A Study of Synthesis and Behavior of Some Heterocyclic Compounds

AHMED MUSTAFA, W. ASKER, AHMED FATHY A. SHALABY,
Z. SELIM, AND CARMEN R. DAGUER

Chemistry Department, Faculty of Science, Cairo University, Cairo, Egypt

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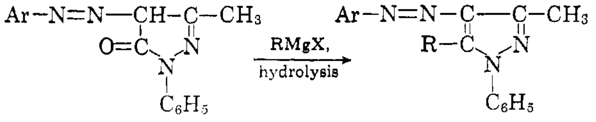
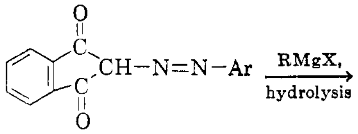
Treatment of 2-arylazo-1,3-indandione (III) with Grignard reagents, followed by hydrolysis yields 2-arylazo(1,3-diaryldihydroxy)indan (IV). 4-Arylazo-3-methylisoxazolin-5-ones (VII) when allowed to react with hydrazine hydrate and/or phenylhydrazine at room temperature undergo hetero-ring opening followed by immediate cyclization in the case of hydrazine hydrate. The intermediate compounds (IX), separated in the case of phenylhydrazine, undergo cyclization, upon heating in glacial acetic acid. Treatment of 4-arylidene-1-phenyl-3-methylpyrazolin-5-ones (XI) with hydrazine hydrate and/or with phenylhydrazine at room temperature leads to the elimination of the arylidene radical and to the formation of the azine of the corresponding aldehyde together with 1-phenyl-3-methylpyrazolin-5-one. 4-Isonitroso-1-phenyl-3-methylpyrazolin-5-one (XII), when subjected to the action of hydrazine hydrate, lithium aluminum hydride, and/or methylmagnesium iodide, now has been found to undergo reduction followed by oxidation to give rubazoic acid (XIII).

Recently, Mustafa and co-workers[1] have undertaken the investigation of the effect of the introduction of the electron-withdrawing group, namely, the phenylazo group in the 4-position of 4-arylazo-1-phenyl-3-methylpyrazolin-5-ones on the reactivity of the carbonyl group toward the action of organomagnesium compounds. Thus, when the highly colored I is treated with organomagnesium compounds, 4-arylazo-1-phenyl-3-methyl-5-arylpyrazoles (II) are obtained (scheme A). The reactivity of the carbonyl function in I parallels the reactivity of the same group in 4-phenylazo-oxazolin-5-one toward the same reagent.[2]

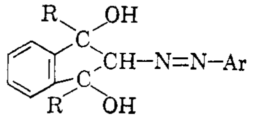


I (Scheme A) II

In extension of our study, we now have investigated the action of organomagnesium compounds on the highly colored 2-arylazo-1,3-indandiones (IIIa–e),[3] and have found that 2-arylazo(1,3-diaryldihydroxy)indan (IVa–k) are obtained (scheme B). The assigned structure for the Grignard products (IVa–k) is inferred from the facts that they are colored and agree in ultimate analysis with that expected. The infrared spectrum of IVa shows no —C=O band strong but —OH group absorption. It was found that the expected hydrazone band (350–400 mμ)[4,5] is present in IVa. A solution of IVa in acetic acid gives upon oxidation with chromic acid *o*-dibenzoylbenzene. Furthermore, treatment of IVa with zinc dust and acetic acid[6] gave 1,3-diphenylindan. The structure of the latter compound was elucidated by its identity with an authentic sample of 1,3-diphenylindan which now has been prepared by reduction of 1,3-diphenylindene[7] with lithium aluminum hydride.



