

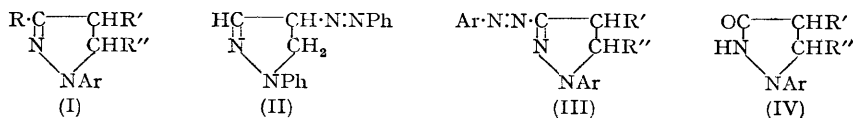
The Reaction of Diazonium Salts with 1-Aryl- Δ^2 -pyrazolines.

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1-Aryl- Δ^2 -pyrazolines (I; R = H), unsubstituted in the 3-position, react with aryl-diazonium chlorides in acetic acid to give 1-aryl-3-arylo- Δ^2 -pyrazolines (III). In alkaline solution the main products are 1:3-diaryl- Δ^2 -pyrazolines (I; R = Ar). 3-Methyl-1-phenyl- and 1:3-diphenyl- Δ^2 -pyrazolines with benzenediazonium chloride, in acid solution only, give 1-*p*-phenylazophenyl derivatives (XIV). Oxidation of the azopyrazolines gives the corresponding azo-pyrazoles and reduction gives the amines (VIII or XIII) which have been synthesized by alternative methods. 3-Amino-1-aryl- Δ^2 -pyrazolines do not behave like aromatic amines and are hydrolysed by mineral acid to 3-pyrazolidones. Reduction of 1-phenyl-3-phenylazopyrazole gives 3-amino-1-phenylpyrazole which has aromatic properties.

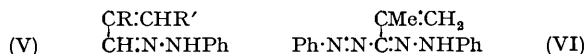
CURTIUS and WIRSING (*J. pr. Chem.*, 1894, **50**, 531), by treating 1-phenyl- Δ^2 -pyrazoline (I; Ar = Ph, R = R' = R'' = H) with benzenediazonium chloride in acetic acid, obtained a 1-phenyl-*x*-phenylazo- Δ^2 -pyrazoline, which Michaelis (*Annalen*, 1905, **338**, 184), without supporting evidence, suggested was the 4-phenylazo-compound (II). Reduction of this azo-compound, however, gave an amine from which, by hydrolysis, 1-phenyl-3-pyrazolidone (IV; Ar = Ph, R' = R'' = H) was obtained, indicating that the amine was 3-amino-1-phenyl- Δ^2 -pyrazoline (VII; Ar = Ph, R' = R'' = H) and the azo-compound 1-phenyl-3-phenylazo- Δ^2 -pyrazoline (III; Ar = Ph, R' = R'' = H).



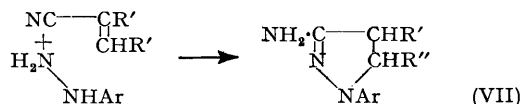
The reactions with diazonium salts, of other 1-phenyl- Δ^2 -pyrazolines, including the 4- and the 5-methyl derivative were also investigated. Although compounds supposed to have the latter structure have been reported, these were really the isomeric phenyl-

hydrazones (V). Thus, the compound (V; R = Me, R' = H) obtained by Shriner and Sharp (*J. Amer. Chem. Soc.*, 1940, **62**, 2245) from phenylhydrazone and α -methylacraldehyde in dilute acetic acid had not the characteristic ultra-violet absorption of a 1-phenyl- Δ^2 -pyrazoline and reacted with benzenediazonium chloride in alkaline solution to give an orange-yellow azo-compound with the properties of a formazan (VI). Similarly, crotonaldehyde and phenylhydrazine, reported by Trener (*Monatsh.*, 1900, **21**, 1111) to give, in the absence of a condensing agent, 5-methyl-1-phenyl- Δ^2 -pyrazoline, yielded only crotonaldehyde phenylhydrazone (cf. Wegscheider and Späth, *Monatsh.*, 1910, **31**, 1024; von Auwers and Kreude, *Ber.*, 1925, **58**, 1974). However, in hot aqueous sodium hydroxide α -methylacraldehyde and phenylhydrazine gave 4-methyl-1-phenyl- Δ^2 -pyrazoline (I; Ar = Ph, R = R' = H, R' = Me), and crotonaldehyde and phenylhydrazine similarly gave the 5-methyl analogue. The ultra-violet absorptions of these pyrazolines are similar to that of 1-phenyl- Δ^2 -pyrazoline and unlike those of the isomeric phenylhydrazones. 4- and 5-Methyl-1-phenyl- Δ^2 -pyrazoline, with benzenediazonium chloride in acetic acid, yielded phenylazo-derivatives, together with 1:3-diphenyl-4- and -5-methyl- Δ^2 -pyrazoline (I; Ar = R = Ph, R' = Me or H, R'' = H or Me, respectively). Shriner and Sharp's compound (*loc. cit.*), under the same conditions, gave no identifiable product. 1:5-Diphenyl-, 1:3-diphenyl-, and 3-methyl-1-phenyl- Δ^2 -pyrazoline gave, with benzenediazonium chloride in acetic acid, only phenylazo-compounds.

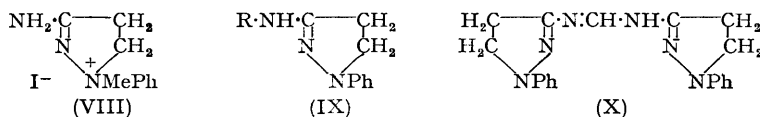
Reduction of the phenylazo-compounds yielded, in all cases, aniline and an amino-substituted 1-phenyl- Δ^2 -pyrazoline. The amines from 1-phenyl-, 4- and 5-methyl-1-phenyl-, and 1:5-diphenyl-phenylazo- Δ^2 -pyrazoline gave an intense blue-green colour with acidic ferric chloride, whereas those from 1:3-diphenyl- and 3-methyl-1-phenyl-phenylazo- Δ^2 -pyrazoline gave none. The former set was also easily hydrolysed by hot dilute mineral acid to an ammonium salt and the corresponding 3-pyrazolidone (IV), thus proving that the amines were 3-amino- Δ^2 -pyrazolines (VII). The other two amines were unaffected under similar conditions.



