TABLE I

ACETATE ESTERS

Formula	Yield, %[a]	B.p. °C.	Mm.	$n^{25}D$	Ester No.[b] Calcd.	Found
$CH_3CH_2CH_2OAc$	10	96–99	...	1.3810	550	516
C_4H_9OAc	33	108–123	...	....	...	...
$CH_3(CH_2)_2CH(CH_3)CH_2OAc$	11	157–159	...	1.4060	389	365
$C_5H_9CH_2OAc$	7	45–50	5	1.4300	395	406
$C_6H_{10}(CO_2H)(CH_2OAc)$[c]	29	150–158	1–2	1.4688	280	274
$C_8H_{17}OAc$	37	60–63	1–2	1.4180	326	283
$C_9H_{19}OAc$	70	55–60	2	1.4225	301	295
$C_{10}H_{14}(CH_2OAc)_2$	19	155–165	2–3	1.4878	401	375
$C_{13}H_{27}OAc$[d]	46	88–90	1–2	1.4350	232	225
$C_{13}H_{27}OAc$[e]	59	88–95	1–2	1.4360	232	232
$C_{17}H_{35}OAc$	54	123–130	1	1.4469	188	183

[a] Yield based on amount of unsaturated material used. [b] The ester, acid or hydroxyl number is the number of milligrams of potassium hydroxide equivalent to the amount of functional group undergoing reaction in one gram of sample. [c] Calculated acid number: 280; found 272. [d] Acetate ester from Sharples triiosbutylene. [e] Acetate ester from Shell tetrapropylene.

acid in the presence of one or two grams of cobalt acetate with a 1:1 gas mixture of carbon monoxide and hydrogen at 225–275° and 700 atm. pressure for one hour in a stainless steel shaker tube (325-cc. capacity). The shaker tube was cooled to room temperature and the pressure released. The resulting liquid products were worked up by distillation. In the case of ethylene and propylene, the propyl acetate and butyl acetates were isolated by steam distillation followed by drying and distillation. Cobalt laurate in the hydroformylation reactions gave comparable results to cobalt acetate. Recycling of the foreshot material (boiling in the range of the olefin) from the hydroformylation of liquid olefins produced substantially no additional acetate esters, indicating that the foreshot material was essentially the saturated hydrocarbon. The yields and properties of the acetate esters are listed in Table I.

Alcohols.—The alcohols were obtained in quantitative yields by methanolysis of the corresponding acetate esters in the presence of traces of sodium methoxide. The properties of the alcohols are given in Table II.

TABLE II

ALCOHOLS

Formula	B.p. °C.	Mm.	$n^{25}D$	OH No. Calcd.	Found
C_4H_9OH[a]	107–114	...	1.3935	...	...
$C_8H_{17}OH$[b]	177–181	...	1.4281	...	...
$C_{13}H_{27}OH$	95–100	2–3	1.4450	281	277
$C_{13}H_{27}OH$	110–117	2–3	1.4460	281	278
$C_{17}H_{35}OH$	140–145	4–5	1.4571	219	216

[a] Analysis of the butanols by the mass spectrograph showed the following composition in mole %: 24.1 *n*-butyl alcohol, 71.6 isobutyl alcohol, 1.8 *n*-butyl formate, 2.5 *n*-butyl acetate. [b] The mass spectrograms of an authentic sample of 2-ethylhexanol and the $C_8H_{17}OH$ fraction were made and found to be quite similar. However, differences were sufficient to indicate that more than one compound was present in one or both of the samples.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Structure of the Self-Condensation Product of 1-Phenyl-2-pyrazoline

BY H. R. SNYDER, FRANK VERBANAC AND D. BRUCE BRIGHT[1]

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The product obtained from the self-condensation of 1-phenyl-2-pyrazoline is shown to be 1,1′-diphenyl-3,3′-bi-2-pyrazoline (II). The structure is proved by characterization of oxidation products and by infrared studies. Oxidation of the substance yields 1,1′-diphenyl-3,3′-bipyrazole (V), identified by independent synthesis. 1,1′-Diphenyl-3,4′-bipyrazole (IV) has also been prepared. The reaction of 3-methyl-1-phenylpyrazole with *n*-butyllithium produces the 5-lithium derivative.