IIIa. Ar = C_6H_5
b. Ar = $C_6H_4CH_3$-*o*
c. Ar = $C_6H_4CH_3$-*m*
d. Ar = $C_6H_4CH_3$-*p*
e. Ar = $C_{10}H_7$-β



IVa. Ar = R = C_6H_5
b. Ar = C_6H_5; R = $C_6H_4CH_3$-*p*
c. Ar = C_6H_5; R = $C_{10}H_7$-α
d. Ar = $C_6H_4CH_3$-*o*; R = C_6H_5
e. Ar = $C_6H_4CH_3$-*o*; R = $C_6H_4CH_3$-*p*
f. Ar = $C_6H_4CH_3$-*m*; R = C_6H_5
g. Ar = $C_6H_4CH_3$-*m*; R = $C_6H_4CH_3$-*p*
h. Ar = $C_6H_4CH_3$-*p*; R = C_6H_5
i. Ar = $C_6H_4CH_3$-*p*; R = $C_6H_4CH_3$-*p*
j. Ar = $C_{10}H_7$-β; R = C_6H_5
k. Ar = $C_{10}H_7$-β; R = $C_6H_4CH_3$-*p*

(Scheme B)

4-Phenylazo-2-phenyloxazolin-5-one (V) rearranges readily with ammonia[5] and with piperidine[2] to give 1,5-diphenyl-3-carbamido-1H-1,2,4-triazole (VIa) and 1,5-diphenyl-3-carbpiperidino-1H-1,2,4-triazole (VIb), respectively. We now have investigated the behavior of the isolog 4-arylazo-3-methylisoxazolin-5-one (VIIa–d) toward the action of hydrazine hydrate and of phenylhydrazine. The

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[1] A. Mustafa, W. Asker, A. F. A. Shalaby, and Z. Selim, *J. Org. Chem.*, **26**, 1779 (1961).

[2] W. Asker and Z. Elagroudi, *ibid.*, **26**, 1441 (1961).

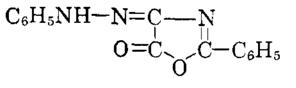
[3] The arylazo derivatives may have the structure in III or one of the tautomeric structures [W. Wislicenus and F. Reitzenstein, *Ann.*, **277**, 363 (1893); E. Gudriniese and G. Vanags, *Zh. Obshch. Khim.*, **28**, 58 (1958); *Chem. Abstr.*, **52**, 12817 (1958)].

[4] R. Wiley and C. H. Jarboe, *J. Am. Chem. Soc.*, **77**, 404 (1955).

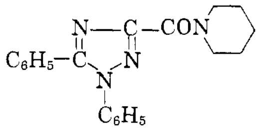
[5] G. W. Sawdey, *ibid.*, **79**, 1955 (1957).

[6] *Cf.* the cleavage action of zinc dust and acetic acid on the arylazo group in 4-methyl-4-phenylazo-1,3-diphenylpyrazolin-5-one; [W. Pelz, W. Puschel, H. Schellenberger, and K. Loffler, *Angew. Chem.*, **72**, 967 (1960)].

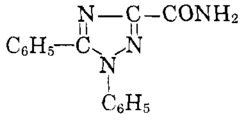
[7] 1,3-Diphenylindene has been reported to give 1,3-diphenylindan by the action of sodium amalgam and boiling alcohol [K. Ziegler, H. Grabbe, and F. Ulrich, *Ber.*, **57**, 1983 (1924)], and by the action of iron in acetic acid [M. C. Dufraisse and L. Enderlin, *Bull. soc. chim. France*, **5**, I, 267 (1934)].



