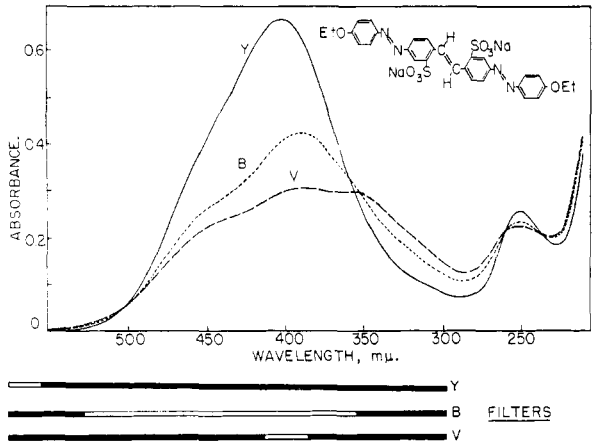

Fig. 3.—Absorption spectra of Chrysophenine in water, irradiated with light transmitted by different filter combinations: Y (———), $\lambda > 567$ mμ; B (. . . .), 354–527 mμ; V (– – – –), 370–413 mμ; concentration 4.3 mg./l.; cell length, 2.00 cm.

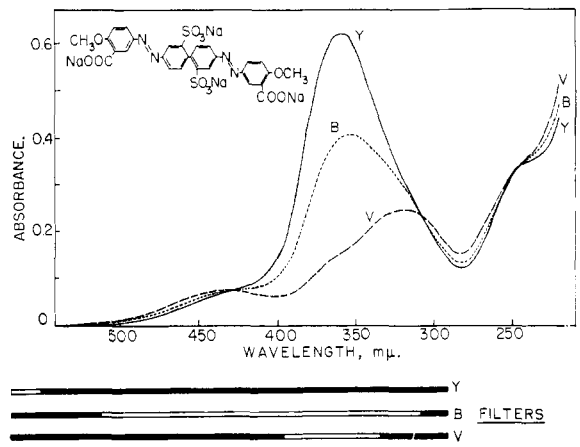

Fig. 4.—Absorption spectra of the sodium salt of 4,4′-bis-(4-methoxy-3-carboxyphenylazo)-biphenyl-2,2′-disulfonic acid in water, irradiated with light transmitted by different filter combinations: Y (———), $\lambda > 545$ mμ; B (. . . .), 305–513 mμ; V (– – – –), 348–386 mμ; concentration, 7.3 mg./l.; cell length, 2.00 cm.

apparent isosbestic points. However, closer examination of the spectra in the 300–315 mμ region, using a more concentrated solution and a slower scanning speed, reveals the absence of a well-defined isosbestic point, thus showing that even in this compound the insulation between the two halves of the molecule is not complete.

On the basis of the findings reported here, it appears that the *cis* isomers of alkoxyazo compounds are sufficiently more stable than those of the corresponding hydroxyazo compounds to permit observation of reversible phototropic *cis–trans* isomerization in aqueous solutions. Further investigation is being conducted on the nature of the solvent effects in the thermal *cis* to *trans* isomerization of these compounds.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE ORGANIC CHEMICAL RESEARCH SECTION AND THE BIOCHEMISTRY RESEARCH SECTION, LEDERLE LABORATORIES DIVISION, AMERICAN CYANAMID CO.]

The Preparation and Identification of the Isomeric 1-Aryl-3(and 5)-methyl-5(and 3)-(4-pyridyl)-pyrazoles