Treatment of 1-phenyl-2-pyrazoline with hydrogen chloride yields a self-condensation product which was referred to as bis-N-phenyl-Δ²-pyrazoline by Curtius and Wirsing.[2] In the present work the reaction was accomplished with boron trifluoride and boron trifluoride etherate as well as with dry hydrogen chloride. The product, a yellow solid which exhibits blue fluoresence in ether solution, was reported[2] to have a melting point of 221° and an empirical formula of $C_{18}H_{20}N_4$. However, the product obtained in this Laboratory melted at 235–237° (cor.), and the empirical formula $C_{18}H_{18}N_4$ was required by the analyses and the molecular weight determinations. Thus, the substance is not a simple dimer but rather the product of an oxidative coupling.

The infrared absorption spectrum of the self-condensation product is characterized by the presence of strong bands at 1596 and 1499 cm.$^{-1}$, the absorption being much more intense than that ordinarily attributed to a phenyl group. Similar bands were observed in the spectra of 1-phenyl-2-pyrazoline, 1,5-diphenyl-2-pyrazoline and 1,5-diphenyl-3-*p*-tolyl-2-pyrazoline. The great similarity of the absorption bands indicates that the structural feature common to these known pyrazolines, *i.e.*, the 1-phenyl-2-pyrazoline system, is also present in the self-condensation product. The spectrum of the unknown substance gave no indication of the presence of an –N–H group. Because

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[1] Atomic Energy Commission Fellow, 1951–1952.

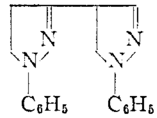
[2] Th. Curtius and F. Wirsing, *J. prakt. Chem.*, [2] 50, 531 (1894).

of the fluorescence of the substance, no detailed study of the ultraviolet absorption was undertaken.

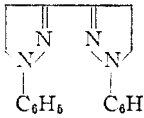
The self-condensation product could not be acetylated by acetic anhydride in pyridine; this test confirms the absence of –N–H groups. No pure product could be isolated after reduction with sodium and *n*-amyl alcohol or with zinc and acetic or hydrochloric acid, or after hydrogenation in the presence of Raney nickel catalyst.

Oxidation with potassium permanganate in pyridine yielded 1-phenylpyrazole-3-carboxylic acid along with a dehydrogenated compound, $C_{18}H_{14}N_4$, evidently a bipyrazole. When this product was reduced with sodium and ethyl alcohol, the yellow color and the fluorescence characteristic of the original substance were again observed.

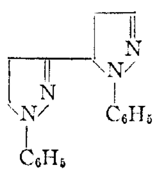
The isolation of the compound $C_{18}H_{14}N_4$ and the 3-carboxylic acid, together with the infrared studies, clearly indicates that the substance is a bi-2-pyrazoline and that the 3-position of one of the pyrazoline units must be a point of union. The possible structures are I, II and III.



I

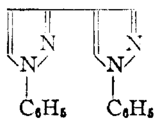


II

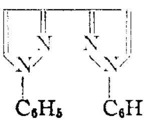


III

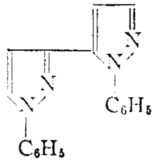
The corresponding bipyrazoles have the structures IV, V and VI.