V

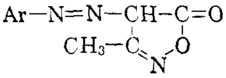


VIb

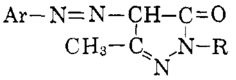


VIa

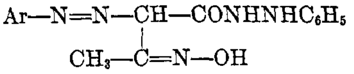
heterocyclic ring in VIIa–d is rapidly opened, followed by immediate cyclization in the case of hydrazine hydrate to form 4-arylazo-3-methylpyrazolin-5-one (VIIIa–d). The intermediate phenylhydrazides (IXa–d) have been successfully isolated in the case of phenylhydrazine. Solutions of IXa–d in boiling acetic acid are readily cyclized to give the corresponding 4-arylazo-1-phenyl-3-methylpyrazolin-5-ones (VIIIe–h).[8] On the other hand replacement of the arylazo group in VII by an arylidene group seems to stabilize the hetero ring against the cleavage[9] action of hydrazine hydrate and of phenylhydrazine. Thus, 4-arylidene-3-methylisoxazolin-5-ones (Xa–b) undergo arylidene elimination by the action of hydrazine hydrate and of phenylhydrazine, at room temperature and in absence of solvent, to yield, *e.g.*, benzaldehyde azine and benzaldehyde phenylhydrazone, together with 3-methylisoxazolin-5-one, in the case of Xa.[10] Now we have also found the heterocyclic ring in 4-arylidene-1-phenyl-3-methylpyrazolin-5-ones (XIa–e) is stable toward the action of the same reagents,[11] but undergo arylidene elimination to give, *e.g.*, anisaldehyde azine and anisaldehyde phenylhydrazone together with 1-phenyl-3-methylpyrazolin-5-one, in the case of XIa.



VIIa. Ar = C_6H_5
b. Ar = $C_6H_4CH_3$-*o*
c. Ar = $C_6H_4CH_3$-*p*
d. Ar = $C_{10}H_7$-*β*

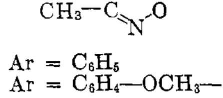


VIIIa. Ar = C_6H_5; R = H
b. Ar = $C_6H_4CH_3$-*o*; R = H
c. Ar = $C_6H_4CH_3$-*p*; R = H
d. Ar = $C_{10}H_7$-*β*; R = H
e. Ar = R = C_6H_5
f. Ar = $C_6H_4CH_3$-*o*; R = C_6H_5
g. Ar = $C_6H_4CH_3$-*p*; R = C_6H_5
h. Ar = $C_{10}H_7$-*β*; R = C_6H_5

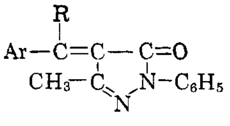


$$Ar{-}N{=}N{-}\underset{CH_3{-}C{=}N{-}OH}{\underset{|}{CH}}{-}CONHNHC_6H_5$$

IXa. Ar = C_6H_5
b. Ar = $C_6H_4CH_3$-*o*
c. Ar = $C_6H_4CH_3$-*p*
d. Ar = $C_{10}H_7$-*β*

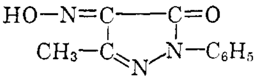


Xa. Ar = C_6H_5
b. Ar = C_6H_4—OCH_3—*p*

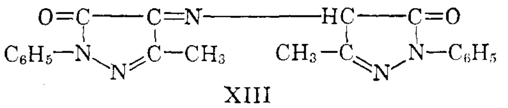


XIa. Ar = $C_6H_4OCH_3$-*p*; R = H
b. Ar = C_6H_4Cl-*o*; R = H
c. Ar = $C_6H_3{=}O{=}CH_2{=}O$; R = H
d. Ar = $C_6H_4NO_2$-*m*; R = H
e. Ar = R = C_6H_5

The arylidene elimination by these reagents is in contrast to the addition of secondary amines, *e.g.*, piperidene and/or morphiline, to the exocyclic double bond in XIa–c.[12] Similarly, the pyrazoline ring in 4-isonitroso-1-phenyl-3-methylpyrazolin-5-one (XII) has now proved to be stable toward the action of hydrazine hydrate and XII is readily converted to rubazoic acid (III)[13] under the given experimental conditions.



XII



XIII

Similarly XIII is obtained upon treatment of XII with lithium aluminum hydride and/or methylmagnesium iodide. On the other hand, reaction of XII and of XIII with aromatic thiols brings about the formation of XIV.

