spectra were taken on an AEI type MS 902 instrument.

1-(1-Methyl-4-pyrazolyl)ethanol (VII).

To methylmagnesium iodide (magnesium 5.85 g., 0.24 mole; methyl iodide, 34.0 g., 0.24 mole) in ether (150 ml.) was added dropwise 22 g. (0.20 mole) 4-formyl-1-methylpyrazole (14) in benzene (500 ml.) during 2 hours with stirring. The mixture was gently refluxed for a further 3 hours, cooled, and hydrolysed, while cooled in ice-water, by the dropwise addition of 25% ammonium chloride solution (200 ml.). The benzene-ether layer was separated from the aqueous layer, dried (magnesium sulfate) and evaporated. The residual yellow oil contained, in addition to some of the desired alcohol, much of the unreacted aldehyde. After being saturated with sodium chloride the aqueous layer was continuously extracted overnight with ether (500 ml.). Evaporation of the dried (magnesium sulfate) ether extract yielded 1-(1-methyl-4-pyrazolyl)ethanol (VII) (21.9 g., 87%) as a pale yellow liquid, n_D^{20} = 1.500. The liquid was used without purification in the next step, being the oxidation to 4-acetyl-1-methylpyrazole (VIII), because distillation even under low pressure causes the compound to lose water (25) to give 1-methyl-4-vinylpyrazole (XI) (see the synthesis of XI).

4-Acetyl-1-methylpyrazole (VIII).

A number of alternative routes have been investigated. Compound VIII could not be prepared by acylation of 1-methylpyrazole by action of acetyl chloride/aluminum trichloride in 1,2-dichloroethane. A reaction to obtain VIII by acylation with boron trifluoride and acetyl chloride has been reported to fail (26). Brooklyn and Finar (10) were able to synthesise 4-acetyl-1-phenylpyrazole from acetyl chloride and 1-phenyl-4-pyrazolylmagnesium bromide, which was prepared from 4-bromo-1-phenylpyrazole and magnesium by use of ethylene dibromide as an entrainer (27,28). This procedure failed for 4-bromo-1-methylpyrazole (29); in our hands 1-methyl-4-pyrazolylmagnesium bromide was not formed, for carbonation with Dry Ice gave no 1-methylpyrazole-4-carboxylic acid.

(a) A solution of 1-(1-methyl-4-pyrazolyl)ethanol (VII) (12.6 g., 0.1 mole) in acetone (80 ml.) was added slowly, with stirring, to a cold acid dichromate solution (500 ml.; 100 g. of sodium dichromate, 250 ml. of concentrated sulphuric acid, 750 ml. of water), while the temperature was maintained below 5° by cooling with an ice bath. After stirring for an additional hour at 0° the mixture was made basic by cautiously adding sodium hydroxide solution (temperature below 20°), filtered and extracted with ether. The ether layer was dried over magnesium sulfate and yielded, after evaporation, 6.2 g. of VIII as a colourless liquid which crystallised as white needles when cooled. The water layer was continuously extracted overnight with ether and the ether extract was dried (magnesium sulfate) and evaporated to give an additional 4.3 g. of VIII. Total yield 10.5 g. (85%) m.p. 50-52°. The ketone was pure enough to be used in the next step. Recrystallisation from petroleum-ether 40-60° or sublimation (60°, 12 mm.) gave a pure product, m.p. 57-59°.

Anal. Calcd. for $C_6H_8N_2O$: C, 58.05; H, 6.50; N, 22.57. Found: C, 58.60; H, 6.68; N, 22.76.

2,4-Dinitrophenylhydrazone m.p. 256° (from methanol).

Anal. Calcd. for $C_{12}H_{12}N_6O_4$: C, 47.37; H, 3.98; N, 27.62. Found: C, 47.26; H, 3.96; N, 27.90.

(b) A solution of 0.61 g. of silver nitrate in 2 ml. of water was added, with stirring, to a mixture of 15 g. (0.136 mole) of 4-ethyl-1-methylpyrazole (16) and 68 g. of ammonium persulfate in 270 ml. of water, which was heated at 50-55° by an oil bath. The internal temperature slowly rose to about 70° and was maintained at 75° for 3 hours. The reaction mixture was cooled to room temperature, made basic with sodium hydroxide solution to *p*H = 9 and saturated with sodium chloride. Continuous extraction with ether overnight yielded after drying (magnesium sulfate) and evaporation of the ether a brown oil, which was vacuum distilled. At 62-63°/15 mm. 8.7 g. 4-ethyl-1-methylpyrazole was collected, followed, at about 130-150°/8 mm., by 2.2 g. of a colourless liquid, which partly crystallised when cooled. 4-Acetyl-1-methylpyrazole (VIII) could be isolated by stirring in cold light petroleum ether 40-60°, followed by filtration. Sublimation yielded 1.1 g. (6.5%) VIII, m.p. 57-59°. A mixed melting point with VIII, prepared under (a) showed no depression.