The structure of the 3-amino-1-phenyl- Δ^2 -pyrazolines was confirmed by unambiguous synthesis from acrylonitrile and phenylhydrazine in the presence of sodium ethoxide. Other 3-amines were similarly formed:



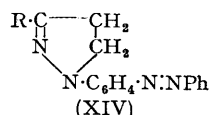
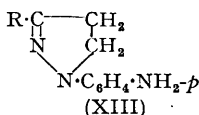
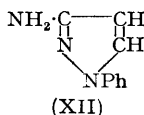
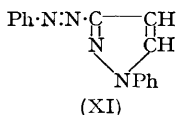
3-Amino-1-aryl- Δ^2 -pyrazolines are colourless, stable monoacid bases which form soluble salts. 3-Amino-1-phenyl- Δ^2 -pyrazoline was investigated more fully. With methyl iodide it gave the monomethiodide (VIII), the structure of which was demonstrated by degradation to *N*-methyl-*N*-phenylhydrazine. With phenyl isothiocyanate it gave a thiourea, assumed to be (IX; R = NHPH·CS) and with ethyl orthoformate an amidine (X). With nitrous acid the amine gave a deep blue insoluble substance, which was also produced by other oxidising agents in acid solution. No evidence of the formation of a diazonium salt could be obtained. The amine readily gave deep yellow Schiff's bases with aromatic aldehydes, but acetylation with acetic anhydride was difficult, tars being also formed. The acetyl derivative was 3-acetamido-1-phenyl- Δ^2 -pyrazoline (IX; R = Ac) since on reduction



with lithium aluminium hydride it gave 3-ethylamino-1-phenyl- Δ^2 -pyrazoline (IX; R = Et), identified by hydrolysis to ethylamine and 1-phenyl-3-pyrazolidone.

Additional evidence that 1-phenyl- Δ^2 -pyrazoline couples at the 3-position was obtained

by oxidising 1-phenyl-3-phenylazo- Δ^2 -pyrazoline with lead tetra-acetate to 1-phenyl-3-phenylazopyrazole (XI). This, unlike 1-phenyl-4-phenylazopyrazole which yields no simple aminopyrazole on reduction (Zincke and Kegel, *Ber.*, 1889, **22**, 1481; Michaelis and Schäfer, *Annalen*, 1915, **407**, 232), was reduced to an amine identical with the hitherto unknown 3-amino-1-phenylpyrazole (XII) obtained by Curtius degradation of 1-phenylpyrazole-3-carboxyhydrazide. 3-Amino-1-phenylpyrazole, unlike 3-amino-1-phenyl- Δ^2 -pyrazoline, behaves as an aromatic amine and can be diazotized like 3-aminopyrazole (Knorr, *Ber.*, 1904, **37**, 3522).



Δ^2 -Pyrazolines with substituents in the 3-position cannot give 3-phenylazo-derivatives. Oxidation of the azo-compound from benzenediazonium chloride and 3-methyl-1-phenyl- Δ^2 -pyrazoline gave a pyrazole which was different from the known 3-methyl-1-phenyl-4-phenylazopyrazole, indicating that the original coupling must have occurred either in the 5-position or in the benzene nucleus. Treating an aqueous solution of *p*-acetamidophenylhydrazine with 4-diethylaminobutan-2-one or β -dimethylaminopropiophenone and then removing the acetyl group gave 1-*p*-aminophenyl- Δ^2 -pyrazolines (XIII; R = Me or Ph) identical with the amines produced by reduction of the phenylazo-derivatives of (I; Ar = Ph, R = Me or Ph, R' = R'' = H). The latter are therefore 1-*p*-phenylazophenyl- Δ^2 -pyrazolines (XIV; R = Me or Ph).

1-Phenyl- Δ^2 -pyrazoline (I; Ar = Ph, R = R' = R'' = H) and an arenediazonium salt in the presence of a base yield, not the arylazo-compound (IV), but a 3-aryl-1-phenyl- Δ^2 -pyrazoline (I; Ar = Ph, R = Ar, R' = R'' = H) with the loss of nitrogen. This reaction appears fairly general for 1-aryl- Δ^2 -pyrazolines unsubstituted in the 3-position, proceeding rapidly at 5–10°. In comparison with those obtained in similar arylations, the yields are remarkably good. Under the same conditions 3-methyl-1-phenyl- and 1:3-diphenyl- Δ^2 -pyrazolines are unaffected. The use of sodium acetate, as the base, in the reaction of 1-phenyl- Δ^2 -pyrazoline with benzenediazonium chloride results in the formation of some 1-phenyl-3-phenylazo- in addition to 1:3-diphenyl- Δ^2 -pyrazoline. All the 1:3-diaryl- Δ^2 -pyrazolines are characterised by the bright blue fluorescence of their solutions in ether and benzene.

The mechanism of arylation of Δ^2 -pyrazolines in alkaline solution is uncertain. Since 1-phenyl-3-phenylazo- Δ^2 -pyrazoline is quite stable in alkaline solution it cannot be regarded as an intermediate in the formation of the 3-phenyl compound. It is suggested that a free-radical mechanism of the type postulated by Hey and Waters (*Chem. Reviews*, 1937, **21**, 169) might best explain the reaction.