4-Benzylidene-1-phenyl-3-methylpyrazolin-5-one and XIa, now have been found to react by addition across the alkene linkage with 1-phenyl-3-methylpyrazolin-5-one, which contains labile hydrogen atoms, to give XVa–b. The elucidation of the given structure for the reaction products has been confirmed by their identity with 4,4-arylmethylidenebis(1-phenyl-3-methylpyrazolin-

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(8) VIIIa–h were obtained by treatment of hot acetic acid solution of VII with hydrazine hydrate and/or phenylhydrazine, [C. Bulow and A. Hecking, *Ber.*, **44**, 468 (1911)].

(9) The instability of the isoxazolone ring in VIIa is in contrast to the behavior of 4-benzylidene-2-phenyl-2-oxazolin-5-one toward the action of hydrazine hydrate ("The Chemistry of Penicillin," Princeton University Press, Princeton, N. J., 1949, p. 735).

(10) G. Minunni and S. Durso, *Gazz. chim. ital.*, **58**, 485 (1928), *Chem. Abstr.*, **23**, 1120 (1929); R. Fusco and E. Musante, *Gazz. chim. ital.*, **67**, 248 (1937), *Chem. Abstr.*, **31**, 8534 (1937).

(11) In contrast to the behavior of 4-arylidene-1,2-diphenyl-3,5-pyrazolindiones (A. Mustafa, M. Kira, and S. Nakhla, *J. Org. Chem.*, **26**, 3389 (1961).

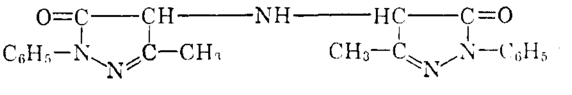
(12) A. Mustafa, W. Asker, A. F. A. Shalaby, S. Khattab, and Z. Selim, *J. Am. Chem. Soc.*, **81**, 6007 (1959).

(13) K. Auwers, *Ann.*, **378**, 218 (1910).

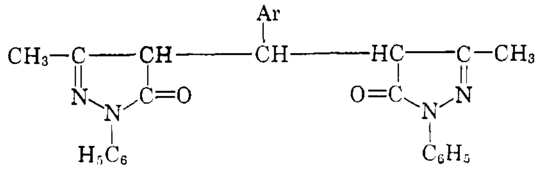
TABLE I

Products IV	M.p.,[a] °C.	Yield, %	Formula	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
IVa	200	92	$C_{27}H_{22}N_2O_2$	79.80	79.80	5.41	5.40	6.89	6.81
IVb	218	87	$C_{29}H_{26}N_2O_2$	80.18	80.11	5.99	5.96	6.45	6.42
IVc	188	75	$C_{35}H_{26}N_2O_2$	83.00	82.91	5.13	5.11	5.53	5.49
IVd	150	90	$C_{28}H_{24}N_2O_2$	80.00	79.89	5.71	5.69	6.66	6.61
IVe	196	82	$C_{30}H_{28}N_2O_2$	80.35	80.29	6.25	6.11	6.25	6.19
IVf	152	85	$C_{28}H_{24}N_2O_2$	80.00	79.88	5.71	6.70	6.66	6.61
IVg	172	77	$C_{30}H_{28}N_2O_2$	80.35	80.11	6.25	6.10	6.25	6.22
IVh	130	87	$C_{28}H_{24}N_2O_2$	80.00	79.88	5.71	5.68	6.66	6.59
IVi	168	70	$C_{30}H_{28}N_2O_2$	80.35	80.21	6.25	6.11	6.25	6.22
IVj	125	91	$C_{31}H_{24}N_2O_2$	81.57	81.50	5.26	5.19	6.14	6.10
IVk	168	84	$C_{32}H_{26}N_2O_2$	81.70	81.66	5.53	5.51	5.95	5.91

[a] Melting points are uncorrected.



XIV



XVa. Ar = C_6H_5
b. Ar = $C_6H_4OCH_3$-*p*

5-ones).[14] The latter compounds have also been obtained by heating an equimolecular mixture of 1-phenyl-3-methylpyrazolin-5-one with benzylideneaniline and/or with *p*-methoxybenzylideneaniline, respectively. When the latter reaction was carried out in the presence of acetic anhydride 4-benzylidene-1-phenyl-3-methylpyrazolin-5-one and XIa were obtained.

