THE INFLUENCE OF SUBSTITUENTS ON THE PROPERTIES OF CERTAIN PYRAZOLINES, WITH PARTICULAR REGARD TO FLUORESCENCE

THESIS FOR THE

Ph.D. DEGREE OF THE UNIVERSITY OF EDINBURGH

SUBMITTED BY:

ROBERT G. M. DAKERS,

B.Sc. (Lond.), with 1st Class Hons. in Chemistry; F.I.C.; Associate of the Heriot-Watt College, Edinburgh.

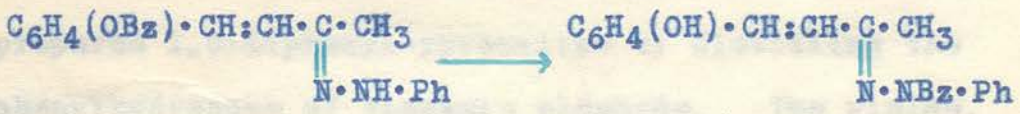
April, 1933.

THE INFLUENCE OF SUBSTITUENTS ON THE PROPERTIES OF CERTAIN PYRAZOLINES, WITH PARTICULAR REGARD TO FLUORESCENCE

By Robert G. M. Dakers

INTRODUCTORY

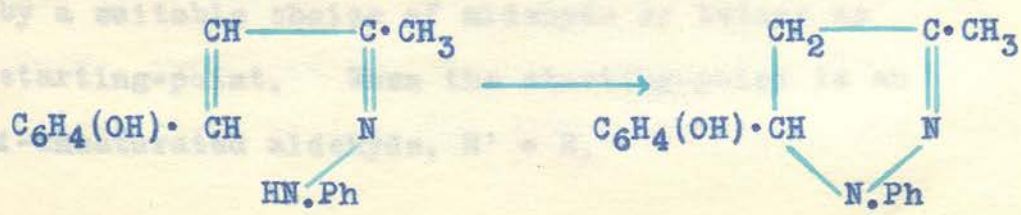
K. v. Auwers and K. Müller (B.41,4230;1908) attempted to convert the O-benzoate of o-hydroxybenzalacetone into the isomeric N-benzoyl derivative by the action of hot glacial acetic acid. The anticipated reaction, viz.:



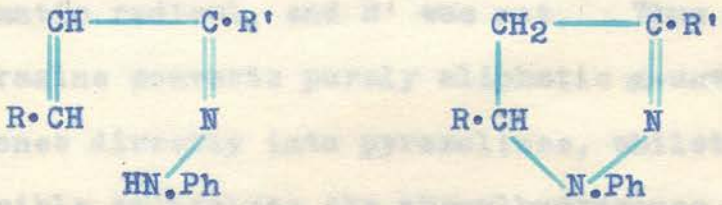
was not realised, although isomeric change did occur.

The product proved, on investigation, to be a pyrazoline, formed by migration of a hydrogen atom from nitrogen to carbon, with simultaneous ring-closure, as follows:

The phenylhydrazone of o-hydroxybenzalacetone itself was shown to behave similarly on warming with glacial acetic acid, yielding 1-phenyl-3-methyl-5-o-hydroxyphenyl-pyrazoline:



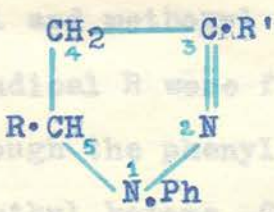
The reaction, indeed, proved to be a general one whereby the phenylhydrazones of α-unsaturated aldehydes and ketones could be converted smoothly, and almost quantitatively, into the isomeric substituted pyrazolines:



Incomplete conversion of hydrazones to pyrazolines had previously been effected by distillation. Laubmann, e.g., (B.21,1212;1888) prepared 1.5-diphenyl-pyrazoline by distilling the phenylhydrazone of cinnamic aldehyde. The yields, however, were invariably poor, as the result of decomposition.

This new and simple general method of converting hydrazones into pyrazolines gave an impetus to the study of the latter compounds.

K. v. Auwers and H. Voss (B.42,4411;1909) studied the influence of constitution on the conversion of phenylhydrazones into pyrazolines, ringing the changes on the groups R and R' in the general formula



by a suitable choice of aldehyde or ketone as starting-point. When the starting-point is an α-unsaturated aldehyde, R' = H.

In many cases the change from hydrazone to pyrazoline occurs with such ease that the phenylhydrazones are not, indeed, isolable and the investigators (loc. cit.) pointed out that phenylhydrazones of ketones of the type R·CH:CH·CO·R' had previously been isolated only when R was an aromatic radical, and R' was not. Thus phenylhydrazine converts purely aliphatic α-unsaturated ketones directly into pyrazolines, whilst it is possible to isolate the phenylhydrazones of cinnamic aldehyde, Ph·CH:CH·CO·H, and methyl styryl ketone, Ph·CH:CH·CO·Me. When R' is an aryl group, however, as in styryl phenyl ketone, Ph·CH:CH·CO·Ph, the change from phenylhydrazone to pyrazoline is spontaneous.

Secondary and tertiary aliphatic radicals, occupying the position R', function as aromatic radicals do, for although the phenylhydrazones of styryl methyl ketone, Ph·CH:CH·CO·Me, styryl ethyl ketone, Ph·CH:CH·CO·Et, styryl n-propyl ketone, Ph·CH:CH·CO·CH_2·Et, styryl n-butyl ketone, Ph·CH:CH·CO·CH_2·CH_2·Et, and styryl n-nonyl ketone, Ph·CH:CH·CO·$(CH_2)_7$·Et, are stable, those of styryl isopropyl ketone, Ph·CH:CH·CO·$CHMe_2$, and styryl tertiary-butyl ketone, Ph·CH:CH·CO·CMe_3, are unstable.