EXPERIMENTAL

Absorption maxima were determined in ethanol.

α -Methylacraldehyde phenylhydrazone (Shriner and Sharpe, *loc. cit.*) had λ_{max} . 2465 (ϵ 9700), 3005 (ϵ 19,600), and 3250 Å (ϵ 23,700).

4-Methyl-1-phenyl- Δ^2 -pyrazoline.—Phenylhydrazine (30 c.c.) and α -methylacraldehyde (25 c.c.) were heated in 3% aqueous sodium hydroxide (300 c.c.) at 100° for 3 hr. After cooling, the precipitated oil was extracted with ether, dried (K_2CO_3), and distilled, to yield 4-methyl-1-phenyl- Δ^2 -pyrazoline as a pale yellow oil, b. p. 118–120°/1.1 mm. (12.5 g., 26%) (Found: C, 75.1; H, 7.4. $\text{C}_{10}\text{H}_{12}\text{N}_2$ requires C, 75.0; H, 7.5%), λ_{max} . 2420 (ϵ 11,000) and 2785 Å (ϵ 21,000).

Crotonaldehyde phenylhydrazone (von Auwers and Kreude, *loc. cit.*) had λ_{max} . 2475 (ϵ 7050), 3010 (ϵ 19,600), and 3230 Å (ϵ 22,200).

5-Methyl-1-phenyl- Δ^2 -pyrazoline.—This compound was obtained from phenylhydrazine and crotonaldehyde by the foregoing method, as a pale yellow oil, b. p. 112–114°/0.6 mm. (24%) (Found: C, 75.4; H, 7.6%), λ_{max} . 2480 (ϵ 10,600) and 2845 Å (ϵ 20,600).

1-Phenyl- Δ^2 -pyrazoline (Fischer and Knoevenagel, *Annalen*, 1887, **239**, 196) had λ_{max} . 2420

(ϵ 11,500) and 2810 Å (ϵ 25,800). 1 : 5-Diphenyl- Δ^2 -pyrazoline (von Auwers and Müller, *Ber.*, 1908, 41, 4232) had λ_{\max} 2440 (ϵ 8400) and 2830 Å (ϵ 14,500).

1-*o*- and 1-*p*-Tolyl- Δ^2 -pyrazoline were prepared by Balbiano's method (*Gazzetta*, 1888, 18, 354), and 1-*m*-tolyl- Δ^2 -pyrazoline similarly from acraldehyde and *m*-tolylhydrazine, as a pale yellow oil, b. p. 152—156°/28 mm. (13%) (Found : N, 17.2. $C_{10}H_{12}N_2$ requires N, 17.5%).

3-Methyl-1-phenyl- Δ^2 -pyrazoline was obtained in improved yield by the following modification of Jacob and Madinaveitia's method (*J.*, 1937, 1929). A solution of phenylhydrazine (10 c.c.) and 4-diethylaminobutan-2-one (11.5 g.) in 2*N*-sulphuric acid (100 c.c.) was heated for 1 hr. at 100°, cooled, and extracted with ether. The extract was washed with dilute aqueous sodium carbonate, dried (K_2CO_3), and evaporated. The solid residue of 3-methyl-1-phenyl- Δ^2 -pyrazoline recrystallized from light petroleum (b. p. 60—80°) in colourless plates, m. p. 73° (8.1 g., 50%), λ_{\max} 2780 Å (ϵ 17,400).

1 : 3-Diphenyl- Δ^2 -pyrazoline.— β -Dimethylaminopropiophenone hydrochloride (21.5 g.), water (150 c.c.), ethanol (100 c.c.), sodium hydroxide (4.5 g.), and phenylhydrazine (15 c.c.) were heated together for 3 hr. at 100°. After cooling to 0° the solid 1 : 3-diphenyl- Δ^2 -pyrazoline was filtered off, washed successively with water and ethanol, and recrystallized from ethanol as pale yellow plates, m. p. 153° (15.3 g., 69%), λ_{\max} 2450 (ϵ 16,800) and 3540 Å (ϵ 26,400).

4-Methyl-1 : 3-diphenyl- Δ^2 -pyrazoline.—Propiophenone (2.4 c.c.), dimethylamine hydrochloride (1.65 g.), and paraformaldehyde (1.0 g.) in ethanol (10 c.c.) were boiled for 16 hr. After removal of ethanol the solid residue was dissolved in 10% aqueous sodium carbonate (38 c.c.), phenylhydrazine (1.8 c.c.) added, and the mixture heated at 100° for 4 hr. The oil which separated rapidly solidified on cooling, and was recrystallized from ethanol as colourless leaflets of 4-methyl-1 : 3-diphenyl- Δ^2 -pyrazoline, m. p. 119° (1.2 g., 28%) (Found : C, 81, 3; H, 6.9. $C_{18}H_{16}N_2$ requires C, 81.4; H, 6.8%).

Action of Aryldiazonium Salts on 1-Aryl- Δ^2 -pyrazolines in Acetic Acid.—The following exemplifies the procedure : Aniline (0.93 g.) in 5*N*-hydrochloric acid (5.0 c.c.) was diazotized at 5—10° with sodium nitrite (0.75 g.) in water (3 c.c.), then added slowly with stirring to a solution of 1-phenyl- Δ^2 -pyrazoline (1.45 g.) in acetic acid (10 c.c.) and water (2 c.c.) at 5—10°. After 1 hr. at 0°, the resulting violet solution was poured into water (100 c.c.) and left overnight. The precipitated solid was washed with water, dried, and recrystallized from methanol to yield 1-phenyl-3-phenylazo- Δ^2 -pyrazoline as orange-red leaflets, m. p. 156° (0.97 g., 39%) (Found : C, 71.7; H, 5.4. Calc. for $C_{15}H_{14}N_4$: C, 72.0; H, 5.6%).

