Synthesis of Pyrazolo[4,3-*d*]oxazoles

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1-Phenyl-3-methyl-5-pyrazolone-4-oxime reacted with benzylamine, methylamine, methyl- and ethyl ioides to give 3-methyl-1,5-diphenyl-1*H*-, 3-methyl-1-phenyl-1*H*- and 3,5-dimethyl-1-phenyl-1*H*-pyrazolo[4,3-*d*]oxazoles I, II. The structure of I was elucidated authentically through other routes by interaction of 1-phenyl-3-methyl-4,5-dioxopyrazolone with benzylamine and/or benzaldehyde and ammonium acetate. Various 3-methyl-5-aryl-1-phenyl-1*H*-pyrazolo[4,3-*d*]oxazoles IV were synthesized by the reaction of 4,5-dioxopyrazolone with aromatic aldehydes in the presence of ammonium acetate. Also, the structure of I was elucidated authentically *via* other routes by the reaction of 1-phenyl-3-methyl-4-imino-5-pyrazolone with each of benzylcyanide, benzylamine, benzaldehyde and benzalaniline.

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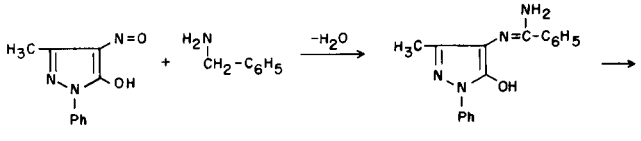
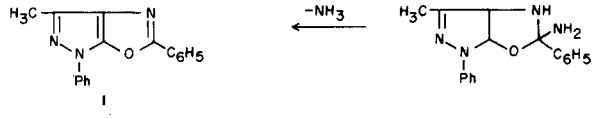
An examination of the literature showed that pyrazolooxazole heterocyclic systems have not been prepared. The only two condensed heterocyclic systems containing pyrazole ring was pyrazoloisoxazole which was prepared by Sammour *et al.* [2]. Fusion of the oxazole ring with a pyrazole nucleus received no attention. Parallel to the work on oxazoloindoles [3], we succeeded in preparing pyrazolooxazoles. The starting materials for such a preparation are: 1-phenyl-3-methyl-5-pyrazolone-4-oxime, 1-phenyl-3-methyl-4-oxo-5-pyrazolone, and 1-phenyl-3-methyl-4-imino-5-pyrazolone.

Benzylamine reacted readily with 1-phenyl-3-methyl-5-pyrazolone-4-oxime in absolute ethanol to give red needles which were identified as 3-methyl-1,5-diphenyl-1*H*-pyrazolo[4,3-*d*]oxazole (I). The product had the following properties: (i) It dissolves in most organic solvents. (ii) It gave a violet colour with methanol and a yellow colour with concentrated sulphuric acid. (iii) It did not dissolve in hydrochloric acid and it was stable towards a concentration of 2.5 *N* of this acid for 5 hours. The structure of the product was established by analytical data and infrared absorption spectra. The ir absorption spectrum showed the following bands: 1575 cm^{-1} for C=N, 1180, 1100 cm^{-1} for a cyclic C-O-C group.

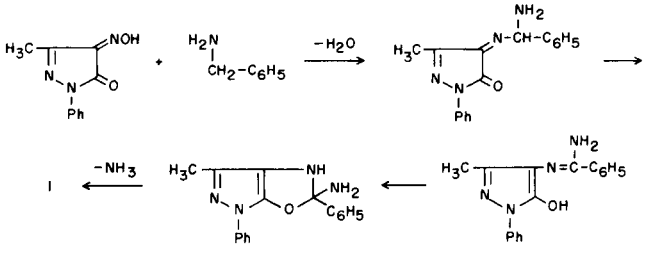
The exceptional behaviour of benzylamine with 1-phenyl-3-methyl-5-pyrazolone-4-oxime may be attributed to the remarkable activity of its methylene group, a condition which is not fulfilled by other amines. The pathway [4] of formation of I can be explained with both the phenolic and ketonic forms of 1-phenyl-3-methyl-5-pyrazolone-4-oxime.