BY WILLIAM B. WRIGHT, JR., HERBERT J. BRABANDER, ROBERT A. HARDY, JR., AND WILLIAM FULMOR

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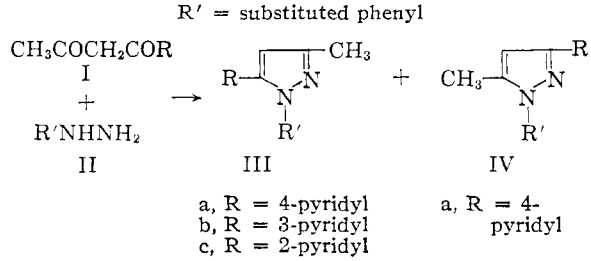
Several pairs of isomeric 1-aryl-3(and 5)-methyl-5(and 3)-(4-pyridyl)-pyrazoles have been prepared by the acid-catalyzed condensation of isonicotinoylacetone with phenylhydrazines. The ultraviolet absorption curves of these isomers are characterized by a hypsochromic shift of λ_{max} and a lower molar extinction coefficient of one member of each pair. This effect may be explained by steric inhibition of resonance and has been used as a basis of structural assignments. The differences in ultraviolet absorption curves of three isomeric pairs of substituted 3(and 5)-methyl-5(and 3)-phenyl-pyrazoles of unequivocal structure may be explained by the same reasoning. A series of 1-aryl-3-methyl-5-(2 and 3-pyridyl)-pyrazoles is also described.

The preparation of pyrazoles from unsymmetrical β-diketones (I) and monosubstituted hydrazines (II) is complicated by the possible formation of two isomers (III and IV).



Jacobs[1] has reviewed and more recently Finar and Simmonds[2] have further investigated this type of reaction. A number of examples exist in which only one isomer was isolated and the structural assignment was equivocal or arbitrary. In other examples two isomeric pyrazoles have been isolated from the same reaction mixture, but the proper structure has not been investigated. Relatively few examples are known in which two isomers have been obtained from the same reaction and the structural assignments investigated. We have iso-

(1) T. L. Jacobs in R. C. Elderfield, Ed., "Heterocyclic Compounds," Vol. 5, J. Wiley and Sons, Inc., New York, N. Y., 1957, pp. 50–55.

(2) I. L. Finar and A. B. Simmonds, *J. Chem. Soc.*, 200 (1958).

TABLE I

THE ULTRAVIOLET ABSORPTION SPECTRA OF PYRAZOLES

R	R′	Type III Compound	Type III λ_{max}, mμ	Type III $\epsilon \times 10^{-4}$	Type IV Compound	Type IV λ_{max}, mμ	Type IV $\epsilon \times 10^{-4}$
C_6H_5	CH_3	V	241	1.46	VI	257	1.96
C_6H_5	C_6H_5	VII	249	1.81	VIII	264	2.26
4-Br deriv. of latter		IX	255	1.53	X	262	1.66
4-Pyridyl	RC_6H_4	IIIa	293–296	1.30–1.51	IVa	294–306	2.01–2.20
3-Pyridyl	RC_6H_4	IIIb	258–259	1.21–1.34			
2-Pyridyl	RC_6H_4	IIIc	297–299	1.13–1.19			

TABLE II

1-ARYL-3-METHYL-5-(4-PYRIDYL)-PYRAZOLES (TYPE IIIa)

Substituent in phenyl ring	Method (Hours)	Yield, %	M.p., °C. Base[a]	M.p., °C. HCl[a]	λmax, mμ	$\epsilon \times 10^{-4}$	Formula[b]	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Halogen, % Calcd.	Halogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
o-Cl	B(7)	25[c]	113–114	227–229	295	1.35	$C_{15}H_{12}ClN_3$	66.7	66.6	4.5	4.7	13.1	13.1	15.6	15.7
m-Cl	A(7); B(5)	77; 14	75–76	241–244	296	1.33	$C_{15}H_{12}ClN_3$	66.7	66.8	4.5	4.6	13.1	13.4	15.6	15.7
p-Cl	A(3); B(5)	60; 10	117–118	254–257	294	1.35	$C_{15}H_{12}ClN_3$	66.7	67.0	4.5	4.4	13.1	13.0	15.6	15.3
p-Br	B(3)	49[c]	124–126	249–253	295	1.37	$C_{15}H_{12}BrN_3$	57.3	57.6	3.9	3.9	25.4	25.2	13.4	13.4
2,4-diCl	B(7)	43[d]	135–136		293	1.40	$C_{15}H_{11}Cl_2N_3$	59.2	59.2	3.6	3.6	23.3	23.0	13.8	14.1
2,5-diCl	A(5)	76	132–134	246–249	295	1.41	$C_{15}H_{11}Cl_2N_3$	59.2	59.0	3.6	3.8	23.3	23.6	13.8	13.7
5-Cl-2-CH_3O	B(8)	8	158–159		293	1.51	$C_{16}H_{14}ClN_3O$	64.1	63.7	4.7	4.9	11.8	11.6	14.0	14.2
3-Cl-2-CH_3	B(7)[d]	24	Oil	213–215	296	1.39	$C_{16}H_{15}Cl_2N_3$[e]	60.0	59.8	4.7	4.9	22.2	22.6	13.1	12.9
m-CH_3O	A(10)[f]	72		136–139[g]	294	1.30	$C_{16}H_{16}N_4O_4$[g]	58.5	58.3	4.9	5.0			17.1	17.4
m-HO	C(24)	55		251–253[h]	293	1.35	$C_{15}H_{14}BrN_3O$[h]	54.2	53.8	4.3	4.3	24.1	24.4	12.7	12.9