Hydroxyl and methoxyl in the ortho position in the aromatic radical R were found to promote ring-closure for, although the phenylhydrazones of o-hydroxystyryl methyl ketone, $C_6H_4(OH)$·CH:CH·CO·Me, and o-methoxystyryl methyl ketone, $C_6H_4(OMe)$·CH:CH·CO·Me, were readily isolable, those of o-hydroxystyryl ethyl ketone, $C_6H_4(OH)$·CH:CH·CO·Et, and

o-methoxystyryl ethyl ketone, $C_6H_4(OMe)\cdot CH{:}CH\cdot CO\cdot Et$, were not. The influence of hydroxyl or methoxyl in the meta or para positions was not studied.

The presence of the nitro group in the radical R was found to confer increased stability on the hydrazone, for the phenylhydrazones of m- and p-nitrostyryl methyl ketone were quite stable.

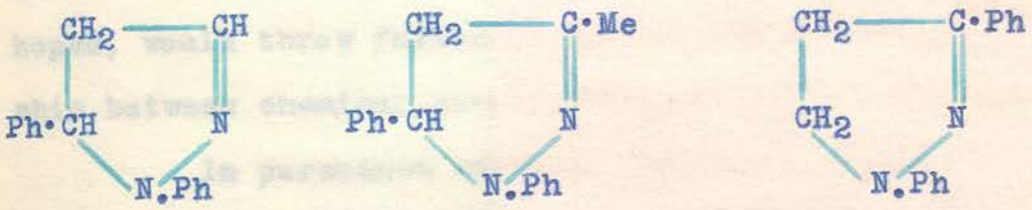
Although their stability, or otherwise, is not of primary interest in the present investigation, the author has indicated, in each case, whether he found it possible or not to isolate the phenylhydrazone as a primary step in the production of the pyrazoline.

Solutions of pyrazolines in organic solvents frequently exhibit fluorescence in daylight and on exposure to X-rays. F. Straus (B.51,1457; 1918) studied the fluorescence of 1.3.5-trisubstituted pyrazolines on exposure to X-rays. He found that the nature of the solvent exercised a marked effect on the intensity of fluorescence; the most brilliant fluorescence was attained in carbon disulphide, benzene and chloroform solutions, in order of diminishing intensity. The compounds investigated by Straus were only feebly fluorescent in alcohol and glacial acetic acid.

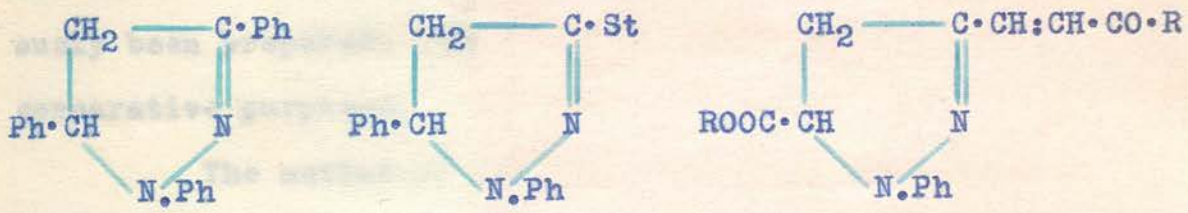
Straus was able to make comparative tests of fluorescence by examining juxtaposed specimens in a light-tight box irradiated from below. By interposing laminae of zinc or lead between the specimen and the source of radiation, he could ascertain at what point fluorescence was inhibited.

Straus came to the conclusion that excitation of fluorescence in pyrazolines by X-rays is associated

with the presence in positions 3 and 5 of unsaturated radicals, including phenyl and carboxyl. When hydrogen, or a saturated aliphatic radical occurred in either of the positions mentioned, the substance did not fluoresce at all on exposure to X-rays. Straus (loc. cit.) cites the following examples:-



Non-fluorescent



Fluorescent

Some pyrazolines which remained non-luminous on exposure to X-rays fluoresced in daylight; but Straus did not conduct exhaustive experiments, using visible rays as the source of excitation. He remarked, however, that fluorescence may possibly be dependent on the occurrence of phenyl in position 1, as fluorescence is not reported in pyrazolines which contain no substituent in that position.

The present investigation was suggested by a realisation that fluorescence in daylight is probably occasioned by its ultraviolet components.

It was readily confirmed that all pyrazolines which fluoresce in daylight do so with enhanced brilliance on exposure to the ultraviolet radiation of a

mercury vapour lamp. Many pyrazolines, moreover, which do not visibly fluoresce in daylight do so on exposure to ultraviolet rays. It was, therefore, decided to investigate the behaviour, on exposure to ultraviolet radiation from the mercury vapour lamp, of a series of pyrazolines sufficiently large to permit of comparative observations which, it was hoped, would throw further light on the relationship between chemical constitution and fluorescence.

In pursuance of this plan, thirty-seven compounds have been prepared for investigation. Of these, as far as can be ascertained by a most thorough search of the literature, twenty-five have not previously been prepared; the remainder were required for comparative purposes.