With the phenolic form the reaction may be represented as follows:





With the ketonic form the reaction proceeds as follows:



The liberated ammonia was detected and estimated by normal qualitative and quantitative methods.

Interaction of alkyl halides such as methyl iodide or ethyl iodide with 1-phenyl-3-methyl-5-pyrazolone-4-oxime in the presence of dry acetone as a solvent and a basic catalyst such as anhydrous potassium carbonate gave the corresponding 3-methyl-1-phenyl-1*H*- and 3,5-dimethyl-1-phenyl-1*H*-pyrazolo[4,3-*d*]oxazoles (IIa,b) respectively.

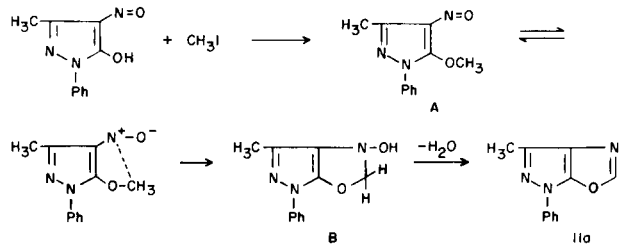
The formation of pyrazolooxazole from the 4-nitroso-5-hydroxypyrazole derivative and an alkyl halide can be suggested to take place by the following steps:

(i) The alkyl halide reacts with the phenolic hydroxyl group giving an intermediate methoxy derivative **A** which is expected to be unstable due to tautomerism.

(ii) This intermediate attains stability by cyclization *via* release of a hydrogen atom as a proton from the methyl group under the influence of the positive nitrogen atom. The proton then attacks the negative oxygen atom of the nitroso group with the formation of **B**.

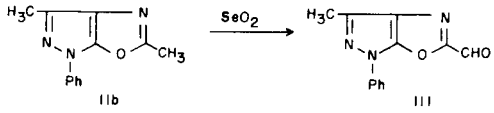
(iii) The intermediate **B** loses the elements of water giving the pyrazolooxazole derivative IIa.

The reaction pathway [5] can be represented as in the following scheme.



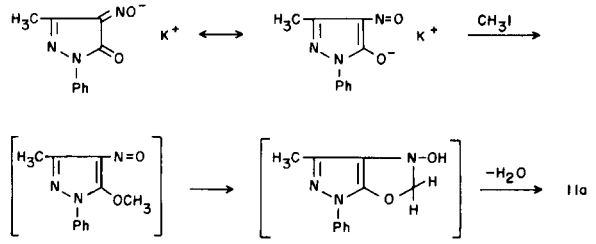
Structure of compound IIa was confirmed by analytical and spectral data. The ir showed absorption bands at 1570 cm^{-1} for C=N, 1175, 1110 cm^{-1} for cyclic C-O-C group.

Using ethyl iodide instead of methyl iodide, 3,5-dimethyl-1-phenyl-1*H*-pyrazolo[4,3-*d*]oxazole (IIb) was obtained. The methyl group was found to be active and could be readily oxidized using selenium dioxide to form 3-methyl-1-phenyl-1*H*-pyrazolo[4,3-*d*]oxazole-5-carboxaldehyde (III).



The structure of this compound was established by elemental analysis and the ir spectra. The ir spectrum showed absorption bands at 1685 cm^{-1} for aldehyde group, 1580 cm^{-1} for C=N and 1000, 1030 cm^{-1} for cyclic C-O-C group.