[a] Recrystallized from ethanol or ethanol by addition of ether. [b] Formulas and analyses are for base unless otherwise noted. [c] A second isomer was not isolated although difficulty of purification indicated that it was present. [d] By purification of fraction B. [e] Hydrochloride. [f] First isolated as distilled base, b.p. 170–180° (0.1 mm.). [g] Nitrate. [h] Hydrobromide.

TABLE III

1-ARYL-5-METHYL-3-(4-PYRIDYL)-PYRAZOLES (TYPE IVa)

Substituent in phenyl ring	Method (Hours)	Yield, %	M.p., °C. Base[a]	M.p., °C. HCl[a]	λmax, mμ	$\epsilon \times 10^{-4}$	Formula[b]	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Halogen, % Calcd.	Halogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
m-Cl	B(5)	8	75–76[c]	208–210	306	2.20	$C_{15}H_{12}ClN_3$	66.8	66.5	4.5	4.7	13.1	13.2	15.6	15.6
p-Cl	B(5)	11	90–92[c]	260–263	306	2.06	$C_{15}H_{12}ClN_3$	66.8	67.0	4.5	4.6	13.1	12.8	15.6	15.6
2,4-diCl	B(7)[d]	10	133–134	244–249	294	2.16	$C_{15}H_{11}Cl_2N_3$	59.2	59.5	3.6	3.9	23.3	23.6	13.8	14.0
5-Cl-2-CH_3O	B(8)	10	140–141		297	2.01	$C_{16}H_{14}ClN_3O$	64.1	64.0	4.7	5.2	11.8	11.8	14.0	13.9
3-Cl-2-CH_3	B(7)[d]	30	Oil	284–290	296	2.14	$C_{16}H_{15}Cl_2N_3$[e]	60.0	59.8	4.7	4.9	22.2	22.1	13.1	13.2

[a] Recrystallized from ethanol or ethanol by addition of ether unless otherwise noted. [b] Formulas and analyses are for base unless otherwise noted. [c] Recrystallized from hexane. [d] From fraction A. [e] Hydrochloride.

lated several pairs of isomeric pyrazoles[3] from the reaction of isonicotinoylacetone with arylhydrazines and have found the ultraviolet absorption spectra useful in assignment of their structures.

The ultraviolet absorption spectra were determined[4] and it was found that the pyrazoles fell into two groups. One isomer (IIIa, Table II) of each pair had an absorption maximum within the limits, λ_{max} 293–296 mμ and $\epsilon \times 10^{-4}$ 1.30–1.51, while in the other isomer (IVa, Table III) a maximum was within the limits, λ_{max} 294–306 mμ and $\epsilon \times 10^{-4}$ 2.01–2.20. When only one isomer was isolated, it also fitted into one of these groups. The spectra of 1-(*m*-chlorophenyl)-3(and 5)-methyl-5(and 3)-(4-pyridyl)-pyrazoles are compared in Fig. 1.

An examination of the structure of these compounds using LaPine atomic models indicated a greater crowding of the pyridine and phenyl rings in IIIa than in IVa. Such crowding would be expected to result in a decrease in the coplanarity of the pyridine and phenyl rings accompanied by steric inhibition of resonance. This observation is consistent with the observed hypsochromic shift and reduced intensity of compounds IIIa as compared to IVa, and was the basis of the assignment of structure to these isomers. It is interesting to note that Burness[5] observed this effect in a series of alkyl substituted 1-(*p*-nitrophenyl)-pyrazoles and showed that the degree of inhibition of resonance depended upon the number, size and position of the alkyl groups.