The method of preparation of the pyrazolines was, in most cases, that of v. Auwers and Müller. In Table I (facing p.7) the source of each pyrazoline is given in the left-hand column; the remaining columns (numbered at the top III. and V., respectively) indicate the substituents present in positions 3 and 5 of the pyrazoline molecule. As the pyrazolines in question were all prepared from phenylhydrazones, the phenyl group occurs in position 1 throughout the series. Thus, the first pyrazoline of the series, prepared from cinnamic aldehyde phenylhydrazone, is 1.5-diphenyl-pyrazoline; the eighteenth member, prepared from p-tolalpinacoline, is 1-phenyl-3-tertiary-butyl-5-p-tolyl-pyrazoline, and so on. This system of tabulation greatly facilitates reference and is used throughout the thesis.

TABLE I.

	Parent Ketone	III.	V.
1.	cinnamic aldehyde	------	phenyl
2.	benzalacetophenone	phenyl	phenyl
3.	banzal-o-hydroxyacetophenone	o-hydroxyphenyl	phenyl
4.	:: -m- :: ::	m- ::	phenyl
5.	:: -p- :: ::	p- ::	phenyl
6.	benzal-o-methoxyacetophenone	o-methoxyphenyl	phenyl
7.	:: -m- :: ::	m- ::	phenyl
8.	:: -p- :: ::	p- ::	phenyl
9.	s-trimethoxyacetophenone	s-trimethoxyphenyl	phenyl
10.	benzal-o-ethoxyacetophenone	o-ethoxyphenyl	phenyl
11.	benzal-o-nitroacetophenone	o-nitrophenyl	phenyl
12.	:: -m- :: ::	m- ::	phenyl
13.	:: -p- :: ::	p- ::	phenyl
14.	benzal-p-aminoacetophenone	p-aminophenyl	phenyl
15.	benzalacetothienone	thienyl	phenyl
16.	dibenzalacetone	styryl	phenyl
17.	benzalpinacoline	tert.-butyl	phenyl
18.	p-tolalpinacoline	tert.-butyl	p-tolyl
19.	p-tolalacetophenone	phenyl	p-tolyl
20.	cinnamylideneacetophenone	anomalous	
21.	cinnamylidenepinacoline	anomalous.	
22.	o-hydroxybenzalacetophenone	phenyl	o-hydroxyphenyl
23.	p- :: :: ::	phenyl	p- ::
24.	o-methoxybenzalacetophenone	phenyl	o-methoxyphenyl
25.	m- :: :: ::	phenyl	m- ::
26.	p- :: :: ::	phenyl	p- ::
27.	benzalacetone	methyl	phenyl
28.	o-hydroxybenzalacetone	methyl	o-hydroxyphenyl
29.	veratralacetophenone	phenyl	3,4-dimethoxyphenyl
30.	veratralpinacoline	tert.-butyl	3,4-dimethoxyphenyl
31.	piperonylidenepinacoline	tert.-butyl	methylene-3,4-dihydroxyphenyl
32.	anisalpinacoline	tert.-butyl	p-methoxyphenyl
33.	o-nitrobenzalacetophenone	phenyl	o-nitrophenyl
34.	m- :: :: ::	phenyl	m- ::
35.	p- :: :: ::	phenyl	p- ::
36.	p-nitrobenzalpinacoline	tert.-butyl	p-nitrophenyl
37.	o-methoxybenzalacetothienone	thienyl	o-methoxyphenyl

EXPERIMENTAL

In the Experimental Section of this thesis, the preparation of thirty-five pyrazolines and two anomalous compounds is described, the compounds being considered in the order in which they appear in Table I.

As the preparation of the unsaturated ketones, from which the pyrazolines were in turn prepared, occupied a considerable proportion of the time devoted to this research, the method employed in each case is clearly indicated; elaborate detail is, however, given only where the starting-material, as well as the pyrazoline is new.

Preparation of α-Unsaturated Ketones

The α-unsaturated ketones, $R{\cdot}CH{:}CH{\cdot}CO{\cdot}R'$, were usually prepared by condensation of an aromatic aldehyde, $R{\cdot}CH{:}O$, with a methyl ketone, $Me{\cdot}CO{\cdot}R'$, in alcoholic solution, in presence of a small amount of 10% NaOH;-

$$R{\cdot}CH{:}O + H_3C{\cdot}CO{\cdot}R' = R{\cdot}CH{:}CH{\cdot}CO{\cdot}R' + H_2O.$$

In most cases, the unsaturated ketone separated on standing for a suitable period at ordinary temperature. Where a phenolic aldehyde was employed, as in the preparation of salicalacetone, and salicalacetophenone (See Nos. 28 and 32 of the series, respectively), the alkaline reaction-mixture had to be acidified in order to liberate the ketone from its sodium salt.

The preparation of p-aminophenyl styryl ketone, $H_2N{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_5$, is of special interest (See No. 14 of the series).

M. Scholtz and L. Hüber (B.37,390-397;1904) pointed out that p-aminoacetophenone, $H_3C \cdot CO \cdot C_6H_4 \cdot NH_2$, contains two groups capable of condensing with aromatic aldehydes. In neutral alcoholic solution, Schiff bases are produced:

$$Ar \cdot CH:O + H_2N \cdot C_6H_4 \cdot CO \cdot CH_3 = Ar \cdot CH:N \cdot C_6H_4 \cdot CO \cdot CH_3 ,$$

whilst in presence of alkali, diarylidene derivatives are formed:

$$2Ar \cdot CH:O + H_2N \cdot C_6H_4 \cdot CO \cdot CH_3 = Ar \cdot CH:N \cdot C_6H_4 \cdot CH:CH \cdot Ar + 2H_2O.$$

The condensation of aldehydes with the amino group is, however, easily reversed on treatment with acids:

$$Ar \cdot CH:CH \cdot CO \cdot C_6H_4 \cdot N:CH \cdot Ar = Ar \cdot CH:CH \cdot CO \cdot C_6H_4 \cdot NH_2 + Ar.CH:O ,$$
$$+ H_2O$$

and this reaction affords a convenient means of preparing p-amino-ω-arylideneacetophenones.