1-Methyl-4-vinylpyrazole (XI).

1-(1-Methyl-4-pyrazolyl)ethanol (VII) (55 g., 0.44 mole) was

slowly heated until distillation over a Vigreux column (20 cm.). At 83°/0.2 mm. a forerun of 2 ml. of a mixture of VII and XI was collected. While the temperature dropped to 54-55°/0.2 mm., XI was collected as a colourless liquid. The eliminated water (7.5 g.) was trapped in the cold finger of the oilpump. Redistillation gave pure 1-methyl-4-vinylpyrazole (XI). Yield 45 g. (94%), b.p. 72°/16 mm., n_D^{21} = 1.5222.

Anal. Calcd. for $C_6H_8N_2$: C, 66.64; H, 7.46; N, 25.91. Found: C, 66.82; H, 7.66; N, 25.85.

1,1'-Dimethyl-3,4'-bipyrazolyl (I) and 1,1'-Dimethyl-4,5'-bipyrazolyl (II).

A mixture of ethyl formate (5.2 g., 0.070 mole) and 4-acetyl-1-methylpyrazole (8.3 g., 0.067 mole) in anhydrous ether (40 ml.) was added dropwise, with stirring, to sodium methoxide (3.6 g., 0.067 mole) in anhydrous ether (60 ml.). The temperature was not allowed to exceed 5°. After a short period of time the sodium salt of 1-(1-methyl-4-pyrazolyl)malonaldehyde separated. The stirring was continued for an additional 1 hour at 0°. The solid was collected and washed with ether followed by hot acetone and dried to give IX (8.5 g., 61%) as a pale yellow powder, m.p. above 250°. Compound IX was used without any further purification.

(a) To IX (4.0 g., 0.023 mole), dissolved in a minimum amount of water, acetic anhydride was added slowly until an acid solution was obtained. During the addition a voluminous precipitate appeared, which filled the whole reaction vessel. To allow stirring the slurry was diluted with water and methylhydrazine (1.7 g., 0.037 mole) was added dropwise. Finally the mixture was heated at 80° for ½ hour and cooled. The resulting clear solution was made basic with sodium hydroxide and saturated with sodium chloride. Continuous extraction overnight with ether gave, after drying (magnesium sulfate) and evaporation of the ether, a mixture of the two isomers (2.8 g.) as a red oil. GLC data showed I/II = 1/9. The separation and isolation was achieved by short column chromatography (20) (silica G nach Stahl, Merck; eluent acetone/hexane 2/1). Compound II was first eluated (2.20 g.) followed by I (0.25 g.). Total yield 2.45 g. (66%). Compound II was further purified by molecular distillation (temp. about 135°/0.01 mm.) to give a colourless liquid, n_D^{20} = 1.5673.

Anal. Calcd. for $C_8H_{10}N_4$: C, 59.24; H, 6.21; N, 34.55. Found: C, 58.98; H, 6.01; N, 34.33.

Picrate, m.p. 211-212° (from benzene).

Anal. Calcd. for $C_{14}H_{13}N_7O_7$: C, 42.97; H, 3.35; N, 25.06. Found: C, 43.43; H, 3.53; N, 24.60.

Compound I crystallised at -10° (white needles), but melted partially at room temperature. The mass-spectrum indicated a pure product. Molecular weight calcd. for $C_8H_{10}N_4$: 162.0905. Found: 162.0909. No picrate could be obtained.

The precipitate, which appeared during the addition of acetic anhydride was investigated in a separate experiment for which it was collected, washed with water and dried. Recrystallisation from ethanol gave white plates, m.p. 147-148°. From the total absence of an aldehyde-hydrogen in the ir and nmr spectra and the appearance of a ν C=O (1760 cm^{-1}) in the ir spectrum the structure of X was assigned; ir (potassium bromide disk): 1760 and 1675 cm^{-1} (acetoxy C=O and α,β-unsaturated C=O); nmr (deuteriochloroform): 2.26 (s, 3, acetoxy), 3.93 (s, 3, N-CH_3), 6.35 (d, 1, J = 12.6 Hz, ethylene), 7.70 (s, 2, 3 and 5-H), 8.13 (d, 1, J = 12.6 Hz, ethylene).