In order to obtain additional evidence in support of the assigned structures, we prepared three isomeric pairs of 3(and 5)-phenyl-pyrazoles whose structure had been previously proved by other investigators[6] (V–X, Table I). As with the (4-pyridyl)-pyrazoles, atomic models indicated that the isomer having an aromatic group in the 5-position (V, VII, IX) would be expected to show the greater inhibition of resonance. The observed shift in λ_{max} and intensity was in agreement and was analogous to results in the (4-pyridyl)-pyrazole series (Table I). Compounds IX and X, in which the large size of the bromo atom would be expected to cause the greatest crowding, showed the largest decrease in intensity.

Pyrazole formation from unsymmetrical dicarbonyl compounds and substituted hydrazines

(3) T. L. Fields, M. J. Weiss and W. B. Wright, Jr., U. S. Patent 2,833,779 (May 6, 1958).

(4) Measurements were made with a Cary model 11 or a Cary model 14 recording spectrophotometer, using 10.00-mm. quartz cells. Samples were prepared by dilution of a 100 γ/ml. solution in methanol to 10–20 γ/ml. with 0.1 *N* HCl.

(5) D. M. Burness, *J. Org. Chem.*, **21**, 97 (1956).

(6) (a) K. v. Auwers and H. Stuhlmann, *Ber.*, **59**, 1043 (1926); (b) K. v. Auwers and K. Schaum, *ibid.*, **62**, 1671 (1929); (c) K. v. Auwers and H. Mauss, *ibid.*, **59**, 611 (1926); (d) L. Knorr and A. Blank, *ibid.*, **18**, 311 (1885); (e) L. Knorr and A. Blank, *ibid.*, **18**, 931 (1885); (f) P. J. Drumm, *Proc. Royal Irish Acad.*, **40**, 106 (1931).

TABLE IV

1-ARYL-3-METHYL-5-(2 AND 3-PYRIDYL)-PYRAZOLES (TYPES IIIb AND IIIc)

Pyridyl	Substituent in phenyl ring	Method (Hours)	Yield, %	Base B.p. (mm.)	Salt	M.p., °C.	λmax, mμ	ε × 10⁻⁴	Formula[a]	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Halogen, % Calcd.	Halogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
2-	H	A(16)[b]	79	136–140(0.2)[b]	HCl	169–171[c]	299	1.13	$C_{15}H_{14}ClN_3$	66.3	66.5	5.2	5.3	13.1	13.2	15.5	15.5
2-	*m*-Cl	A(16)[b]	85	156–162(0.2)	HCl	154–156[d]	297	1.15	$C_{15}H_{13}Cl_2N_3$	58.8	58.6	4.3	4.2	23.2	23.1	13.7	14.0
2-	*p*-Cl	A(16)[e]	74	94–96[c,f]	HCl	187–189[d]	298	1.19	$C_{15}H_{13}Cl_2N_3$	58.8	58.9	4.3	4.5	23.2	22.9	13.7	13.7
3-	H	A(6)[b]	87	160–170(2)[i]	HNO_3	153–155[c]	259	1.21	$C_{15}H_{14}N_4O_3$	60.5	60.4	4.7	5.0			18.8	19.0
3-	*m*-Cl	A(6)[b]	52	156–162(0.2)	HNO_3	144–145[d]	258	1.34	$C_{15}H_{13}ClN_4O_3$	54.1	53.8	4.0	4.1	10.7	10.9	16.8	17.1
3-	*m*-CH_3O	A(10)[b]	72	165–170(0.5)	HCl	168–170[d]	258	1.30	$C_{16}H_{16}ClN_3O$	63.7	63.5	5.3	5.5	11.8	12.1	13.9	14.1
3-	*m*-HO	C(24)[g]	90	130–132[c,f]	HNO_3	126 dec.[d]	258	1.29	$C_{15}H_{14}N_4O_4$	57.3	57.2	4.5	4.4			17.8	17.8

[a] Empirical formulas and analyses are for the salt. [b] Product isolated as the distilled base. [c] Recrystallized from ethanol. [d] Recrystallized from ethanol by the addition of ether. [e] The base crystallized on cooling. [f] Melting point. [g] Isolated as a base by addition of aqueous sodium bicarbonate to the crude hydrobromide. [h] Micko, *Monatsh.*, **17**, 448 (1896), reported b.p. 215° (15 mm.). [i] Ferenczy, *ibid.*, **18**, 674 (1897), described an oil which was not characterized.