Preparation of Phenylhydrazones

The method adopted for the attempted preparation of phenylhydrazones was that described by K. v. Auwers and H. Voss (B.42,4411;1909):- The aldehyde or ketone, dissolved in the minimum quantity of 96% alcohol, is treated with the calculated quantity of phenylhydrazine dissolved in a little alcohol, with addition of 1c.c. of glacial acetic acid for each 1 g. of phenylhydrazine. The small amount of acetic acid was found to favour separation of the hydrazone in a crystalline state, whilst it did not, in the cold, tend to promote pyrazoline formation.

Preparation of Pyrazolines

The conversion of the phenylhydrazones to pyrazolines was effected, where it did not occur spontaneously, by boiling with glacial acetic acid for ½ to 1 hour. The pyrazoline frequently crystallised on cooling; in many cases, however, precipitation with water was resorted to, followed by crystallisation from a suitable solvent.

When the pyrazoline, as frequently happened, separated as an oil, crystallisation was induced by trituration with methyl alcohol.

Separate experiments were usually conducted with the object of obtaining the phenylhydrazone or, alternatively, the pyrazoline. The latter may usually be very satisfactorily prepared by warming the unsaturated ketone with the theoretical amount of phenylhydrazine in glacial acetic acid solution. (Cf. Kyohei Murakami: Science Reports, Tôhoku Imp. Univ., 1st Series - 18,651-660;1929 -- Amer. Chem. Abs., 24,2455;1930, who states that the best yields of certain pyrazolines were obtained by refluxing the unsaturated ketone in alcohol with the equivalent quantity of phenylhydrazine and 3 to 5 parts of glacial acetic acid for ½ to 1 hour.).

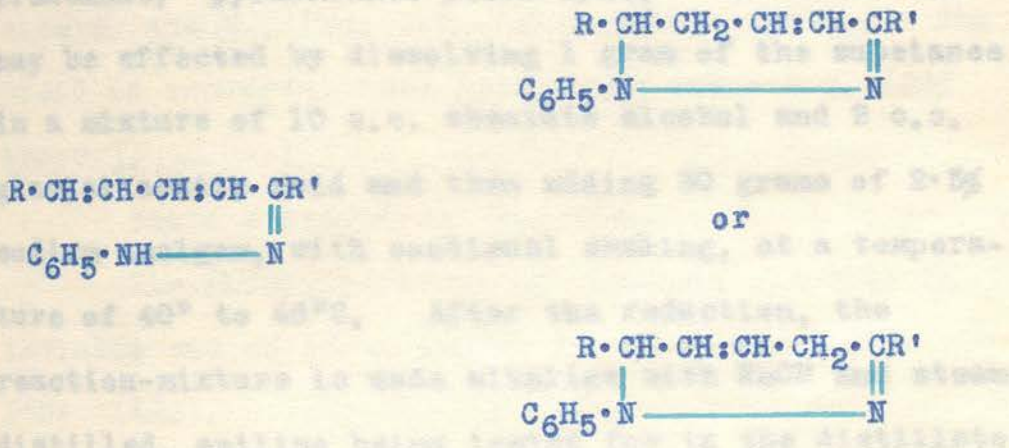
Note on Anomalous Behaviour of Certain Cinnamylidene Compounds

K. v. Auwers and H. Voss (B.42,4411;1909) noted that the phenylhydrazones of cinnamylideneacetophenone and dicinnamylideneacetone were changed by boiling with glacial acetic acid; but they did not investigate the products in order to prove whether or not

they were pyrazolines.

F. Straus (B.51,1457;1918) stated that these substances were definitely not pyrazolines, basing this opinion on the feeble luminescence of the products on exposure to X-rays, and the non-formation of pyrazole-carboxylic acids on oxidation.

As the substances in question yielded no aniline on reduction with sodium amalgam, a cyclic structure was assumed, and the following mechanism suggested:



(R' = C_6H_5 or CH:CH·CH:CH·C_6H_5.)

The series of compounds at present under investigation contains the products of the action of glacial acetic acid on the phenylhydrazones of cinnamylideneacetophenone and cinnamylidenepinacoline (Nos. 20 and 21 of the series, respectively). Their behaviour on exposure to ultraviolet rays has been compared with that of undoubted pyrazolines and the results are discussed in the appropriate part of this thesis.

Criteria of Pyrazoline Formation

The majority of pyrazolines containing an aryl group in position 1 give brilliant colours

(green, blue or magenta) on adding a speck of sodium nitrite, or a drop of ferric chloride solution, to the solution in concentrated sulphuric acid. This test, known as Knorr's test, is extremely delicate; it is, therefore, useless for the distinction of a pyrazoline from a phenylhydrazone which may contain a mere trace of the pyrazoline.