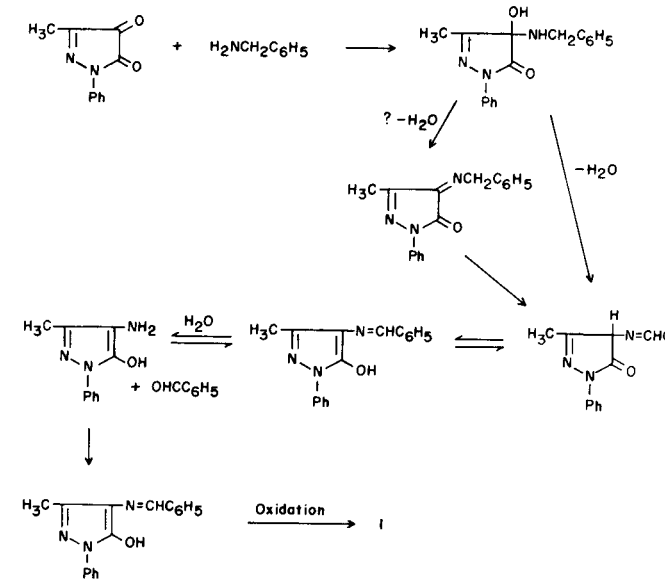
When the potassium salt of 1-phenyl-3-methyl-4-nitroso-5-hydroxypyrazole was treated with methyl iodide in dry acetone and in the presence of anhydrous potassium carbonate, the reaction took place to give the parent pyrazolooxazole (IIa). The sequence of reactions [5] can be represented as in the following scheme:



When ether was used instead of acetone, the reaction yield was highly reduced. This may give an indication of the direct influence of the solvent on this reaction. This is probably due to the increase of the potassium salt ionisation.

The structure of this product has been confirmed by analytical data, mp and mixed mp with the product obtained from the action of methyl iodide on the nitroso compound itself.

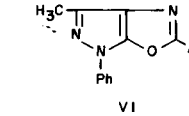
We have found that benzylamine reacted with 1-phenyl-3-methyl-4,5-dioxopyrazolone to form 3-methyl-1,5-diphenyl-1*H*-pyrazolo[4,3-*d*]oxazole (I). The reaction proved to be *via* transamination. This can be represented as follows:



The structure of this product was confirmed by analytical data as well as the infrared spectrum. The reaction product was found to be identical with that formed by previous methods.

The pyrazolooxazole derivatives IVa-f were obtained by heating aromatic aldehydes with 1-phenyl-3-methyl-4,5-dioxopyrazolone in the presence of ammonium acetate and glacial acetic acid for one hour.

The reaction mechanism may be explained on the basis of imino formation. As expected, only one carbonyl group at position 4 is active and forms the monoimine derivative *in situ*. The other carbonyl group is amidic and could not give an imino derivative. The imine then condensed with the aldehyde forming 3-methyl-5-aryl-1-phenyl-1*H*-pyrazolo[4,3-*d*]oxazoles IVa-f.



VI

IVa, Ar = C_6H_5; b, Ar = p-$CH_3OC_6H_4$; c, Ar = p-ClC_6H_4; d, Ar = p-$NO_2C_6H_4$; e, Ar = p-OHC_6H_4; f, Ar = p-$CH_3C_6H_4$

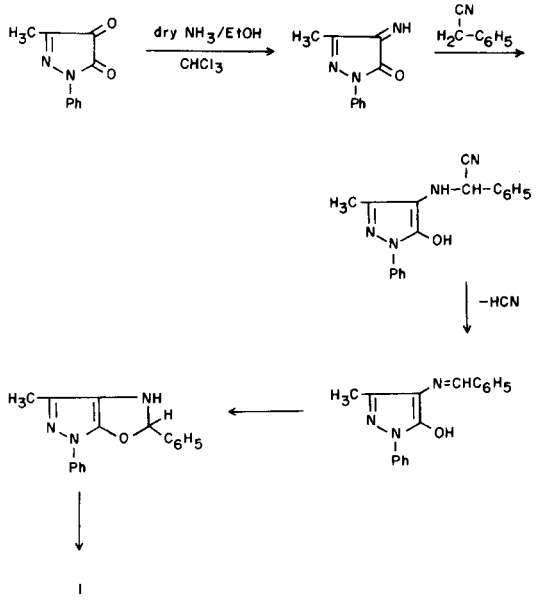
These products IVa-f are coloured needles, which are easily soluble in most organic solvents and give a pink colour with methanol and an orange colour with concentrated sulphuric acid, which turns pale yellow upon dilution.