IV



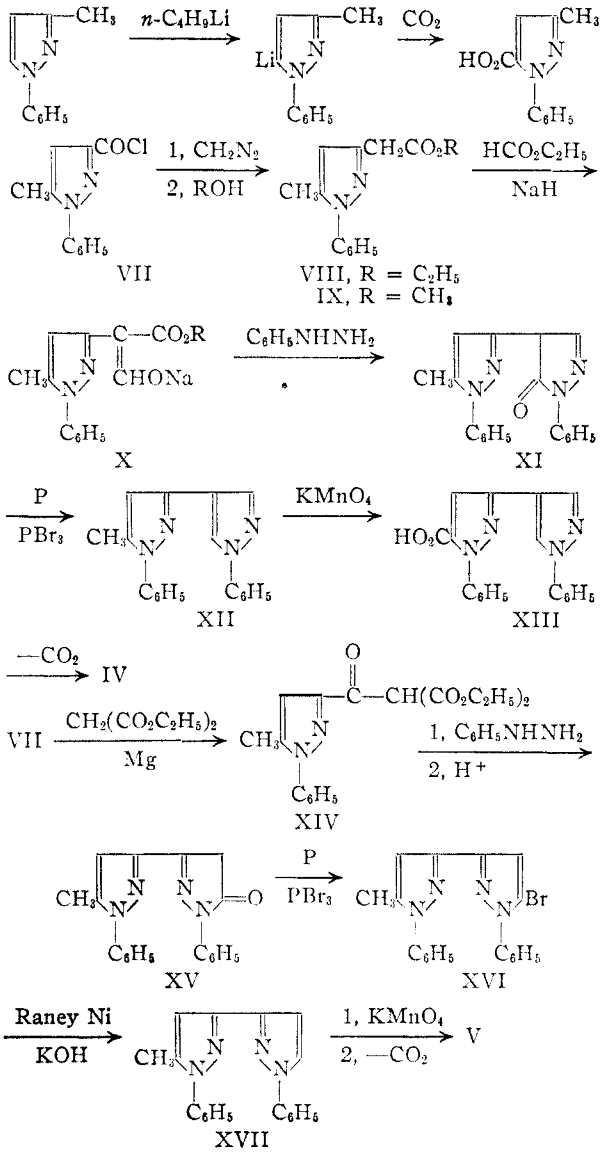
V



VI

The synthesis of these bipyrazoles was undertaken in order to elucidate the structure of the oxidation product $C_{18}H_{14}N_4$. The 3,4'-bipyrazole (IV) was prepared from 1-phenyl-5-methylpyrazole-3-carboxylic acid. Application of the Arndt–Eistert reaction to this acid was most successful when the silver benzoate catalyst of Newman and Beal[3] was employed. The homologous ester (IX) was formylated by the use of ethyl formate in the presence of sodium hydride and a trace of methyl alcohol, and the hydroxymethylene salt (X, probably a mixture of methyl and ethyl esters) was converted directly to the pyrazolone (XI) by treatment with acetic acid and phenylhydrazine. The reduction of XI with phosphorus and phosphorus tribromide proceeded smoothly to the bipyrazole (XII). Subsequent oxidation and decarboxylation produced IV. This bipyrazole proved to be different from the compound $C_{18}H_{14}N_4$ obtained by oxidation of the self-condensation product.

An attempt to synthesize 3-(1-phenylpyrazolyl)-acetic acid (related to VIII and IX) by a lithium–hydrogen exchange between *n*-butyllithium and 3-methyl-1-phenylpyrazole, followed by carbonation, was unsuccessful. The lithium exchange took place at the 5-position of the pyrazole, and 3-methyl-1-phenylpyrazole-5-carboxylic acid[4] was obtained.



1,1'-Diphenyl-3,3'-bipyrazole (V) was also prepared from 1-phenyl-5-methylpyrazole-3-carbonyl chloride (VII). The acylmalonic ester (XIV), characterized as the 2,4-dinitrophenylhydrazone, was made from VII and diethyl malonate. Treatment with phenylhydrazine followed by hydrolysis and decarboxylation yielded the pyrazolone (XV). The attempted reduction of XV resulted in the formation of a bromopyrazole (probably XVI) rather than the bipyrazole (XVII). However, XVI was readily debrominated with Raney nickel catalyst. Oxidation of the methyl group and decarboxylation gave V.

A mixed melting point determination and comparison of the infrared spectra showed V to be identical with the $C_{18}H_{14}N_4$ compound obtained by oxidation of the self-condensation product. Therefore, the original bipyrazoline must be 1,1'-diphenyl-3,3'-bi-2-pyrazoline (II). The carbon–ni-

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[3] M. S. Newman and P. F. Beal III, THIS JOURNAL, **72**, 5163, 1950)

[4] L. Claisen and P. Roosen, *Ann.*, **278**, 274 (1893).

trogen skeleton is fixed by the oxidative conversion to V. The location of the double bonds is based on the infrared absorption characteristics. The color of the compound also suggests that the double bonds are conjugated.

Experimental[5,6]

"**Bis-1-phenyl-Δ²-Pyrazoline.**" 1. **Boron Fluoride Catalyst.**—The general method of Snyder and Smith[7] for the boron trifluoride catalyzed Fischer indole synthesis was employed. A solution of 7.3 g. of 1-phenyl-2-pyrazoline[8] in 80 ml. of dry benzene was placed in a 500-ml. 3-necked flask, fitted with a gas inlet, a condenser and a gas outlet. Boron trifluoride gas was passed through the refluxing solution for 1.5 hours at a rate of 2–3 bubbles per second. The reaction mixture turned successively blue-green, light green and dark green, and a dark, oily material separated. The mixture was allowed to cool, and the benzene solution was washed with 5% sodium carbonate, water, 2 *N* hydrochloric acid and twice more with water. After drying overnight over potassium hydroxide pellets, the solution was concentrated, chilled and allowed to stand overnight. The dark yellow crystals were filtered, washed four times with 5-ml. portions of cold benzene and dried. Fractional crystallization from benzene finally yielded a yellow material, m. p. 235–239°, which exhibited the characteristic fluorescence described by Curtius and Wirsing.[2]