A reliable criterion of pyrazoline formation is the absence of aniline on reduction with sodium amalgam. All phenylhydrazones yield aniline on such treatment; pyrazolines yield none. The reduction may be effected by dissolving 1 gram of the substance in a mixture of 10 c.c. absolute alcohol and 2 c.c. glacial acetic acid and then adding 30 grams of 2·5% sodium amalgam, with continual shaking, at a temperature of 40° to 45°C. After the reduction, the reaction-mixture is made alkaline with NaOH and steam-distilled, aniline being tested for in the distillate (K. v. Auwers and H. Voss: B.42,4411;1909).

No known phenylhydrazone can withstand boiling with glacial acetic acid so that, even when the hydrazone cannot be isolated, the pyrazoline may safely be assumed to be formed when such treatment has constituted part of the mode of preparation.

In the sequel, the preparation of hitherto unknown pyrazolines is described in detail and reference is made to the original literature in the case of compounds already known.

. . . . . .

PREPARATION OF INDIVIDUAL PYRAZOLINES

1. 1,5-Diphenyl-pyrazoline (Laubmann: B.21,1212; 1888. K. v. Auwers and K. Müller: B.41, 4230; 1908.)

3·3 g. Cinnamaldehyde and 2·7 g. phenylhydrazine were boiled for ½ h. with 20 c.c. glacial AcOH. The pyrazoline crystallised on cooling and, recrystallised from glacial AcOH, was obtained in the form of small pale yellow crystals, m.p. 138°C. (L., also A. and M., loc. cit., give 137° - 138°C.) The yield of recrystallised pyrazoline was 4·6 g. (83% theory).

Knorr's reaction: Magenta.

The phenylhydrazone of cinnamic aldehyde is isolable and melts at 168°C. (E. Fischer: B.17, 573; 1884).

---

2. 1,3,5-Triphenyl-pyrazoline (Knorr and Laubmann: B.21,1209;1888.)

5·2 g. Benzalacetophenone (phenyl styryl ketone) (Claisen: B.20,657;1887. Organic Syntheses, II.,1.) and 2·7 g. phenylhydrazine were boiled for 1 h. with 10c.c. glacial AcOH. The pyrazoline crystallised on cooling and, recrystallised from absolute EtOH, was obtained as pale yellow needles, m.p. 132° - 133°C. (K. and L., loc. cit., 134° - 135°C.). Yield: 6·9 g. (92·6% th.).

The phenylhydrazone of benzalacetophenone is not isolable (K. v. Auwers and H. Voss: B.42,4411; 1909).

Knorr's reaction: Blue.

---

3. 3-o-Hydroxyphenyl-1,5-diphenyl-pyrazoline

o-Hydroxyphenyl styryl ketone, m.p. 88° - 89°C., was prepared by boiling o-methoxyacetophenone (See No. 6 of this series) with HCl (Edelstein and v. Kostanecki: B.31,715;1898):

$$MeO\cdot C_6H_4\cdot CO\cdot Me + HCl = HO\cdot C_6H_4\cdot CO\cdot Me + MeCl ,$$

and condensing the resulting o-hydroxyacetophenone with $Ph\cdot CH{:}O$ in alcoholic solution, in presence of NaOH (Feuerstein and v. Kostanecki: B.31,715;1898):

$$Ph\cdot CH{:}O + H_3C\cdot CO\cdot C_6H_4\cdot OH = Ph\cdot CH{:}CH\cdot CO\cdot C_6H_4\cdot OH + H_2O .$$

Preparation of Pyrazoline:- 2·2 g. o-Hydroxyphenyl styryl ketone and 1 g. phenylhydrazine, in 10c.c. glacial AcOH, were boiled for ½ h. On diluting with water, the pyrazoline was precipitated. Recrystallised from alcohol, it was obtained in small pinkish-white crystals, m.p. 136°C. Yield 2·5 g. (80% th.).

An attempt to isolate the phenylhydrazone was unsuccessful, the pyrazoline being formed directly.

On keeping in the dark for several days, the pyrazoline lost its pink colour, becoming colourless. This phototropic effect is reversible and is shared by the 3-m- (and p-) hydroxyphenyl-1,5-diphenyl-pyrazolines, the 3-o- (and m-) methoxyphenyl-1,5-diphenyl-pyrazolines, and 3-o-ethoxyphenyl-1,5-diphenyl-pyrazoline.

The pyrazoline yielded no aniline on reduction with Na/Hg.

Knorr's reaction: Green.

Estimation of Nitrogen:-

0·1421 g. gave 11·4c.c. N_2 at 16·8°C. and 748 mm., measure over 40% KOH.

$$N = 11{\cdot}4 \times \frac{273}{284} \times \frac{739}{760} \times \frac{0{\cdot}126}{0{\cdot}1421} = 9{\cdot}44\%.$$

(Theory for $C_{21}H_{18}ON_2$ = 8·92%.)