The structure of these compounds IVa-f was confirmed by analytical and spectral data (*cf.* Table 1).

The compound IVa was found to be identical with I which was obtained in the previous methods by mp and mixed mp determinations. Also, the infrared absorption spectrum was found to be a finger print with those previously described.

Reaction of benzyl cyanide with 1-phenyl-3-methyl-4-imino-5-pyrazolone in the presence of anisole as a solvent

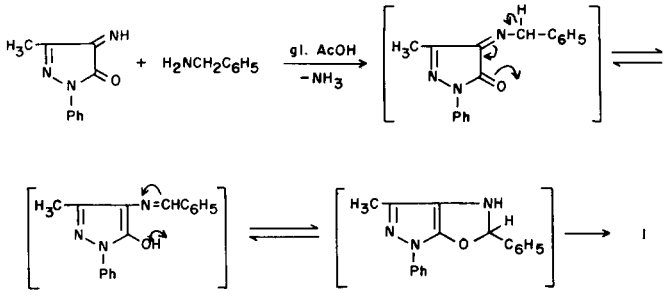
gave red needles of a product which proved to be I. The reaction scheme [6] can be represented as follows:



The product was found to be identical with the compound obtained by previous methods.

The reactivity of the imino group attached to heterocyclic rings is well known, and it was of interest to attempt the synthesis of pyrazolooxazole system I using such imino derivatives. The reaction between 1-phenyl-3-methyl-4-imino-5-pyrazolone and benzylamine in the presence of glacial acetic acid as a solvent gives rise to 3-methyl-1,5-diphenyl-1*H*-pyrazolo[4,3-*d*]oxazole (I), as deep red needles.

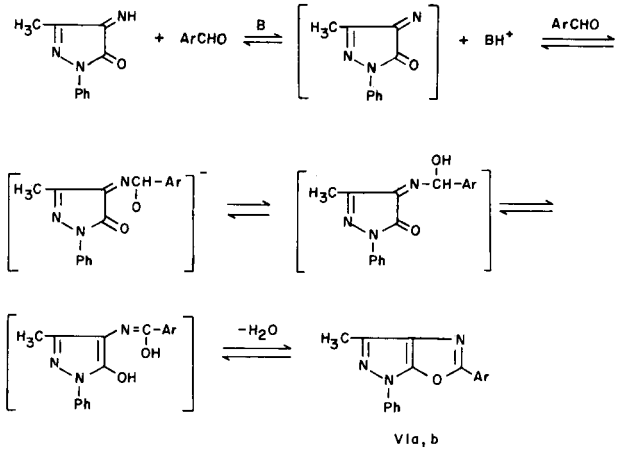
The pathway [7] of formation of this product is proposed as the following:



The structure of this product was confirmed by analytical data as well as by the infrared spectrum.

The product obtained from this method was identical in all respects with that obtained by previously mentioned methods.

Arylpyrazolooxazoles IVa,b were prepared by reaction of aromatic aldehydes with 1-phenyl-3-methyl-4-imino-5-pyrazolone in glacial acetic acid as a solvent medium and in the presence of piperidine as a basic catalyst. The following sequence [8,9] is proposed for this reaction.



The above scheme indicates an aldol-type of condensation as the first step in the reaction. This is followed by an allylic type shift of hydrogen and subsequently by the splitting out of water to form arylpyrazolooxazoles IVa,b.

These products exhibit a deep red colour in methanol and give a pink colour upon dilution. Also they give a pale yellow colour in concentrated sulphuric acid. The structure of these products was confirmed by elemental analyses and infrared spectra.

Many trials have been carried out in different solvents such as benzene, toluene, anisole, acetone, ethanol, ethylene glycol in the presence of piperidine with the aim of synthesizing arylpyrazolooxazoles, but in all cases a resinous material has been obtained.