Experimental

Action of Arylmagnesium Halides on III.—The following illustrates the procedure. To a Grignard solution (prepared from 1.0 g. of magnesium and the appropriate quantity of the aryl halide in 150 ml. of dry ether) was added a solution of 2 g. of III[3] in 50 ml. of dry benzene. The reaction mixture was refluxed for 1 hr. and kept overnight at room temperature, then decomposed by about 100 ml. of saturated aqueous ammonium chloride solution, and extracted with ether. The ethereal layer was separated, dried, and evaporated. The oily residue, so obtained, was washed with petroleum ether (b.p. 30–50°) until it solidified and was crystallized from the appropriate solvent (*cf.* Table I).

The Grignard products (IVa–k) listed in Table I are al. colored. They are generally soluble in benzene and xylenel but are sparingly soluble in petroleum ether (b.p. 80–100°), Their alcoholic solutions give no color with ferric chloride. They develop deep violet color with concentrated sulfuric acid.

Action of Chromic Acid Solution on IVa.—A mixture of 1 g. of IVa dissolved in 15 ml. of glacial acetic acid and 1 g. of chromic acid in 10 ml. of glacial acetic acid, was heated on a steam bath for 2 hr. The reaction mixture was kept overnight at room temperature, poured over crushed ice; colorless crystals separated. They were collected by filtration, recrystallized from ethyl alcohol and identified as *o*-dibenzoylbenzene (not depressed when admixed with an authentic sample).[15]

Action of Lithium Aluminum Hydride on 1,3-Diphenylindene.—To a 0.7 g. of pulverized lithium aluminum hydride (New Metals and Chemicals Ltd., London) was added 50 ml. of dry ether. After 15 min., 30 ml.of benzene containing 1 g. of 1,3-diphenylindene[7] was added. The reaction mixture was refluxed for 2 hr. The cold reaction mixture was poured slowly over concentrated ammonium chloride solution. The ether–benzene layer was separated, dried and evaporated. The solid, so obtained, was washed with light petroleum (b.p. 40–60°) and recrystallized from alcohol as colorless crystals m.p. 157° [7]; yield 0.85 g.

Anal. Calcd. for $C_{21}H_{18}$: C, 93.33; H, 7.14. Found: C, 93.30; H, 7.10.

Reduction of IVa.—A mixture of a solution of 1 g. of IVa in 15 ml. of glacial acetic acid, 1 g. of zinc dust, and 5 drops of platinum chloride solution (0.083%) was refluxed for 5 hr., and then poured over ice. The reaction mixture was left overnight at room temperature. The colorless crystals that separated were collected by filtration, recrystallized from alcohol, and were identified as 1,3-diphenylindan, m.p. 157° (not depressed when admixed with the above sample).

Action of Hydrazine Hydrate of VIIa–d. General Procedure.—A mixture of equimolecular amounts (0.01 mole) of each of VIIa–d[16] and hydrazine hydrate (80%) was left overnight at room temperature. During the reaction, evolution of gas was observed and the solid substance went into solution. The reaction mixture was poured over crushed ice and acidified with dilute hydrochloric acid solution. The solid so obtained, was collected by filtration and recrystallized from ethyl alcohol and identified as VIIIa–d.[8]

Action of Phenylhydrazine on VIIa–d. General Procedure.—A mixture of equimolecular amounts (0.01 mole) of each of VIIa–d and phenylhydrazine was left overnight at room temperature. During the reaction, the solid went into solution. The reaction mixture was poured over crushed ice and acidified with dilute hydrochloric acid solution. The solid so obtained, was collected and recrystallized from the proper solvent and identified as IXa–d (*cf.* Table II). IXa–d were crystallized from dry solvents. They are insoluble in petroleum ether and in cold benzene. They give a red color when treated with concentrated sulfuric acid.