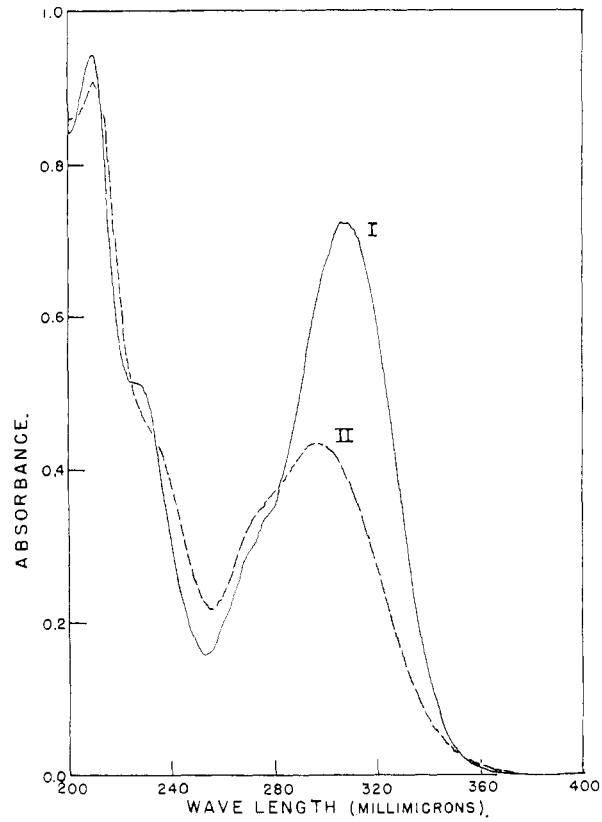


Fig. 1.—Ultraviolet absorption spectra: I, 1-(*m*-chlorophenyl)-5-methyl-3-(4-pyridyl)-pyrazole hydrochloride; II, 1-(*m*-chlorophenyl)-3-methyl-5-(4-pyridyl)-pyrazole hydrochloride. Samples were prepared by dilution of a 100 γ/ml. solution in methanol to 10 γ/ml. with 0.1 *N* HCl.

may be considered a complex example of competitive carbonyl addition reactions.[7] The nucleophilic reagent, the hydrazine derivative, has two non-equivalent reactive centers which can react sequentially (or possibly simultaneously) with the carbonyl reagent which also has two non-equivalent reactive centers. The ratio of pyrazole isomers should be governed by the relative reactivities of all four of these centers. Hinman[8] has investigated the relative reactivity of the two nitrogen atoms of substituted hydrazines toward various reagents including anhydrides and esters. Hydrazone formation is subject to general acid catalysis,[9] and pyrazole formation would also be expected to be a balance between two opposing factors; namely, the increased reactivity of the carbonyl group and the decreased reactivity of one or both nitrogen atoms due to salt formation. The influence of acid catalysis by disproportionately affecting the reactivity of the four centers could then be expected to alter the proportions of the two pyrazole isomers. This was observed when isonicotinoylacetone was treated with both *m*-chlorophenylhydrazine and *p*-chlorophenylhydrazine. When isonicotinoylacetone and *m*-chloro-

(7) Reference 1, p. 55.

(8) R. L. Hinman, *J. Org. Chem.*, **23**, 1587 (1958); R. L. Hinman and D. Fulton, THIS JOURNAL, **80**, 1895 (1958).