Anal. Calcd. for $C_9H_{10}N_2O_3$: C, 55.66; H, 5.19; N, 14.43. Found: C, 55.84; H, 5.09; N, 14.15.

(b) To IX (6.6 g., 0.038 mole), dissolved in a minimum amount of water, was added dilute sulfuric acid until a solution of *p*H=5 was obtained. Methylhydrazine (2.3 g., 0.050 mole) was added dropwise, with stirring to the clear solution, which became warm and a red oil separated. The mixture was heated for ½ hour at 80°, cooled, and worked up as described above under (a). Glc data showed I/II = 1/9. Short column chromatography (20) yielded II (2.20 g.) and I (0.25 g.); total yield 2.45 g. (33%).

1,1'-Dimethyl-4,4'-bipyrazolyl (III).

The potassium salt of 1,1,2,2 ethanetetracarboxyaldehyde (XII) (0.20 g., 9.10^{-4} mole), prepared by the procedure of Trofimenko from 3,4-furandicarboxaldehyde (13), was added, with stirring, to a solution of methylhydrazine (0.23 g., 5.10^{-3} mole) in 5 ml. of water. The solution which immediately became yellow, was stirred at room temperature for 15 hours, saturated with sodium chloride and extracted overnight with ether. The ether extract was dried (magnesium sulfate) and evaporated to give a light brown residue, which was sublimated twice. 1,1'-Dimethyl-4,4'-bipyrazolyl (III) was obtained as white crystals, m.p. 159-160°. Yield 0.08 g. (54%). The mass spectrum showed a pure product. Molecular weight calcd. for $C_8H_{10}N_4$: 162.0905. Found: 162.0910.

1,1'-Dimethyl-3,3'-bipyrazolyl (IV), 1,1'-Dimethyl-5,5'-bipyrazolyl (V) and 1,1'-Dimethyl-3,5'-bipyrazolyl (VI).

A solution of methylhydrazine (7.4 g., 0.16 mole) in anhydrous ether (40 ml.) was added at once to a solution of XIII (8.0 g., 0.04 mole), prepared according to Effenberger's procedure (12) in anhydrous ether (80 ml.), while keeping it below -12°. The reaction mixture was allowed to stand for 20 hours at -12°. The solvent was evaporated and the residue was boiled with 4*N* hydrochloric acid and decolourising carbon, filtered and made basic with sodium hydroxide solution, saturated with sodium chloride and continuously extracted overnight with ether. The ether-layer was dried (magnesium sulfate) and filtered. GLC data showed IV/V/VI = 1/2/2. Evaporation was achieved under vacuum without external heating. Half way this evaporation was interrupted to collect a precipitate on a Büchner funnel. This precipitate was a mixture of IV and V. Separation by fractional sublimation gave V at 90-100°/10 mm. and IV at 120-135°/10 mm. The residue, a red oil, obtained on further evaporation contained a mixture of all three isomers IV, V and VI. Isolation of the reaction products was achieved by short column chromatography (20) (silica G nach Stahl, Merck; eluent: acetone/hexane 2/1). The three products were obtained in the following order: respectively VI, V and IV. The total yield was 25-34% based on XIII. Compounds IV and V were purified by sublimation twice and VI was recrystallised from petroleum ether 80-100°.

1,1'-Dimethyl-3,3'-bipyrazolyl (IV), white needles, m.p. 149-150°.

Anal. Calcd. for $C_8H_{10}N_4$: C, 59.24; H, 6.21; N, 34.55. Found: C, 59.24; H, 6.26; N, 34.84.

1,1'-Dimethyl-5,5'-bipyrazolyl (V), white needles, m.p. 97-98°.

Anal. Calcd. for $C_8H_{10}N_4$: C, 59.24; H, 6.21; N, 34.55. Found: C, 59.32; H, 6.28; N, 34.48.

1,1'-Dimethyl-3,5'-bipyrazolyl (VI), white needles, m.p. 45.5-46.5°.

Anal. Calcd. for $C_8H_{10}N_4$: C, 59.24; H, 6.21; N, 34.55. Found: C, 59.24; H, 6.31; N, 34.76.

Both the time in which the methylhydrazine was added (at once or over a period of 30 minutes) and the polarity of the solvent (ether, ether/methanol 2/1 or methanol) turned out to

affect the ratio fo the three isomers, but in a small degree and the total yield did not exceed 34% of theoretical.

Acknowledgment.

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