Analogues, similarly obtained, are recorded in Table I.

TABLE I. 1-Aryl-3-arylamino- Δ^2 -pyrazolines (III).

Ar	R'	R''	M. p.*	(Yield %)	Found (%)		Formula	Required (%)	
					C	H		C	H
Ph	H	Ph	154°	49	77.35	5.7	$C_{21}H_{18}N_4$	77.4	5.55
<i>o</i> -Tolyl	H	H	92	53	72.7	6.35	$C_{17}H_{18}N_4$	73.3	6.45
<i>m</i> -Tolyl	H	H	150	82	73.2	6.4	$C_{17}H_{18}N_4$	73.3	6.45
<i>p</i> -Tolyl	H	H	184	60	73.5	6.4	$C_{17}H_{18}N_4$	73.3	6.45
Ph	Me	H	101	38 ^a	72.6	6.6	$C_{16}H_{16}N_4$	72.4	6.4
Ph	H	Me	107	43 ^b	72.5	6.4	$C_{16}H_{16}N_4$	72.4	6.4

^a Together with 4-methyl-1 : 3-diphenyl- Δ^2 -pyrazoline (18%), separated by chromatography from activated alumina in light petroleum. ^b Together with 5-methyl-1 : 3-diphenyl- Δ^2 -pyrazoline (2%) separated as in (a).

* The products form red needles, except the third and fifth which form orange plates; all were crystallized from methanol, except for the last two which crystallized from light petroleum.

3-Methyl-1-*p*-phenylazophenyl- Δ^2 -pyrazoline, obtained from 3-methyl-1-phenyl- Δ^2 -pyrazoline by the same method, crystallized from methanol as orange plates, m. p. 152° (36%) (Found : C, 72.25; H, 6.4. $C_{16}H_{16}N_4$ requires C, 72.4; H, 6.4%).

3-Methyl-1-*p*-phenylazophenylpyrazole.—The last-named pyrazoline (2.1 g.) was treated in acetic acid (30 c.c.) with lead tetra-acetate (5.0 g.). An exothermic reaction took place and the orange solution became yellow. Dilution with water gave an oil which rapidly solidified. Recrystallization from ethanol gave 3-methyl-1-*p*-phenylazophenylpyrazole as bright yellow plates, m. p. 117° (0.78 g., 38%) (Found : C, 73.3; H, 5.7; N, 21.4. $C_{16}H_{14}N_4$ requires C, 73.4; H, 5.4; N, 21.4%).

3-Phenyl-1-*p*-phenylazophenyl- Δ^2 -pyrazoline.—1 : 3-Diphenyl- Δ^2 -pyrazoline (10 g.) was dissolved in warm acetic acid (500 c.c.), the solution cooled to 14°, and a solution of benzenediazonium chloride [prepared from aniline (4.5 c.c.), 5*N*-hydrochloric acid (25 c.c.), and sodium

nitrite (3.7 g.) in water (10 c.c.)] stirred in with further cooling. The mixture was then left overnight at room temperature and the blue solution poured into a mixture of sodium hydroxide (400 g.) and ice (2 kg.). A red solid was precipitated, filtered off, washed with water and methanol, dried, and extracted with boiling benzene (500 c.c.) from a brown insoluble substance (2.0 g.). Evaporation of the benzene gave a reddish tar which, with acetone (50 c.c.), gave deep red needles (4.6 g.). Recrystallization from benzene yielded 3-phenyl-1-p-phenylazophenyl- Δ^2 -pyrazoline as dark red needles with a blue reflex, m. p. 185—186° (2.3 g., 29%) (Found: C, 77.5; H, 5.75. $C_{21}H_{18}N_4$ requires C, 77.4; H, 5.55%).

1: 5-Diphenyl-3-isopropenylformazan.—A solution of benzenediazonium chloride, prepared from aniline (3.8 c.c.), 5*N*-hydrochloric acid (21 c.c.), and sodium nitrite (3.1 g.) in water (10 c.c.), was added with stirring at 5—7° to one of α -methylacraldehyde phenylhydrazone (7.3 g.) in ethanol (100 c.c.) and 40% sodium hydroxide (11.4 c.c.). The mixture was well cooled and after 1 hr. the dark red precipitate was filtered off rapidly, washed with cold methanol (4 \times 10 c.c.), dried *in vacuo*, and recrystallized from methanol, to give the *formazan* as deep red needles, m. p. 109° (9.2 g., 72%) (Found: C, 72.5; H, 6.2; N, 21.0. $C_{16}H_{16}N_4$ requires C, 72.7; H, 6.05; N, 21.2%).

Addition of a benzenediazonium chloride solution to α -methylacraldehyde phenylhydrazone in 90% acetic acid gave a violet solution from which nitrogen was slowly evolved. Only a tar was isolated.

Reduction of Arylazo- Δ^2 -pyrazolines (III) or (XIV).—Two general methods were used: (A) 1-Phenyl-3-phenylazo- Δ^2 -pyrazoline (10 g.) was dissolved in ethanol (80 c.c.) and acetic acid (20 c.c.) on a water-bath. Zinc dust was added gradually until the reaction had moderated and the yellow colour disappeared. The mixture was boiled for 10 min. then filtered hot from zinc dust, and the filtrate was made alkaline with 10% aqueous sodium hydroxide to precipitate a pale buff solid which was collected and recrystallized from benzene. This gave 3-amino-1-phenyl- Δ^2 -pyrazoline as colourless leaflets, m. p. 169° (3.4 g., 53%) (Found: C, 67.35; H, 6.8; N, 26.0. $C_9H_{11}N_3$ requires C, 67.2; H, 6.85; N, 26.1%). Ether-extraction of the aqueous solution yielded aniline (73%).