(9) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp. 246–251.

phenylhydrazine were refluxed in ethanol and then treated with hydrogen chloride, the only product isolated was 1-(*m*-chlorophenyl)-3-methyl-5-(4-pyridyl)-pyrazole hydrochloride (IIIa, R″ = *m*-chlorophenyl). The purified yield was 77%. However, when the same reaction was carried out in the presence of one or more equivalents of hydrochloric acid, the isolated product had a lower melting point and was difficult to purify. Fractional recrystallization showed that both isomeric pyrazoles had formed. The reaction with *p*-chlorophenylhydrazine gave similar results; the details are given in Tables II and III. When isonicotinoylacetone was allowed to react in the presence of acid with other phenylhydrazines it was found that they also generally formed two isomeric pyrazoles which could be purified and characterized.

A series of (2-pyridyl)- and (3-pyridyl)-pyrazoles also was prepared (Table IV). These reactions were not acid-catalyzed and only one isomer was isolated. These compounds have been assigned the type III structure based on the low molar extinction coefficients observed.

Acknowledgment.—We wish to thank Dr. M. W. Bullock,[10] Dr. J. H. Clark and co-workers for the preparation of many of the intermediates, Mr. L. Brancone and associates for the microanalyses, and Mr. G. O. Morton for the ultraviolet absorption data.

Experimental

Known methods were used for the preparation of 1,3-dimethyl-5-phenylpyrazole,[6a] 1,5-dimethyl-3-phenylpyrazole,[6a] 3-methyl-1,5-diphenylpyrazole,[6d] 5-methyl-1,3-diphenylpyrazole,[6e] 4-bromo-3-methyl-1,5-diphenylpyrazole[6d] and 4-bromo-5-methyl-1,3-diphenylpyrazole.[6e] Physical constants were in agreement with those previously reported.

The 1-aryl-3(and 5)-methyl-5(and 3)-pyridylpyrazoles were prepared from known intermediates by one of the following general methods. The procedures are typical; the multiple examples are given to illustrate modifications in the purification necessary to separate various pairs of isomers.

Method A. Condensation in the Absence of Acid. 1-(*m*-Chlorophenyl)-3-methyl-5-(4-pyridyl)-pyrazole Hydrochloride.—A mixture of 16.4 g. (0.1 mole) of isonicotinoylacetone and 14.3 g. (0.105 mole) of *m*-chlorophenylhydrazine in 200 ml. of ethanol was allowed to stand at room temperature for a short time, heated on the steam-bath for 7 hours and cooled. Precipitation did not occur. The solution was treated with 24 ml. (0.1 mole) of 4.2 *N* ethanolic hydrogen chloride. On cooling, 15.3 g. (50%) of yellow crystals, m.p. 241–244°, separated. One recrystallization from ethanol resulted in 10.7 g. of pure 1-(*m*-chlorophenyl)-3-methyl-5-(4-pyridyl)-pyrazole hydrochloride as white needles, m.p. 241–244°. Recovery by concentration by the mother liquors increased the yield to 77%.

The base was obtained by dissolving the hydrochloride in water and adding concentrated ammonia. It was purified by recrystallization from ethanol.

Method B. Condensation in the Presence of Acid. 1-(*m*-Chlorophenyl)-3-methyl-5-(4-pyridyl)-pyrazole Hydrochloride and 1-(*m*-Chlorophenyl)-5-methyl-3-(4-pyridyl)-pyrazole Hydrochloride.—*m*-Chlorophenylhydrazine (14.3 g., 0.105 mole) was added to a solution of 16.4 g. (0.1 mole) of isonicotinoylacetone in 200 ml. of ethanol and 28.8 ml. (0.12 mole) of 4.2 *N* ethanolic hydrogen chloride. The mixture was refluxed for five hours and cooled. Precipitation did not occur, so the solution was concentrated to about 50 ml. and again cooled. Precipitate A, 13.4 g., m.p. 190–195°, was obtained. When the mother liquor was concentrated nearly to dryness and triturated with ether, precipitate B, 9.2 g., m.p. 181–185°, was isolated.

Fraction A was recrystallized from ethanol and 4.2 g. (14%) of the previously described 1-(*m*-chlorophenyl)-3-methyl-5-(4-pyridyl)-pyrazole hydrochloride, m.p. 238–242°, was obtained.