Schiff's base was interacted with 1-phenyl-3-methyl-4-imino-5-pyrazolone in presence of glacial acetic acid as a solvent for 25 hours and then, the reaction mixture was oxidized by air to give arylpyrazolooxazole derivatives IVa, d. The reaction can be represented as follows:

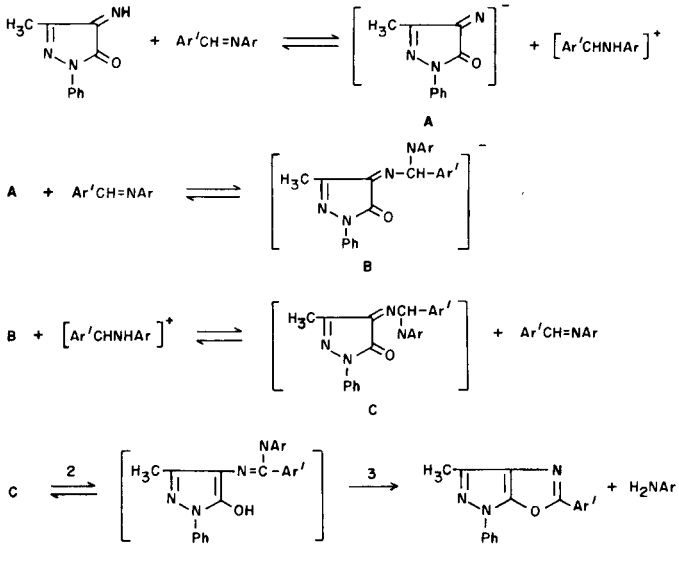
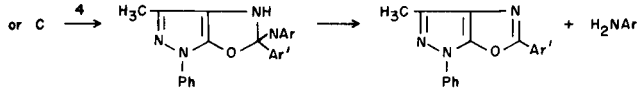


Table 1

3-Methyl-5-aryl-1-phenyl-1*H*-pyrazolo[4,3-*d*]oxazoles VIa-f

Compound No.	Ar	Mp °C [a]	Yield %	Formula	Analysis % Calcd./Found C	H	N	ν (ir) cm^{-1}
IVa	C_6H_5	171-173	55	$C_{17}H_{13}N_3O$	74.18	4.72	15.27	C=N 1575
					73.95	4.97	15.10	C-O-C 1180, 1210
IVb	*p*-$CH_3OC_6H_4$	174-176	40	$C_{18}H_{15}N_3O_2$	70.81	4.91	13.77	C=N 1590
					71.20	5.05	13.97	C-O-C 1180, 1210
IVc	*p*-ClC_6H_4	175-177	42	$C_{18}H_{15}N_3OCl$	65.91	3.87	13.57	C=N 1590
					66.28	4.20	13.96	C-O-C 1180, 1210
IVd	*p*-$NO_2C_6H_4$	173-174	69	$C_{17}H_{12}N_4O_3$	63.75	3.75	12.13	C=N 1580
					63.25	3.88	12.36	C-O-C 1180, 1210
IVe	*p*-OHC_6H_4	171-172	55	$C_{17}H_{13}N_3O_2$	70.10	4.46	14.43	C=N 1580
					70.55	4.77	14.72	C-O-C 1180, 1210
IVf	*p*-$CH_3C_6H_4$	168-170	42	$C_{18}H_{15}N_3O$	74.74	5.19	14.53	C=N 1580
					74.54	5.05	14.83	C-O-C 1180, 1210

[a] Crystallization from petroleum ether (40-60°).



IVa,d

The reaction pathway of the above reaction can be explained on the same basis as that mentioned previously in the preparation of oxazolo[5,4-*b*] indole derivatives [3].

These products were found to be identical with the products obtained by the previous methods.

EXPERIMENTAL

The infrared absorption spectra were determined with a Beckmann IR 20 spectrophotometer using the potassium bromide wafer technique. All melting points are uncorrected.

1-Phenyl-3-methyl-5-pyrazolone.

A mixture of phenylhydrazine (10.8 g, 0.1 mole) and methyl acetoacetate (11.6 g, 0.1 mole) was dissolved in 50 ml of ethanol and the reaction mixture was allowed to remain below 50° for 1 hour, then refluxed on a water bath for 6 hours. The product obtained after cooling was filtered off and crystallized from ethanol as pale yellow crystals in quantitative yield, mp 125-126°.