(B) 1-Phenyl-3-phenylazo- Δ^2 -pyrazoline (5.0 g.) was refluxed with 5*N*-hydrochloric acid (21 c.c.), ethanol (10 c.c.), and stannous chloride (10.1 g.) for 10 min. The resulting colourless solution was filtered and made alkaline by addition of 10% aqueous sodium hydroxide (150 c.c.), to precipitate a buff solid which was collected, dried, and recrystallized from benzene as colourless plates, m. p. and mixed m. p. 169° (2.1 g., 65%).

Analogous experiments are reported in Table 2.

TABLE 2. *Reduction of azo-compounds (III) to amines: properties of the amine.*

Ar	R'	R''	Azo-cpd.	Amine ^a	Method	Yield (%)	M. p.	Found (%) ^e	
								C	H
<i>m</i> -Tolyl	H	H	(III)	(VII)	<i>B</i>	55	110° ^b	68.9	7.5
<i>p</i> -Tolyl	H	H	"	"	<i>B</i>	65	143° ^b	69.0	7.4
Ph	H	Me	"	"	<i>B</i>	64	106° ^c	68.4	7.4
Ph	Me	H	"	"	<i>B</i>	47	82° ^c	68.4	7.4
Ph	H	Ph	i,	"	<i>A</i>	70	195° ^c	76.3	6.5 ^f
R = Me			(XIV)	(XIII)	<i>A</i>	35	126° ^d	68.6	7.3
R = Ph			"	"	<i>B</i>	70	135° ^c	76.0	6.3

^a All (VII) were colourless needles; (XIII; R = Me) formed colourless plates, and (XIII; R = Ph) pale yellow plates. ^b From benzene. ^c From ethanol. ^d From light petroleum. ^e $C_{16}H_{13}N_3$ requires C, 68.7; H, 7.45; but for the fifth and the last amine, $C_{15}H_{11}N_3$ requires C, 76.0; H, 6.3%. ^f Found: N, 17.6. Req'd.: N, 17.75%.

Reaction of Arylhydrazines with $\alpha\beta$ -Unsaturated Nitriles.—The following exemplifies the procedure: Sodium (2.0 g.) was dissolved in ethanol (100 c.c.), and phenylhydrazine (40 c.c.) and acrylonitrile (26 c.c.) were added in that order. The mixture was refluxed for 6 hr., filtered hot, and cooled. The buff plates which separated were washed with ethanol and recrystallized from benzene, giving 3-amino-1-phenyl- Δ^2 -pyrazoline as colourless leaflets, m. p. 169° (48 g., 74%) (Found: C, 67.4; H, 6.65; N, 25.9%). The *hydrochloride* was obtained from concentrated hydrochloric acid as colourless plates, m. p. 96—97° (Found: Cl, 16.3. $C_9H_{11}N_3 \cdot HCl \cdot H_2O$ requires Cl, 16.5%), and the *picrate* from ethanol as yellow needles, m. p. 169° (decomp.) (Found: N, 20.7. $C_9H_{11}N_3 \cdot C_6H_3O_7N_3$ requires N, 21%).

Analogous syntheses are recorded in Table 3.

3-Amino-1-methyl-1-phenyl- Δ^2 -pyrazolinium Iodide.—3-Amino-1-phenyl- Δ^2 -pyrazoline (10 g.) and methyl iodide (20 c.c.) were heated under reflux for 4 hr., the mixture was cooled, and the solid was collected and washed with ether. After recrystallization from ethanol, the iodide formed colourless plates, m. p. 157° (5.2 g., 28%) (Found: I, 42.0. $C_{10}H_{14}N_3I$ requires

TABLE 3. Synthesis of 3-amino-1-aryl- Δ^2 -pyrazolines (VII).

Amine (VII) ^a			M. p.	Yield (%)	Found (%)		Formula	Required (%)	
Ar	R'	R''			C	H		C	H
<i>From acrylonitrile</i>									
<i>o</i> -Tolyl	H	H	74° ^b	8.5	68.8	7.6	} $C_{10}H_{13}N_3$	68.7	7.45
<i>m</i> -Tolyl ...	H	H	110° ^b	47	68.9	7.5			
<i>p</i> -Tolyl ...	H	H	143° ^b	70	69.0	7.5			
<i>p</i> - C_6H_4Cl ...	H	H	135° ^c	42	55.15	4.95° ^e	$C_9H_{10}N_3Cl$	55.25	5.15
<i>From cinnamonnitrile</i>									
Ph	H	Ph	195° ^c	40	75.7	6.0° ^f	See Table 2		
<i>m</i> -Tolyl ...	H	Ph	152° ^c	22	76.6	6.9	} $C_{16}H_{17}N_3$	76.7	6.8
<i>p</i> -Tolyl ...	H	Ph	195° ^b	31	76.6	7.1			
<i>p</i> - C_6H_4Cl ...	H	Ph	129° ^c	37	65.85	4.85			
<i>From crotononitrile</i>									
Ph	H	Me	106° ^c	29	68.4	7.4	See Table 2		
<i>From methylacrylonitrile</i>									
Ph	Me	H	82° ^d	43	68.4	7.2	See Table 2		

^a All colourless needles, except that the first three formed colourless plates, and the sixth and seventh buff-coloured needles. ^b From benzene. ^c From ethanol. ^d From light petroleum. ^e Found: Cl, 18.2. Reqd.: Cl, 18.15%. ^f Found: N, 17.9%.