When 0.5 g. of each of IXa–d was refluxed in 20 ml. of glacial acetic acid for 2 hr.; then the reaction mixture was cooled, orange crystals were separated and were identified as VIIIe–h.[8]

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[14] XVa is described to be obtained after boiling two moles of ethyl acetoacetate phenylhydrazone and one mole of benzaldehyde at 60°, [B. Lachowicz, *Monatsh.*, **17**, 357 (1896)] or by refluxing two moles of 1-phenyl-3-methylpyrazolin-5-one and one mole of benzaldehyde in benzene [F. Stolz, *Ber.*, **28**, 631 (1895)].

[15] H. Bauer, *Ber.*, **38**, 240 (1905).

[16] C. Bulow and A. Hecking, *ibid.*, **44**, 238 (1911).

TABLE II

Products IX	Solvents	M.p.,[a] °C.	Yield, %	Formula	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
IXa	Benzene	228	88	$C_{16}H_{17}N_5O_2$	61.73	61.70	5.46	5.41	22.18	22.09
IXb	Xylene	236	79	$C_{17}H_{19}N_5O_2$	62.76	62.70	5.84	5.81	21.53	21.50
IXc	Benzene	166	85	$C_{17}H_{19}N_5O_2$	62.76	62.69	5.84	5.79	21.53	21.52
IXd	Xylene	242	81	$C_{20}H_{19}N_5O_2$	66.48	66.41	5.66	5.00	19.39	19.33

[a] Melting points are uncorrected.

Action of Hydrazine Hydrate on XIa–e. General Procedure.—A mixture of 1 g. of each of the highly colored XIa–e[12] and 3 g. of hydrazine hydrate (80%) was left aside overnight at room temperature. During the reaction, the deep color of the reaction mixture faded gradually till it became completely colorless. The reaction mixture was poured over 50 g. of crushed ice and acidified with dilute hydrochloric acid. The solid, that separated, was collected by filtration, recrystallized from alcohol, and identified as the corresponding aldehyde azine.

The acidified mother liquor was evaporated to dryness. The solid residue, so obtained, was recrystallized from dilute ethyl alcohol as colorless crystals, m.p. 96°; yield *ca.* 0.25 g. It was identified as the hydrochloride of 1-phenyl-3-methylpyrazolin-5-one[17] (m.p. and mixed m.p. determination).

In case of XIe, benzophenone hydrazone together with 1-phenyl-3-methylpyrazolin-5-one were obtained.

Action of Phenylhydrazine on XIa–e.—The above procedure was adopted and the solid so obtained was recrystallized from alcohol. The products were identified as the corresponding Ar—C(R)═N—NHC$_6$H$_5$. In the mother liquors the presence of the hydrochloride of 1-phenyl-3-methylpyrazolin-5-one was also detected.

Action of Hydrazine Hydrate on XII.—A 1.5-g. sample of XII was heated with 4 g. of hydrazine hydrate under the same experimental conditions described above. XIII[17] was obtained as red crystals m.p. 181°; yield *ca.* 0.9 g. (not depressed when admixed with an authentic sample).

Anal. Calcd. for $C_{20}H_{17}N_5O_2$: C, 66.85; H, 4.73; N, 19.49. Found: C, 66.79; H, 4.71; N, 19.41.

Action of Lithium Aluminum Hydride on XII.—A 1-g. sample of pulverized lithium aluminum hydride was refluxed in 60 ml. of dry ether. After 15 min., 40 ml. of dry benzene containing 1.5 g. of XII was added. The reaction mixture was heated on a steam bath for 4 hr. and left aside to cool at room temperature. It was poured over a cooled saturated ammonium chloride solution. The ether–benzene layer was separated, dried, and evaporated. The solid so obtained was recrystallized as red crystals of XIII; yield 1.1 g.

Action of Methylmagnesium Iodide on XII.—A solution of 1.5 g. of XII in 40 ml. of dry benzene was added to an ethereal solution of methylmagnesium iodide (prepared from 1 g. of magnesium, 7 g. of methyl iodide, and 30 ml. of dry ether). The reaction mixture was heated on a steam bath for 2 hr. and left aside to cool. The reaction mixture was worked up in the usual manner and the solid so obtained was collected. It was crystallized from ethyl acetate as red crystals of XIII, m.p. 181°; yield 0.8 g.