1-Phenyl-3-methyl-5-pyrazolone-4-oxime.

1-Phenyl-3-methyl-5-pyrazolone (17.4 g, 0.1 mole) was dissolved in a mixture of hydrochloric acid (30 ml, 0.1 mole) and 10 ml of ethanol, then cooled in an ice bath at zero degrees. A cold solution of sodium nitrite (82.8 g, 1.2 moles) was added dropwise during a period of one half an hour. The reaction mixture was allowed to stand for 24 hours in the refrigerator. The product was fitlered off, washed with water and dried. The crude product was crystallized from ethanol to give yellow needles, mp 155-157° (lit [10] 157-158°).

Interaction of Benzylamine with 1-Phenyl-3-methyl-5-pyrazolone-4-oxime. Formation of 3-Methyl-1,5-diphenyl-1*H*-pyrazolo[4,3-*d*]oxazole (I).

A solution of 1-phenyl-3-methyl-5-pyrazolone-4-oxime (2.03 g, 0.01 mole) in 50 ml ethanol was refluxed with benzylamine (1.1 ml, 0.01 mole) for 5 hours. Ammonia was evolved during this period and detected by the usual method. The reaction mixture was concentrated, cooled and the precipitated red product was collected. It was crystallized from petroleum ether (40-60°) as red needles, mp 171-173°, yield 1.9 g (69%).

Anal. Calcd. for $C_{17}H_{13}N_3O$: C, 74.18; H, 4.72; N, 15.27. Found: C, 74.58; H, 5.05; N, 15.61.

Acid Hydrolysis of I.

A mixture of 0.5 g of I and 20 ml of 2.5 *N* hydrochloric aicd was heated for 4 hours. On cooling the reaction mixture precipitated a red solid material which was collected and crystallized from petroleum ether (40-60°) as red needles. The reaction product was identified as unchanged 3-methyl-1,5-diphenyl-1*H*-pyrazolo[4,3-*d*]oxazole, mp and mixed mp 171-173°. This indicates that such compounds are stable towards mineral acids.

Reaction of Alkyl Halides with 1-Phenyl-3-methyl-5-pyrazolone-4-oxime or its Potassium Salt.

3-Methyl-1-phenyl-1*H*-pyrazolo[4,3-*d*]oxazole (IIa).

A mixture of 1-phenyl-3-methyl-5-pyrazolone-4-oxime (2.03 g, 0.01 mole), anhydrous potassium carbonate (5 g, 0.03 mole), and methyl iodide (3.73 ml, 0.06 mole) in 70 ml of dry acetone was heated under reflux for 6 hours on a water bath. The reaction mixture was filtered and acetone was removed by evaporation. The viscous residue was extracted with petroleum ether (60-80°). On concentrating and cooling the extract, orange needles were precipitated, collected and dried, mp 97-100°, yield 1.1 g (55%).

Anal. Calcd. for $C_{11}H_9N_3O$: C, 66.33; H, 4.52; N, 21.10. Found: C, 66.73; H, 4.77; N, 21.36.

3,5-Dimethyl-1-phenyl-1*H*-pyrazolo[4,3-*d*]oxazole (IIb).

A mixture of 1-phenyl-3-methyl-5-pyrazolone-4-oxime (2.03 g, 0.01 mole), anhydrous potassium carbonate (5 g, 0.03 mole) and ethyl iodide (5 ml, 0.06 mole) in dry acetone (70 ml) was heated under reflux for 6 hours on a water bath. The usual working up procedure gave orange needles, mp 84-85°, yield 1.2 g (56%).

Anal. Calcd. for $C_{12}H_{11}N_3O$: C, 67.60; H, 5.16; N, 19.71. Found: C, 67.85; H, 5.36; N, 19.92.