Anal. Calcd. for $C_{18}H_{18}N_4$: C, 74.45; H, 6.24; N, 19.30. Calcd. for $C_{18}H_{20}N_4$: C, 73.94; H, 6.89; N, 19.17. Found: C, 74.69; H, 6.28; N, 19.18.

2. **Boron Fluoride Etherate Catalyst.**—A solution of 1.5 g. of boron trifluoride etherate and 1.5 g. of 1-phenyl-2-pyrazoline in 40 ml. of dry benzene was refluxed for 1.5 hours. The light brown reaction mixture turned green at the reflux temperature. After the refluxing, a dark oily material separated and the green color disappeared. After cooling, the benzene solution was decanted into a separatory funnel, and the dark residue was triturated with a hot mixture of benzene and 5% sodium carbonate solution. Most of the residue was unaffected by this treatment. The mixture of the sodium carbonate solution and the benzene solution was decanted into the separatory funnel. The benzene layer was separated and washed once more with 15 ml. of 5% sodium carbonate, followed by three 15-ml. water extractions. The yellow benzene solution was dried over magnesium sulfate, filtered and concentrated. The cooled solution yielded yellow needles, m.p. 234–237°. The identity of this product with that described just above and just below was established by mixed melting points and by comparison of the infrared absorptions.

Anal. Found: C, 74.51; H, 6.28; N, 19.32.

3. **Hydrogen Chloride Catalyst.**—The method of Curtius and Wirsing[2] was used. The crude product was obtained in 70% yield. It was recrystallized from hot benzene to give fine yellow needles, m.p. 235–237°.

Anal. Found: C, 74.36, 74.41; H, 6.48, 6.22; N, 19.05.

Since the analytical data differed from those given by Curtius and Wirsing,[2] a second sample was prepared by three recrystallizations from cyclohexanol followed by four recrystallizations from benzene.

Anal. Found: C, 74.50; H, 6.08; N, 19.50, 19.48.

Oxidation of "Bis-N-phenyl-Δ²-pyrazoline."—A solution of 1 g. of the bispyrazoline and 2 g. of potassium permanganate in 20 ml. of pyridine containing 5 ml. of water was refluxed until the permanganate color disappeared. A solution of 2 g. of potassium permanganate in 10 ml. of pyridine and 5 ml. of water was added, and the refluxing was continued for one hour. The reaction mixture was diluted with 20 ml. of water and filtered. The filtrate was washed with ether and the ether extracted with 7.5% aqueous sodium hydroxide. These extracts were combined with the original water layer and the whole concentrated to a small volume. The resulting solution was filtered, acidified with 50% sulfuric acid and then exhaustively extracted with ether. The ether extract was dried over magnesium sulfate, and the ether was removed by distillation. The slightly yellow, oily residue was decolorized with Darco and repeatedly recrystallized from water to give a solid of m.p. 142–143°.

Anal. Calcd. for $C_{10}H_8O_2N_2$: C, 63.82; H, 4.29; N, 14.89. Found: C, 63.81; H, 4.38; N, 14.75.

A mixed melting point determination with 1-phenylpyrazole-3-carboxylic acid[9] showed no depression.

The ether extract first obtained was washed successively with water, 5% hydrochloric acid and water. It was then dried over magnesium sulfate and the solvent removed by distillation. After crystallization from benzene, treatment with decolorizing charcoal and recrystallization from alcohol, 300 mg. of white needles was obtained, m.p. 183–184°.

Anal. Calcd. for $C_{18}H_{14}N_4$: C, 75.50; H, 4.93; N, 19.57. Found: C, 75.55; H, 5.11; N, 19.66.

To 20 mg. of this oxidation product dissolved in 30 cc. of alcohol was added an excess of sodium in several portions. A yellow color developed in the reaction mixture as the addition of the sodium progressed. A part of the alcohol was evaporated and the residual mixture was diluted with 30 ml. of water and extracted with benzene. The benzene solution was of a clear yellow color and exhibited the fluorescence characteristic of the bispyrazoline.