---

4. 3-m-Hydroxyphenyl-1,5-diphenyl-pyrazoline

m-Hydroxyacetophenone was prepared by reducing m-nitroacetophenone (See No. 12 of this series) to m-aminoacetophenone by means of Fe and AcOH (Rupe, Braun and v. Zembrzuski: B.34,3522;1901), diazotising the latter and decomposing the diazonium salt by boiling with water (Besthorn, Bauzhaf and Jaeglé: B.27, 3042;1894):

$$Me{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2 \longrightarrow Me{\cdot}CO{\cdot}C_6H_4{\cdot}NH_2 \longrightarrow Me{\cdot}CO{\cdot}C_6H_4{\cdot}OH\ .$$

The m-hydroxyacetophenone was converted into m-hydroxyphenyl styryl ketone by condensation with $Ph.CH{:}O$ in alcoholic solution, in presence of NaOH (v. Kostanecki and Tambor: B.32,1924;1899). M.p. 124°C. (K. and T., loc. cit., 126°C.):

$$Ph{\cdot}CH{:}O + H_3C{\cdot}CO{\cdot}C_6H_4{\cdot}OH = Ph{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}OH + H_2O.$$

Preparation of Pyrazoline:-

4·5 g. m-Hydroxystyryl ketone and 2·2 g. phenylhydrazine were boiled with 10c.c. glacial AcOH for ½ h. The pyrazoline was precipitated, after cooling, by

addition of water. Recrystallised from EtOH, it was obtained in pinkish-white needles, m.p. 147°C., which showed the same phototropic effect as the ortho isomer, q.v. Yield 4·7 g. (75% th.).

The pyrazoline yielded no aniline on reduction with Na/Hg.

An attempt to isolate the phenylhydrazone was unsuccessful.

Knorr's reaction: Green.

Estimation of Nitrogen:-

0·1376 g. gave 10·8c.c. N_2 at 15°C. and 752 mm., measured over 40% KOH.

$$N = 10{\cdot}8 \times \frac{273}{288} \times \frac{744}{760} \times \frac{0{\cdot}126}{0{\cdot}1376} = 9{\cdot}18\%.$$

(Theory for $C_{21}H_{18}ON_2$ = 8·92%.)

---

5. 3-p-Hydroxyphenyl-1,5-diphenyl-pyrazoline

p-Hydroxyphenyl styryl ketone was prepared by diazotising p-aminoacetophenone, decomposing the diazonium salt with hot water (Klingel: B.18,2691; 1885), and condensing the resulting p-hydroxyacetophenone with Ph·CH:O in alcoholic solution, in presence of NaOH (v. Kostanecki and Tambor: B.32,1924; 1899). M.p. 176°C. (v. K. and T., loc. cit., 172° - 173°C.).

Preparation of Pyrazoline:-

4·5 g. p-Hydroxyphenyl styryl ketone and 2·2 g. phenylhydrazine were boiled with 10c.c. glacial AcOH

for ½ h. The pyrazoline, isolated by precipitation with water, was recrystallised from alcohol. It was similar in appearance to, and showed the same photo-tropic behaviour as the ortho and meta isomers. M. p. 153°C. Yield 4·9g. (78% th.).

The pyrazoline yielded no aniline on reduction with Na/Hg.

An attempt to isolate the phenylhydrazone was unsuccessful.

Knorr's reaction: Green.

Estimation of Nitrogen:-

0·1549 g. gave 12·1c.c. N_2 at 17·5°C. and 738 mm., measured over 40% KOH.

$$N = 12{\cdot}1 \times \frac{273}{290{\cdot}5} \times \frac{729}{760} \times \frac{0{\cdot}126}{0{\cdot}1549} = 8{\cdot}88\%.$$

(Theory for $C_{21}H_{18}ON_2$ = 8·92%.)

Preparation of Methoxyacetophenones

For the preparation of the three isomeric 3-o-(m- and p-)methoxyphenyl-1.5-diphenyl-pyrazolines (Nos. 6, 7 and 8 of this series) it was necessary, in the first place, to prepare the corresponding methoxy-acetophenones; this was carried out as follows:-

o- (m- or p-) Hydroxybenzoic ester was methylated by means of Me_2SO_4 in presence of NaOH. The methoxybenzoic ester was converted into the methoxybenzoylacetic ester by condensation with ethyl acetate in presence of metallic sodium (Tahara: B.25,1306;1892):

$HO \cdot C_6H_4 \cdot COOEt + Me_2SO_4 + NaOH = MeO \cdot C_6H_4 \cdot COOEt + MeNaSO_4 + H_2O$,

$MeO \cdot C_6H_4 \cdot COOEt + Me \cdot COOEt = MeO \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot COOEt + EtOH.$

The benzoylacetic ester was then hydrolysed by prolonged boiling with dil. H_2SO_4, as described for o-methoxyacetophenone by Tahara (loc. cit.):-

$MeO \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot COOEt + H_2O = MeO \cdot C_6H_4 \cdot CO \cdot Me + EtOH + CO_2.$

---

6. 3-o-Methoxyphenyl-1,5-diphenyl-pyrazoline

o-Methoxyphenyl styryl ketone:- 80 g. ethyl salicylate, dissolved in 100c.c. 40% NaOH, treated with 63c.c. Me_2SO_4, yielded 65 g. (75% th.) o-methoxybenzoic ester, distilling 255° - 260°C.

55 g. o-Methoxybenzoic ester, 33 g. ethyl acetate and 7·1 g. sodium, refluxed for 18 h., yielded 45 g. (66% th.) o-methoxybenzoylacetic ester, in the form of a dark oil which could not be distilled without decomposition, even in vacuo.

On hydrolysis of this oil with 30% H_2SO_4, 21 g. o-methoxyacetophenone (42% th., calculated on o-methoxybenzoic ester), distilling 243° - 250°C., were obtained.

11·5 g. o-Methoxyacetophenone and 11 g. Ph·CH:O in 125c.c. 75% EtOH + 25c.c. 10% NaOH yielded, after 8 days, 19 g. (80% th.) of a brown oil which was separated and used directly for the preparation of the pyrazoline.