A mixture of potassium salt of 1-phenyl-3-methyl-5-pyrazolone-4-oxime (1.21 g, 0.005 mole) anhydrous potassium carbonate (3 g) (or its absence), dry acetone (70 ml) and methyl iodide (3 ml) was heated under reflux for 6 hours on a water bath. The usual work up procedure gave orange needles of IIa, mp 97-100°, yield 1 g (50%). The mp was undepressed on admixture with the product obtained in the foregoing experiment.

Anal. Calcd. for $C_{11}H_9N_3O$: C, 66.33; H, 4.52; N, 21.10. Found: C, 66.65; H, 4.95; N, 21.52.

3-Methyl-1-phenyl-1*H*-pyrazolo[4,3-*d*]oxazole-5-carboxaldehyde (III).

Compound IIb (0.229 g, 0.01 mole) was dissolved in ethanol. This solution was treated with a solution of selenium dioxide (0.111 g, 0.001 mole) in ethanol. The reaction mixture was boiled under reflux for 3 hours. The solution was filtered, cooled and the precipitated selenium was eliminated by filtration. The filtrate was concentrated and cooled to give III which was crystallized from petroleum ether (60-80°) as orange needles, mp 77°, yield 0.17 g, (75%).

Anal. Calcd. for $C_{12}H_9N_3O_2$: C, 63.43; H, 3.96; N, 18.50. Found: C, 63.88; H, 4.50; N, 18.92.

1-Phenyl-3-methyl-4,5-dioxopyrazolone.

It was prepared by a method patented by Eastman Kodak Co. [11].

Reaction of Benzylamine with 1-Phenyl-3-methyl-4,5-dioxopyrazolone. Formation of I.

A mixture of 1-phenyl-3-methyl-4,5-dioxopyrazolone (0.188 g, 0.001 mole) and benzylamine (0.11 ml, 0.001 mole) was dissolved in 50 ml of absolute ethanol. The reaction mixture was refluxed for 3 hours on a water bath and then allowed to cool. The precipitated solid material was collected and crystallized from petroleum ether (40-60°) to give red needles, mp 175-176°, yield 0.17 g (62%).

Anal. Calcd. for $C_{17}H_{13}N_3O$: C, 74.18; H, 4.72; N, 15.27. Found: C, 74.58; H, 5.15; N, 15.30.

Reaction of Aromatic Aldehydes with 1-Phenyl-3-methyl-4,5-dioxopyrazolone in the Presence of Ammonium Acetate and Glacial Acetic Acid. Formation of IVa-f.

General Procedure.

A mixture of 1-phenyl-3-methyl-4,5-dioxopyrazolone (0.001 mole), ammonium acetate (0.015 mole) and aromatic aldehyde (0.001 mole) was dissolved in glacial acetic acid (30 ml) and refluxed for 2 hours. The reaction mixture was then concentrated and cooled. The product was filtered, collected and recrystallized from the proper solvent. The results are given in Table 1.

1-Phenyl-3-methyl-4-imino-5-pyrazolone.

1-Phenyl-3-methyl-4,5-dioxopyrazolone (1.88 g, 0.01 mole) in dry chloroform (20 ml) was mixed with 25 ml of a saturated solution of ammonia gas in absolute ethanol. The reaction mixture was allowed to stand in dry atmosphere at room temperature for 12 hours. After this time, the reaction mixture was concentrated under reduced pressure to give pale yellow solid material. This product was recrystallized from absolute ethanol saturated with dry ammonia (maximum temperature 50°) as pale yellow plates, mp 157-158°, yield 1.7 g (91%). On heating this compound with dilute hydrochloric acid for one minute gave the corresponding quinone, mp and mixed mp 119-120°.

Interaction of Benzylcyanide with 1-Phenyl-3-methyl-4-imino-5-pyrazolone. Formation of I.

A mixture of 1-phenyl-3-methyl-4-imino-5-pyrazolone (0.187 g, 0.001 mole) and benzyl cyanide (0.117 g, 0.001 mole) in anisole (10 ml) was refluxed for 1 hour. The anisole had been evaporated to give deep red needles. The product was recrystallized from petroleum ether (40-60°) to give red needles, mp 177-178°, undepressed on admixture with a sample, which was prepared by the previous methods.