I, 41.9%). It (5.0 g.) was heated at 100° for 4 hr. with *N*-sodium hydroxide (40 c.c.). After cooling, the precipitated oil was extracted with ether, dried, and distilled, yielding *N*-methyl-*N*-phenylhydrazine, b. p. 128—132°/15 mm. (1.5 g., 75%) (benzylidene derivative, m. p. and mixed m. p. 107°).

3-Acetamido-1-phenyl- Δ^2 -pyrazoline.—3-Amino-1-phenyl- Δ^2 -pyrazoline (50 g.) and acetic anhydride (50 c.c.) were stirred without cooling for 1 hr. The mixture was then cooled to precipitate the crystalline *acetyl* derivative. From ethanol this formed pale yellow needles, m. p. 192° (9.2 g., 15%) [Found: C, 65.2; H, 6.4%; *M* (ebullioscopic in EtOH), 199. $C_{11}H_{13}ON_3$ requires C, 65.0; H, 6.4%; *M*, 203].

3-Ethylamino-1-phenyl- Δ^2 -pyrazoline.—Reduction of 3-acetamido-1-phenyl- Δ^2 -pyrazoline (3.7 g.) in dry ether (100 c.c.) with lithium aluminium hydride (2.0 g.), vigorous at first, was continued for 16 hr. under reflux. Decomposition with ethanol, addition of water (200 c.c.), filtration, evaporation of the ethereal filtrate, and recrystallization from light petroleum (b. p. 60—80°) yielded 3-ethylamino-1-phenyl- Δ^2 -pyrazoline as colourless plates, m. p. 74° (2.9 g., 85%) (Found: C, 70.0; H, 8.15; N, 22.0. $C_{11}H_{15}N_3$ requires C, 69.8; H, 7.95; N, 22.2%). The amine (3.3 g.) was refluxed for 60 hr. with water (10 c.c.) and concentrated sulphuric acid (0.84 c.c.). On cooling, crystals were deposited which, recrystallized from water, yielded 1-phenyl-3-pyrazolidone, m. p. 121° (2.2 g., 79%). The aqueous solution from the hydrolysis was made alkaline by sodium hydroxide and distilled into saturated aqueous picric acid, giving ethylamine picrate, m. p. and mixed m. p. 168°.

3-Benzylideneamino-1-phenyl- Δ^2 -pyrazoline.—3-Amino-1-phenyl- Δ^2 -pyrazoline (16 g.) and benzaldehyde (10 c.c.) were boiled in ethanol (50 c.c.) for 2 hr. The precipitated 3-benzylideneamino-1-phenyl- Δ^2 -pyrazoline crystallized from dioxan as orange-yellow leaflets, m. p. 182° (14.3 g., 57%) (Found: C, 77.0; H, 6.1. $C_{16}H_{15}N_3$ requires C, 77.2; H, 6.0%).

3-*p*-Chlorobenzylideneamino-1-phenyl- Δ^2 -pyrazoline formed orange-red leaflets (from dioxan), m. p. 207° (84%) (Found: Cl, 12.6. $C_{16}H_{14}N_3Cl$ requires Cl, 12.5%).

NN'-Di-(1-phenyl- Δ^2 -pyrazolin-3-yl)formamidine.—3-Amino-1-phenyl- Δ^2 -pyrazoline (3.2 g.) in warm acetic acid (10 c.c.) was treated with ethyl orthoformate (2 c.c.). The solution became yellow and after a few minutes a copious yellow precipitate was formed. Recrystallization from acetic acid gave the yellow *formamidine*, m. p. 200° (2.4 g., 73%) (Found: C, 68.7; H, 6.2. $C_{19}H_{20}N_6$ requires C, 68.7; H, 6.0%).

***N*-Phenyl-*N'*-(1-phenyl- Δ^2 -pyrazolin-3-yl)thiourea.**—3-Amino-1-phenyl- Δ^2 -pyrazoline (5.0 g.)

and phenyl isothiocyanate (3.8 c.c.) in boiling ethanol (25 c.c.) gave the *thiourea* as pale yellow needles (from ethanol), m. p. 196° (3.1 g.) (Found: S, 10.85. $C_{16}H_{16}N_4S$ requires S, 10.8%).

Hydrolysis of 3-Amino- Δ^2 -pyrazolines.—The following exemplifies the procedure: 3-Amino-1-phenyl- Δ^2 -pyrazoline (10 g.) was dissolved in a mixture of concentrated sulphuric acid (3.32 c.c.) and water (40 c.c.), and the solution boiled for 6 hr. On cooling, the colourless crystals were collected and crystallized from water, yielding 1-phenyl-3-pyrazolidone as colourless needles, m. p. 121° (8.6 g., 86%) (Found: C, 66.75; H, 6.1. Calc. for $C_9H_{10}ON_2$: C, 66.7; H, 6.15%).

Similar experiments are reported in Table 4.

TABLE 4. *Hydrolysis of 3-amino- Δ^2 -pyrazolines (VII).*

3-Pyrazolidone (IV) ^a			M. p.	Yield (%)	Found (%)		Formula	Required (%)	
Ar	R'	R''			C	H		C	H
<i>p</i> -Tolyl ...	H	H	163° ^b	34	68.2	6.9	$C_{10}H_{12}ON_3$	68.2	6.8
<i>p</i> - C_6H_4Cl ...	H	H	117° ^b	20	55.65	4.9	$C_9H_9ON_2Cl$	55.7	4.9
Ph	Me	H	135° ^c	31	68.3	6.75	$C_{10}H_{12}ON_3$	68.2	6.8
Ph	H	Ph	159° ^c	60	75.5	5.95	$C_{15}H_{14}ON_2$	75.7	5.9

^a The first two formed colourless plates, the last two colourless needles. ^b From benzene. ^c From benzene-light petroleum.