Ethyl 3-(5-Methyl-1-phenylpyrazolyl)-acetate (VIII).—A solution of 5.5 g. of 5-methyl-1-phenylpyrazole-3-carbonyl chloride,[10] m.p. 91.5–92.5°, in 75 ml. of anhydrous ether was added slowly to 125 ml. of a continuously swirled ether solution of diazomethane prepared from 12.0 g. of N-nitrosomethylurea. The temperature was maintained at 0–5°. After the evolution of nitrogen subsided, the reaction mixture was allowed to stand for 3.5 hours. The solvent was removed *in vacuo* at 30–35° (hood). The residue (a thick yellow oil) was dissolved in 75 ml. of absolute alcohol, and the solution was warmed to 60–65°. To the continuously swirled solution an alcohol slurry of silver oxide (prepared from 10 ml. of 10% silver nitrate solution) was added in small portions. The formation of a silver mirror and the evolution of nitrogen were observed. The mixture was refluxed for several hours and filtered. The filtrate was refluxed with another slurry of silver oxide for ten hours. It was then treated with Darco and filtered. Two-thirds of this solution was vacuum distilled. Two fractions were collected, 0.34 g., b.p. 162–165° (about 1 mm.), n^{20}_D 1.5525; and 0.55 g., b.p. 165° (about 1 mm.), n^{20}_D 1.5538. The last fraction was redistilled through a microfractionating column, n^{20}_D 1.5538.

Anal. Calcd. for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 69.09; H, 6.84; N, 11.73.

Methyl 3-(5-Methyl-1-phenylpyrazolyl)-acetate (IX).—The general method of Newman and Beal[3] was employed. The diazoketone was prepared by a procedure similar to that described above, from 28 g. of VII and a diazomethane solution prepared from 61.8 g. of N-nitrosomethylurea. The residue of the crude diazoketone consisted of 25 g. of a crystalline yellow material, m.p. 77–85° (the melting point could be raised to 85–86° by recrystallization from dilute alcohol). To a solution of the diazoketone in 250 ml. of absolute methanol were added portions of a 10% solution of silver benzoate in triethylamine at intervals such that the evolution of nitrogen did not cease. After 30 hours 94% of the theoretical amount of nitrogen had been evolved, and no more reaction took place. The solution was treated with Darco and the mixture was refluxed for 15 minutes. After filtration the solvents were removed by distillation, and the residue was dissolved in ether. Some solid material was removed by filtration, and the filtrate was washed with 10% sodium bicarbonate. After the ether was removed, the residue was vacuum distilled, yielding 16.9 g. (58%) of light yellow liquid, b.p. 145–155° at about 0.5 mm., n^{20}_D 1.5610.

Anal. Calcd. for $C_{13}H_{14}N_2O_2$: C, 67.83; H, 6.08. Found: C, 67.97; H, 6.05.

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[5] All melting points are corrected and boiling points are uncorrected.

[6] The authors are indebted to Mrs. Katherine Pih, Mrs. Jean Fortney, Miss Emily Davis, Mrs. Jane Wood and Mr. Maurice Dare for microanalyses and to Miss Elizabeth M. Petersen for infrared analyses.

[7] H. R. Snyder and C. W. Smith, THIS JOURNAL, **65**, 2452 (1943).

[8] E. Fischer and O. Knoevenagel, *Ann.*, **239**, 194 (1887).

[9] L. Balbiano and O. Severini, *Gazz. chim. ital.*, **23**, **I**, 354 (1893).

[10] C. A. Rojahn and A. Seitz, *Ann.*, **437**, 297 (1924).

1-Phenyl-4-(1-phenyl-5-methyl-3-pyrazolyl)-5-pyrazolone (XI).—To a mixture of 2.75 g. of IX and 9.2 g. of ethyl formate in 11 ml. of dry ether was added 0.6 g. of finely ground sodium hydride. The reaction was run under a nitrogen atmosphere. When the initial vigorous reaction had subsided, a few drops of methanol was added. Continuous, mild gas evolution ensured as the mixture gradually turned orange. In 30 minutes the contents of the reaction flask had turned into an orange paste. This material was filtered and washed with two 10-ml. portions of dry ether, which removed most of the color. A yield of 2.75 g. (78%) of crude X was obtained.