Preparation of Pyrazoline:-

The brown oil (19 g.) from the previous preparation was treated with 8·7 g. phenylhydrazine in 30c.c.

glacial AcOH. Considerable heat was evolved. The pyrazoline crystallised on cooling, after refluxing ½ h. It was recrystallised 4 times from EtOH, with the aid of animal charcoal, being finally obtained as a pale yellow crystalline powder, m.p. 153°C. Yield of purified product 16·3 g. (62% th.).

The pyrazoline showed the same phototropic properties as the 3-hydroxyphenyl-1,5-diphenyl-pyrazolines.

No aniline was obtained on reducing the pyrazoline with Na/Hg.

An attempt to isolate the phenylhydrazone was unsuccessful.

Knorr's reaction: Green.

Estimation of Carbon and Hydrogen:-

0·1346 g. gave 0·0761 g. H_2O and 0·3948 g. CO_2.

$$H = 0{\cdot}0761 \times \frac{1}{9} \times \frac{100}{0{\cdot}1346} = 6{\cdot}28\% \text{ (Theory = 6·10\%);}$$

$$C = 0{\cdot}3948 \times \frac{3}{11} \times \frac{100}{0{\cdot}1346} = 80{\cdot}00\% \text{ (Theory = 80·49\%).}$$

Estimation of Nitrogen:-

0·1185 g. gave 9·3c.c. N_2 at 17·5°C. and 750 mm., measured over 40% KOH.

$$N = 9{\cdot}3 \times \frac{739{\cdot}4}{750{\cdot}0} \times \frac{273}{290{\cdot}5} \times \frac{0{\cdot}126}{0{\cdot}1185} = 9{\cdot}04\% \text{ (Th. = 8·54\%).}$$

(Empirical formula: $C_{22}H_{20}ON_2$.)

---

7. 3-m-Methoxyphenyl-1,5-diphenyl-pyrazoline

m-Methoxyphenyl styryl ketone:-

50 g. Ethyl m-hydroxybenzoate yielded 44 g. (81% th.) m-methoxybenzoic ester, a pale yellow oil distilling 245° - 255°C. (Béhal and Tiffeneau: Bl.IV.,3,316; 1862 give b.p. 250° - 252°C.).

44 g. m-Methoxybenzoic ester, treated exactly as in the case of the ortho compound, yielded 32 g. (59% th.) m-methoxybenzoylacetic ester, a yellow oil which cannot be distilled without decomposition, even in vacuo. On hydrolysis, this oil gave 15 g. (42% th, calculated on m-methoxybenzoic ester) m-methoxyacetophenone, distilling 235° - 245°C. (Béhal and Tiffeneau: C.r.,141,597;1905 give b.p. 240°C.)

15 g. m-Methoxyacetophenone, treated with 11 g. Ph·CH:O in 125c.c. 75% EtOH + 25c.c. 10% NaOH, yielded, after 8 days, 17 g. (71% th.) benzal-m-methoxyacetophenone, a brown oil which was at once converted into the pyrazoline.

Preparation of Pyrazoline:-

15 g. Benzal-m-methoxyacetophenone + 6·9 g. phenylhydrazine in 30c.c. glacial AcOH were boiled ½ h. The pyrazoline crystallised on cooling and, recrystallised from alcohol, formed pale yellow needles, m.p. 115°C. Yield 16 g. (77% th.) of the recrystallised product.

The pyrazoline yielded no aniline on reduction with Na/Hg. It showed the same phototropic effect as the ortho isomer.

The phenylhydrazone could not be isolated.

Knorr's reaction: Green.

Estimation of Carbon and Hydrogen:-

0·1546 g. gave 0·0845 g. H_2O and 0·4570 g. CO_2.

$$C = 0{\cdot}4570 \times \frac{3}{11} \times \frac{100}{0{\cdot}1546} = 80{\cdot}65\% \text{ (Th. = 80·49\%)};$$

$$H = 0{\cdot}0845 \times \frac{1}{9} \times \frac{100}{0{\cdot}1546} = 6{\cdot}07\% \text{ (Th.= 6·10\%)}.$$

Estimation of Nitrogen:-

0·1107 g. gave 8·7c.c. N_2 at 18·5°C. and 748 mm., measured over 40% KOH.

$$N = 8{\cdot}7 \times \frac{736{\cdot}7}{760} \times \frac{273}{291{\cdot}5} \times \frac{0{\cdot}126}{0{\cdot}1107} = 9{\cdot}00\% \text{ (Th. = 8·54\%)}.$$

(Empirical formula: $C_{22}H_{20}ON_2$.)

---

8. 3-p-Methoxyphenyl-1,5-diphenyl-pyrazoline

(K. v. Auwers and Maria Seyfried: Ann.484, 171-211;1930.)

50 g. Ethyl-p-hydroxybenzoate yielded, on methylation with Me_2SO_4 in presence of NaOH, 43 g. (70% th.) p-methoxybenzoic ester, distilling 250° - 260°C. (Cahours: 250° - 255°C.).

43 g. p-Methoxybenzoic ester yielded 34 g. (65% th.) p-methoxybenzoylacetic ester, a brown oil which could not be distilled without decomposition, even in vacuo.

34 g. p-Methoxybenzoylacetic ester yielded, on hydrolysis, 17 g. (74% th.) p-methoxyacetophenone, m.p. 37°C. from ether (Gattermann, Erhardt and Maisch: B,23,1202;1890 give 38° - 39°C.).