Fraction B was recrystallized from ethanol and 2.4 g. (8%) of the second isomer, 1-(*m*-chlorophenyl)-5-methyl-3-(4-pyridyl)-pyrazole hydrochloride, m.p. 205–207°, was obtained. This compound was shown to be different from A by a depressed mixture melting point and a different ultraviolet absorption curve. A portion of this hydrochloride was converted to the base by treatment with aqueous ammonia. After purification by recrystallization from hexane, it melted at 75–76° and gave a depressed mixture melting point with the base from A. A sample of this was reconverted to the hydrochloride. The purified hydrochloride melted at 208–210°.

1-(*p*-Chlorophenyl)-3-methyl-5-(4-pyridyl)-pyrazole and 1-(*p*-Chlorophenyl)-5-methyl-3-(4-pyridyl)-pyrazole.—*p*-Chlorophenylhydrazine hydrochloride (17.9 g., 0.1 mole) was added to a solution of 16.4 g. (0.1 mole) of isonicotinoylacetone in 200 ml. of ethanol and 4.8 ml. (0.02 mole) of 4.2 *N* ethanolic hydrogen chloride. The mixture was refluxed for 5 hours and then cooled. The reaction mixture was filtered and the product was washed with ether and dried in a desiccator. This was fraction A, 20.2 g., m.p. 232–236°. The mother liquor was concentrated to a sirup, fraction B.

Recrystallization of A from ethanol did not give satisfactory purification, so the material was slurried in 7 parts of water, and filtered. The white precipitate was treated with ammonia and filtered, 7.5 g., m.p. 60–63°. This product was recrystallized from hexane until pure 1-(*p*-chlorophenyl)-5-methyl-3-(4-pyridyl)-pyrazole, m.p. 90–92°, was obtained.

The water-soluble portion from fraction A was precipitated by the addition of ammonia, 2.7 g., m.p. 90–105°. Additional material, 5.2 g., m.p. 80–85°, was obtained by a similar water–ammonia treatment of fraction B. The combined solids were recrystallized from hexane or ethanol until pure 1-(*p*-chlorophenyl)-3-methyl-5-(4-pyridyl)-pyrazole, m.p. 117–118°, was obtained.

1-(5-Chloro-2-methoxyphenyl)-3-methyl-5-(4-pyridyl)-pyrazole and 1-(5-Chloro-2-methoxyphenyl)-5-methyl-3-(4-pyridyl)-pyrazole.—A solution of 16.4 g. (0.1 mole) of isonicotinoylacetone and 20.9 g. (0.1 mole) of 5-chloro-2-methoxyphenylhydrazine hydrochloride in 100 ml. of ethanol was refluxed for 8 hours and cooled. Precipitation did not occur. The reaction was concentrated to a sirup and again cooled. The solid which formed was washed onto a filter with ethanol, fraction A. The filtrate was concentrated to a sirup, fraction B.

Fraction A was recrystallized twice from ethanol. The hydrochloride was slurried in water and treated with ammonia. The precipitate which separated was 1-(5-chloro-2-methoxyphenyl)-3-methyl-5-(4-pyridyl)-pyrazole and melted at 158–159° before and after recrystallization from ethanol.

Fraction B dissolved easily in water and was treated with ammonia. The precipitate which separated was filtered and recrystallized twice from ethanol. Pure 1-(5-chloro-2-methoxyphenyl)-5-methyl-3-(4-pyridyl)-pyrazole melted at 140–141°.

Additional material was obtained by reworking the filtrates. The difference in the water solubility of the hydrochlorides was very useful in separating these materials.

Method C. Hydrolysis of Phenolic Ether. 1-(*m*-Hydroxyphenyl)-3-methyl-5-(4-pyridyl)-pyrazole Hydrobromide.—A mixture of 2.5 g. of 1-(*m*-anisyl)-3-methyl-5-(4-pyridyl)-pyrazole and 25 ml. of 48% hydrobromic acid was heated on the steam-bath for 24 hours and then concentrated. The gum was warmed with 5 ml. of ethanol, cooled, filtered, and the tan crystals were recrystallized once from ethanol. The yield of pure 1-(*m*-hydroxyphenyl)-3-methyl-5-(4-pyridyl)-pyrazole hydrobromide, m.p. 251–253°, was 55%.

PEARL RIVER, N. Y.

(10) M. W. Bullock and J. J. Hand, THIS JOURNAL, **78**, 5854 (1956).