A mixture of 3.5 g. (0.012 mole) of X and 1.3 g. (0.012 mole) of phenylhydrazine in 30 ml. of glacial acetic acid was refluxed for 1.5 hours. The addition of water to the cooled reaction mixture caused the precipitation of 3.1 g. of a light green substance, m.p. 120–125°. Treatment with Darco and crystallization from a water–alcohol mixture gave 2.4 g. of white crystals, m.p. 123.5–126°. Three recrystallizations raised the melting point to 128–129°.

Anal. Calcd. for $C_{19}H_{16}N_4O$: C, 72.13; H, 5.06; N, 17.71. Found: C, 71.89; H, 5.09; N, 17.83.

1,1′-Diphenyl-5-methyl-3,4′-bipyrazole (XII).—The method of Stoermer and Martinsen[11] was followed with some modifications. A mixture of 1.6 g. of XI, 2.0 g. of freshly distilled phosphorus tribromide, and 0.25 g. of red phosphorus was heated in a sealed tube at 240–255° for 9.5 hours. The contents of the tube was treated with alcohol and Darco. Two crystallizations after filtration yielded 0.6 g. (40%) of white needles, m.p. 96–98°. A sample prepared for analysis melted at 97.5–98°.

Anal. Calcd. for $C_{19}H_{16}N_4$: C, 75.98; H, 5.37; N, 18.65. Found: C, 75.74; H, 5.36; N, 18.61.

1,1′-Diphenyl-3,4′-bipyrazole-5-carboxylic Acid (XIII).—To a mixture of 0.6 g. of XII, 10 g. of potassium permanganate and 15 ml. of pyridine was added sufficient water to effect solution. The mixture was heated for 3.5 hours. The manganese dioxide was filtered and washed with three portions of hot 3:1 pyridine–water solution. The combined filtrates were diluted with 50 ml. of 3% sodium hydroxide, washed with chloroform, concentrated, treated with Darco, filtered and acidified to congo red paper with concentrated hydrochloric acid to yield 0.13 g. of a light tan solid, m.p. 206–207° (dec.). Two crystallizations from methanol resulted in the formation of white needles, m.p. 224–225° (dec.).

Anal. Calcd. for $C_{19}H_{14}O_2N_4$: C, 69.09; H, 4.27; N, 16.96. Found: C, 69.21; H, 4.21, 4.26; N, 16.82.

From the chloroform extracts 0.4 g. of XII was recovered.

1,1′-Diphenyl-3,4′-bipyrazole (IV).—In a small Pyrex test-tube was placed 0.13 g. of XIII. The test-tube was heated in a Wood's metal-bath at 210–230° for 20 minutes. The black reaction mixture was treated with 5 ml. of hot alcohol and Darco. When cooled 35 mg. of solid was obtained. Recrystallization from a water–alcohol mixture yielded white crystals, m.p. 125.5–126.5°.

Anal. Calcd. for $C_{18}H_{14}N_4$: C, 75.50; H, 4.93. Found: C, 75.35; H, 5.06.

Reaction of 3-Methyl-1-phenylpyrazole with *n*-Butyllithium.—A solution of 5.0 g. of 3-methyl-1-phenylpyrazole[12] in 20 ml. of anhydrous ether was added dropwise to 0.04 mole of freshly prepared butyllithium in 65 ml. of ether. The mixture was stirred for two hours after the addition and then poured into a slurry of solid carbon dioxide in ether. The carbon dioxide was allowed to evaporate, and 50 ml. of water was cautiously added. The water layer was separated, concentrated and acidified with concentrated hydrochloric acid. A white material precipitated after chilling, and it was recrystallized from hot water; m.p. 178.5–179.5°.

Anal. Calcd. for $C_{11}H_{10}N_2O_2$: C, 65.33; H, 4.98; N, 13.86. Found: C, 65.48; H, 5.13; N, 13.94.

The amide was prepared and recrystallized from methanol; m.p. 177–178°. The melting point of 3-methyl-1-phenylpyrazole-5-carboxamide is 181°.[4] The monocarboxylic acid was oxidized by potassium permanganate in the usual manner, and an acid was obtained, m.p. 257–258° (dec.). The melting point of authentic 1-phenylpyrazole-3,5-dicarboxylic acid is 260°.[4] A mixed melting point determination showed no depression. The diamides of the dibasic acids were prepared. The melting point of the authentic diamide was 192–194° (lit.[4] 190°). The melting point of the diamide derived from the acid obtained from the *n*-butyllithium reaction was 190–192°; mixed m.p. 190–193°.