Action of Nitrous Acid on 3-Amino-1-phenyl- Δ^2 -pyrazoline.—The amine (3.2 g.) was treated in 5*N*-hydrochloric acid (10 c.c.) at 0° with sodium nitrite (1.5 g.) in water (4 c.c.) with stirring. Nitrogen was evolved and a dark blue substance, m. p. 260—270° (2.9 g.), precipitated. The substance was almost insoluble in all organic solvents, but dissolved in concentrated acids to give intense blue solutions. Similar substances were obtained from other 3-amino- Δ^2 -pyrazolines with nitrous acid or acid oxidizing agents.

1-p-Aminophenyl-3-methyl- Δ^2 -pyrazoline.—The double salt of stannic chloride and *p*-acetamidophenylhydrazine hydrochloride (Franzen and von Fürst, *Annalen*, 1917, **412**, 35) (10 g.) was treated in water (100 c.c.) with potassium carbonate (5.0 g.). After 2 hr. the precipitate was filtered off, and 4-diethylaminobutan-2-one (Hagemeyer, *J. Amer. Chem. Soc.*, 1949, **71**, 1120) (4.5 c.c.) added to the aqueous filtrate. The mixture was warmed for 1 hr. at 100°, then well cooled. Crystals which separated were recrystallized from water, to yield 1-*p*-acetamidophenyl-3-methyl- Δ^2 -pyrazoline as pale yellow plates, m. p. 181° (3.7 g., 57%) (Found: C, 66.6; H, 6.8. $C_{12}H_{15}ON_3$ requires C, 66.4; H, 6.9%). The acetyl compound (2.0 g.) was warmed at 100° for 10 min. with concentrated hydrochloric acid (10 c.c.), and the solution cooled, diluted with water (50 c.c.), and made alkaline with 40% sodium hydroxide (12 c.c.). Ether-extraction removed a solid which recrystallized from ethanol as pale buff needles, m. p. 126° (0.85 g., 52%) (Found: C, 68.9; H, 7.4%), identical with 1-*p*-aminophenyl-3-methyl- Δ^2 -pyrazoline obtained as above.

1-p-Aminophenyl-3-phenyl- Δ^2 -pyrazoline.—By a similar process, β -dimethylaminopropiophenone hydrochloride yielded 1-*p*-acetamidophenyl-, yellow leaflets (from acetic acid), m. p. 220° (78%) (Found: C, 73.25; H, 6.35. $C_{17}H_{17}ON_3$ requires C, 73.2; H, 6.1%), and 1-*p*-aminophenyl-3-phenyl- Δ^2 -pyrazoline, pale yellow plates (from aqueous ethanol), m. p. 135° (63%) (Found: C, 75.9; H, 6.2%).

1-Phenyl-3-phenylazopyrazole.—1-Phenyl-3-phenylazo- Δ^2 -pyrazoline (2.5 g.) was dissolved in acetic acid (25 c.c.), and lead tetra-acetate (6.0 g.) added at 20°. The temperature rose to 44° and the colour of the solution changed from orange to yellow. Addition of water (200 c.c.) precipitated a yellow oil which rapidly solidified. Recrystallization from benzene gave 1-phenyl-3-phenylazopyrazole as bright yellow needles, m. p. 101° (1.51 g., 61%) (Found: C, 72.65; H, 4.8; N, 22.15. $C_{15}H_{12}N_4$ requires C, 72.8; H, 4.85; N, 22.6%).

Reduction of 1-Phenyl-3-phenylazopyrazole.—The azo-compound (5.0 g.) was heated in ethanol (50 c.c.) and concentrated hydrochloric acid (25 c.c.) with tin (10 g.) for 15 min., the resulting colourless solution was filtered hot, and the filtrate made alkaline with 2*N*-sodium hydroxide (250 c.c.). The ethanol was then removed by distillation and the residue cooled to precipitate colourless needles. Recrystallized from water these gave 3-amino-1-phenylpyrazole, m. p. 101° (1.0 g., 31%) (Found: C, 68.0; H, 5.5; N, 26.2. $C_9H_9N_3$ requires C, 67.9; H, 5.65; N, 26.4%). It readily gave the acetyl derivative, colourless needles (from aqueous ethanol), m. p. 129° (Found: C, 65.7; H, 5.6. $C_{11}H_{11}ON_3$ requires C, 65.7; H, 5.5%).

1-(1-Phenylpyrazol-3-ylazo)-2-naphthol.—3-Amino-1-phenylpyrazole (0.32 g.) was diazotized in *n*-hydrochloric acid (5 c.c.) at 0° with sodium nitrite (0.15 g.) in water (1 c.c.). The yellow solution was added to a solution of β -naphthol (1.0 g.) in *n*-sodium hydroxide (30 c.c.). The

precipitate, recrystallized from acetic acid, yielded 1-(1-phenylpyrazol-3-ylazo)-2-naphthol as black needles with a green lustre, m. p. 178° (0.3 g.) (Found: C, 72.2; H, 4.65. $C_{19}H_{14}ON_4$ requires C, 72.5; H, 4.45%).