Anal. Calcd. for $C_{17}H_{13}N_3O$: C, 74.18; H, 4.72; N, 15.27. Found: C, 74.52; H, 4.62; N, 15.21.

Interaction of Benzylamine with 1-Phenyl-3-methyl-4-imino-5-pyrazolone. Formation of I.

A mixture of quinonimine (0.187 g, 0.001 mole) and benzylamine (0.11 ml, 0.001 mole) was dissolved in glacial acetic acid (25 ml) and refluxed for 2 hours. The reaction mixture was concentrated and cooled. The product was collected and crystallized from petroleum ether (40-60°) to give red needles, mp 177-178°. The mp was undepressed on admixture with the product obtained in the previous experiments.

Anal. Calcd. for $C_{17}H_{13}N_3O$: C, 74.18; H, 4.72; N, 15.27. Found: C, 74.38; H, 4.92; N, 15.35.

Reaction of Aromatic Aldehydes with 1-Phenyl-3-methyl-4-imino-5-pyrazolone. Formation of IVa,b.

3-Methyl-1,5-diphenyl-1*H*-pyrazolo[4,3-*d*]oxazole (IVa).

A mixture of quinonimine (0.187 g, 0.001 mole) and benzaldehyde (0.106 g, 0.001 mole) was dissolved in glacial acetic acid (30 ml) in presence of few drops of piperidine. The reaction mixture was refluxed for 2 hours, then concentrated and cooled. The product was filtered and dried. It was crystallized from petroleum ether (40-60°) to give red needles, mp 177-179°, undepressed on admixture with the products, which have been previously prepared.

Anal. Calcd. for $C_{17}H_{13}N_3O$: C, 74.18; H, 4.72; N, 15.72. Found: C, 74.44; H, 4.79; N, 15.52.

3-Methyl-5-(*p*-methoxyphenyl)-1-phenyl-1*H*-pyrazolo[4,3-*d*]oxazole (IVb).

A mixture of quinonimine (0.187 g, 0.001 mole) and anisaldehyde (0.136 g, 0.001 mole) was dissolved in glacial acetic acid (30 ml) and in presence of few drops of piperidine and was refluxed for 2 hours. The usual working up procedure gave red needles, mp 175-177°. The compound was proved to be identical with the product obtained in the previous method (mp and mixed mp determinations).

Anal. Calcd. for $C_{18}H_{15}N_3O_2$: C, 70.81; H, 4.91; N, 13.77. Found: C, 70.62; H, 5.05; N, 13.87.

Interaction of Schiff's Base with 1-Phenyl-3-methyl-4-imino-5-pyazolone. Formation of IVa,d.

a) With Benzalaniline.

A mixture of quinonimine (0.187 g, 0.001 mole) and benzalaniline (0.181 g, 0.001 mole) was dissolved in glacial acetic acid (50 ml). The reaction mixture was refluxed for 25 hours, then it was oxidized by air and evaporated to dryness. the residual material was extracted with petroleum ether (40-60°). The extract was concentrated and cooled. The product was filtered and dried. It was crystallized from petroleum ether (40-60°) as deep red needles, yield 0.1 g (36%), mp 177-178°, undepressed on admixture with the product obtained from the previously mentioned methods.

Anal. Calcd. for $C_{17}H_{13}N_3O$: C, 74.18; H, 4.72; N, 15.27. Found: C, 73.95; H, 4.88; N, 15.44.

b) With *p*-Nitrobenzalaniline.

A mixture of quinonimine (0.187 g, 0.001 mole) and *p*-nitrobenzalaniline (0.214 g, 0.001 mole) was dissolved in glacial acetic acid (50 ml) and the reaction mixture was refluxed for 25 hours. The usual working up procedure gave red needles, yield 0.15 g (47%), mp 174-175°, undepressed on admixture with the products obtained from the previously mentioned methods.

Anal. Calcd. for $C_{17}H_{12}N_4O_3$: C, 63.75; H, 3.75; N, 13.12. Found: C, 63.92; H, 3.66; N, 13.44.

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