Diethyl 1-Phenyl-5-methylpyrazole-3-carboxylmalonate (XIV).—To a mixture of 2.7 g. of magnesium, 5 ml. of absolute alcohol and 0.5 ml. of carbon tetrachloride, heated a few minutes on the steam-bath, was added 50 ml. of dry ether with stirring. A mixture of 16 g. of diethyl malonate, 6.7 ml. of absolute alcohol and 25 ml. of dry ether was added slowly at reflux temperature. When the mixture had refluxed for three hours, a solution of 22.0 g. of VII in 300 ml. of ether was slowly added over a period of 15 minutes. The white precipitate that formed was decomposed with 350 ml. of 10% sulfuric acid. The aqueous layer was extracted with two 150-ml. portions of ether. The combined ether solutions were dried over magnesium sulfate and evaporated to dryness, yielding 28.3 g. (82%) of crude XIV. The 2,4-dinitrophenylhydrazone of XIV served to characterize it. The derivative was recrystallized four times from a 95% ethanol–ethyl acetate mixture and once from *t*-butyl alcohol; m.p. 209° (dec.).

Anal. Calcd. for $C_{24}H_{24}O_8N_6$: C, 54.96; H, 4.61; N, 16.03. Found: C, 55.26; H, 4.92; N, 16.17.

1-Phenyl-3-(1-phenyl-5-methyl-3-pyrazolyl)-5-pyrazolone (XV).—A solution of 4.0 g. of crude XIV and 1.25 g. of phenylhydrazine in 25 ml. of glacial acetic acid was refluxed for 1.5 hours. To the mixture was added 68 ml. of 25% sulfuric acid, and refluxing was continued for five hours. The addition of water caused 2.5 g. of yellow material to precipitate, m.p. 160–175°. Treatment with Darco and two crystallizations from 95% alcohol yielded white crystals, m.p. 187–188.5°.

Anal. Calcd. for $C_{19}H_{16}ON_4$: C, 72.13; H, 5.06; N, 17.71. Found: C, 72.18; H, 5.15; N, 17.73.

1,1′-Diphenyl-5-methyl-5′-bromo-3,3′-bipyrazole (XVI).—This reaction was carried out by the procedure described for the preparation of XII, except that the sealed tube was heated at 225–240° for 12 hours. This resulted in the formation of a white crystalline material, m.p. 162–164°, in 33% yield. After two recrystallizations from 95% alcohol the melting point was 166–167°.

Anal. Calcd. for $C_{19}H_{16}N_4Br$: C, 60.19; H, 3.99; N, 14.77. Found: C, 60, 17; H, 4.15; N, 14.76.

1,1′-Diphenyl-5-methyl-3,3′-bipyrazole (XVII).—A mixture of 1.3 g. of XVI (m.p. 162–164°), about 4 g. of Raney nickel catalyst and 40 ml. of a 10% solution of potassium hydroxide in alcohol was refluxed for 30 minutes. Filtration and concentration gave 0.8 g. (78%) of a white crystalline material, m.p. 162–163°. A small portion was purified by two recrystallizations from a water–alcohol mixture; m.p. 162–163°.

Anal. Calcd. for $C_{19}H_{16}N_4$: C, 75.98; H, 5.37; N, 18.65. Found: C, 76.08; H, 5.26; N, 18.63.

1,1′-Diphenyl-3,3′-bipyrazole-5-carboxylic Acid.—This reaction was run as described above (XIII). One recrystallization from methanol produced white crystals, m.p. 225–226° (dec.).

Anal. Calcd. for $C_{19}H_{14}N_4O_2$: C, 69.09; H, 4.27. Found: C, 68.73; H, 4.50.

1,1′-Diphenyl-3,3′-bipyrazole (V).—Employment of the procedure used for IV yielded 25 mg. of nearly colorless crystals, m.p. 182–184°, from 96 mg. of 1,1′-diphenyl-3,3′-bipyrazole-5-carboxylic acid. The infrared spectrum of the product is identical with that of the $C_{14}H_{18}N_4$ oxidation product of the bis-compound; mixed m.p. 183–184°.

Anal. Calcd. for $C_{18}H_{14}N_4$: C, 75.50; H, 4.93; N, 19.57. Found: C, 75.73; H, 5.13; N, 19.41.

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