Action of Thiophenol and/or *p*-Thiocresol on XII and on XIII.—One gram each of XII and XIII was treated with 2 g. of the mercaptan and 2 drops of freshly distilled piperidine. The reaction mixture was warmed on a steam bath for 5 hr., cooled, and triturated with cold light petroleum ether (b.p. 40–60°). The solid so obtained was crystallized from benzene as orange crystals of XIV, m.p. 210°; yield is 60%.

Anal. Calcd. for $C_{20}H_{19}N_5O_2$: C, 66.48; H, 5.26; N, 19.39. Found: C, 66.39; H, 5.20; N, 19.11.

Action of 1-Phenyl-3-methylpyrazolin-5-one on 4-Benzylidene-1-phenyl-3-methylpyrazolin-5-one and/or XIa.—To a solution of sodum ethoxide (prepared from 30 ml. of absolute ethyl alcohol and the equivalent amount of metallic sodium) 0.01 mole of 1-phenyl-3-methylpyrazolin-5-one was added, followed by the addition of 0.01 mole of the corresponding 4-arylidene-1-phenyl-3-methylpyrazolin-5-one. The reaction mixture was refluxed on a steam bath for 12 hr. and left aside to cool. The cooled reaction mixture was poured slowly over 200 g. of crushed ice and acidified with dilute hydrochloric acid solution, whereby a colorless solid separated. The solid was collected by filtration and crystallized from ethyl alcohol as colorless crystals of XVa[14]; yield, 75% (m.p. and mixed m.p. determination) and/or XVb.

Anal. Calcd. for $C_{27}H_{24}N_4O_2$: C, 74.31; H, 5.50; N, 12.84. Found: C, 74.25; H, 5.48; N, 12.80.

XVb gives colorless crystals, m.p. 235°; yield, 80%.

Anal. Calcd. for $C_{28}H_{26}N_4O_3$: C, 72.10; H, 5.58; N, 12.02. Found: C, 71.99; H, 5.50; N, 12.00.

Benzylideneaniline and/or p-Methoxybenzylideneaniline. Dry Reaction.—A mixture of 1-phenyl-3-methylpyrazolin-5-one and 7 g. of the appropriate anil was heated in an oil bath at 175–180°. A vigorous reaction occurred and heating was continued for 5 hr. The cooled reaction mixture was poured over water. A solid was separated, collected by filtration, and recrystallized from ethyl alcohol as colorless crystals of XVa, m.p. 167°; yield, 80% and/or XVb, m.p. 235°; yield, 75%, respectively (m.p. and mixed m.p. determinations).

Wet Reaction.—A mixture of 5 g. of 1-phenyl-3-methylpyrazolin-5-one, 8 g. of the appropriate anil and 30 ml. of acetic anhydride was heated in an oil bath at 155–160° for 2 hr., during which time the reaction mixture acquired a deep red color. The cooled reaction mixture was poured over water, and the red solid that separated was collected by filtration and washed with dilute sodium carbonate solution (5%). It was crystallized from ethyl alcohol as orange crystals of 4-benzylidene-1-phenyl-3-methylpryazolin-5-one and/or XIa, respectively (m.p. and mixed m.p. determinations). 4-Benzylidene-1-phenyl-3-methylpyrazolin-5-one, m.p. 107°; yield 5 g.

Anal. Calcd. for $C_{17}H_{14}N_2O$: C, 77.86; H, 5.34; N, 10.68. Found: C, 77.85; H, 5.29; N, 10.59.

XIa has a m.p. 127°, yield 5.5 g.

Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.97; H, 5.48; N, 9.59. Found: C, 73.91; H, 5.44; N, 9.55.

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[17] L. Knorr, *Ann.*, **238**, 137 (1887).