3-Amino-1-phenylpyrazole.—1-Phenylpyrazole-3-carboxylic acid (Claisen and Roosen, *Annalen*, 1894, 278, 294) (7.5 g.) was boiled with ethanol (25 c.c.) and sulphuric acid (0.1 c.c.) for 20 hr. After neutralization of the free acid, the ethanol was evaporated to leave the crude ethyl ester as a syrup (5.1 g., 60%) which was dissolved in ethanol (20 c.c.), and 90% hydrazine hydrate (5.0 c.c.) added. The solution was boiled for 3 hr., cooled, and diluted with water (20 c.c.). The precipitate, recrystallized from aqueous ethanol, gave 1-phenylpyrazole-3-carboxyhydrazide as colourless needles, m. p. 138° (3.5 g., 75%) (Found: C, 58.7; H, 6.0. $C_{10}H_{12}N_4$ requires C, 58.8; H, 5.9%). The hydrazide (3.0 g.) was dissolved at 5° in *n*-nitric acid (15 c.c.), and sodium nitrite (1.0 g.) in water (3 c.c.) added with stirring. An oil was precipitated which rapidly solidified and after 1 hr. was collected and dried *in vacuo*, giving colourless 1-phenylpyrazole-3-carboxyazide, m. p. 74° (decomp.) (2.9 g., 87%) (Found: N, 31.8. $C_{10}H_9ON_5$ requires N, 32.5%). The azide (2.35 g.) was boiled for 5 hr. with ethanol (20 c.c.), and the solution diluted with water (20 c.c.) and kept overnight at 0°. 1-Phenylpyrazol-3-yl-urethane separated and was obtained from ethanol as colourless needles, m. p. 102° (1.9 g., 75%) (Found: C, 62.4; H, 5.8. $C_{12}H_{13}O_2N_3$ requires C, 62.3; H, 5.65%). The urethane (1.5 g.) was heated at 100° for 4 hr. with 10% sodium hydroxide solution (40 c.c.). On cooling, crystals separated which, recrystallized from water, gave 3-amino-1-phenylpyrazole as colourless matted needles, m. p. 101° (0.7 g., 54%) (Found: C, 67.8; H, 5.7%).

Arylation of 1-Aryl- Δ^2 -pyrazolines.—1:3-Diphenyl- Δ^2 -pyrazoline was obtained by the following three procedures: (a) A solution of benzenediazonium chloride prepared from aniline (0.9 c.c.), 5*N*-hydrochloric acid (5 c.c.), and sodium nitrite (0.75 g.) in water (3 c.c.) was added with stirring to 1-phenyl- Δ^2 -pyrazoline (1.45 g.) in pyridine (20 c.c.) at 5–10°. Nitrogen was evolved throughout the addition. After 10 min. water (50 c.c.) was added to precipitate a mass of brown needles. Recrystallization from methanol gave 1:3-diphenyl- Δ^2 -pyrazoline as yellow needles, m. p. 152° (1.26 g., 56%) (Found: C, 81.2; H, 6.5. Calc. for $C_{15}H_{14}N_2$: C, 81.0; H, 6.3%).

(b) Experiment (a) was repeated but with 3% alcoholic sodium hydroxide (30 c.c.) instead of pyridine. 1:3-Diphenyl- Δ^2 -pyrazoline (75%) was again obtained.

(c) A diazonium solution as in (a) was added with stirring to 1-phenyl- Δ^2 -pyrazoline (1.46 g.) and sodium acetate (5 g.) in ethanol (30 c.c.) at 0°. A deep yellow solution was produced initially, but rapidly became colourless with evolution of nitrogen and separation of yellow crystals of 1:3-diphenyl- Δ^2 -pyrazoline, m. p. 150° (0.9 g., 40%). The filtrate, on dilution with water, gave a tar which was dissolved in light petroleum and chromatographed from alumina, to give 1:3-diphenyl- Δ^2 -pyrazoline (0.4 g., 18%) and 1-phenyl-3-phenylazo- Δ^2 -pyrazoline as orange-red plates, m. p. 156° (0.21 g., 8.5%).

By procedure (a) the compounds of Table 5 were prepared.

TABLE 5. 1:3-Diaryl- Δ^2 -pyrazolines (I).

Ar	R	R'	R''	M. p.	Yield (%)	Found (%)		Formula	Required (%)	
						C	H		C	H
Ph	<i>m</i> -Tolyl	H	H	77° ^a	33	82.0	6.75	$C_{16}H_{16}N_2$	81.4	6.75
<i>m</i> -Tolyl	<i>m</i> -Tolyl	H	H	120° ^a	65	81.55	7.05	$C_{17}H_{18}N_2$	81.65	7.2
<i>m</i> -Tolyl	Ph	H	H	89° ^a	28	81.6	6.9	$C_{16}H_{16}N_2$	81.4	6.75
Ph	<i>p</i> -C ₆ H ₄ Br	H	H	133° ^a	62	59.6	4.4	$C_{16}H_{13}N_2Br$	59.8	4.35
Ph	<i>p</i> -C ₆ H ₄ Cl	H	H	132° ^b	34	70.0	5.3	$C_{16}H_{13}N_2Cl$	70.2	5.05
Ph	Ph	Me	H	119° ^c	40	81.3	6.8	$C_{16}H_{16}N_2$	81.4	6.75
Ph	Ph	H	Me	107° ^c	33	81.5	6.9			
Ph	Ph	H	Ph	133° ^d	31	84.2	6.3	$C_{21}H_{18}N_2$	84.6	6.05

^a Pale yellow needles from methanol. ^b Buff leaflets from methanol. ^c Colourless leaflets from ethanol. ^d Colourless needles from ethanol.

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