15 g. p-Methoxyacetophenone and 11 g. benzaldehyde in 125c.c. 75% EtOH + 25c.c. 10% NaOH yielded, almost immediately, a crop of colourless crystals, m.p. 106°C., after recrystallisation from EtOH. (Stockhausen and Gattermann: B.25,3536;1892 give 106° - 107°C.) Yield of anisyl styryl ketone 20·5 g. (86% th.).

Preparation of Pyrazoline:-

15·8 g. Anisyl styryl ketone and 6·9 g. phenylhydrazine, boiled in 30c.c. glacial AcOH for ½ h., yielded a crop of colourless crystals on cooling. Recryst. from EtOH, the pyrazoline melted at 139°C. (K. v. A. and M. S., loc. cit., give 140·5° - 141·5°C.)

This pyrazoline did not exhibit the phototropic change shown by the ortho and meta isomers. It yielded no aniline on reduction with Na/Hg.

An attempt to isolate the phenylhydrazone was unsuccessful.

Knorr's reaction: Green.

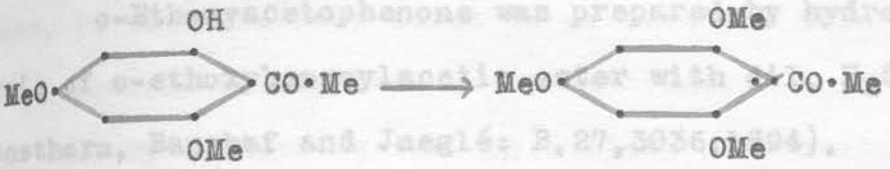
---

9. 3-s-Trimethoxyphenyl-1,5-diphenyl-pyrazoline

2-Hydroxy-4,6-dimethoxyacetophenone, m.p. 87°C., was available by the courtesy of Messrs. T and H. Smith, Ltd., Blandfield Chemical Works, Edinburgh, who isolate it from residues remaining after the extraction of santonin from Artemisia Brevifolia.

s-Trimethoxyphenyl styryl ketone:- 9·8 g. of the starting-material were dissolved in 40c.c. 10% NaOH and shaken with 6·3 g. Me_2SO_4. The resulting s-trimethoxyacetophenone was recrystallised from a mixture of alcohol and ether. The yield of purified

ketone was 8·4 g. (80% th.), m.p. 99°C. (v. Kostanecki and Tambor: B.32,2261;1899 give 100°C.)



4·2 g. s-Trimethoxyacetophenone and 2·2 g. Ph·CH:O in 10c.c. absolute EtOH and 5c.c. 10% NaOH gave, after 48 h., colourless crystals of s-trimethoxyphenyl styryl ketone, m.p.92°C. Yield 4·3 g. (72% th.).

Preparation of Pyrazoline:-

4·3 g. s-Trimethoxyphenyl styryl ketone and 1·6 g. phenylhydrazine were boiled with 20c.c. glacial AcOH for 1 h. After cooling, the pyrazoline was precipitated with water and recrystallised from EtOH. Colourless needles, m.p. 165°C. Yield 3·7 g. (66% theory).

The pyrazoline yielded no aniline on reduction with Na/Hg.

The phenylhydrazone could not be isolated.

Knorr's reaction: Green, turning brown.

Estimation of Nitrogen:-

0·1605 g. gave 10·1c.c. N_2 at 17·5°C. and 768 mm., measured over 40% KOH.

$$N = 10{\cdot}1 \times \frac{273}{290{\cdot}5} \times \frac{757}{760} \times \frac{0{\cdot}126}{0{\cdot}1605} = 7{\cdot}43\%.$$

(Theory for $C_{24}H_{24}O_3N_2$ = 7·22%.)

10. 3-o-Ethoxyphenyl-1,5-diphenyl-pyrazoline

o-Ethoxyphenyl styryl ketone:-

o-Ethoxyacetophenone was prepared by hydrolysis of o-ethoxybenzoylacetic ester with dil. H_2SO_4 (Besthorn, Banzhaf and Jaeglé: B.27,3036;1894). Prisms from dil. EtOH, m.p. 37°C. (Fittig and Claus: A.269,10 give 38·5° - 39·5°C.)

o-Ethoxyphenyl styryl ketone was obtained by condensation of the above with Ph·CH:O in alcoholic NaOH solution, m.p. 74° - 75°C. (Cf. Stockhausen and Gattermann: B.25,3535;1892)

Preparation of Pyrazoline:-

5 g. o-Ethoxyphenyl styryl ketone and 2·2 g. phenylhydrazine were boiled with 10c.c. glacial AcOH for 1 h. The pyrazoline crystallised on cooling. It melted at 133°C., after recrystallisation from dil. EtOH. Yield of recrystallised product 4·7 g. (69% th.).

An attempt to isolate the phenylhydrazone was unsuccessful.

The pyrazoline gave no aniline on reduction with Na/Hg.

Knorr's reaction; Green.

Estimation of Nitrogen:-

0·1347 g. gave 9·9c.c. N_2 at 17°C. and 745 mm., measured over 40% KOH.

$$N = 9{\cdot}9 \times \frac{273}{290} \times \frac{735}{760} \times \frac{0{\cdot}126}{0{\cdot}1347} = 8{\cdot}43\%.$$

(Theory for $C_{23}H_{23}ON_2$ = 8·19%.)

For the preparation of the three isomeric (o-, m- and p-) 3-nitrophenyl-1,5-diphenyl-pyrazolines, it was necessary first to prepare the three corresponding nitrophenyl styryl ketones. This was done by condensing the appropriate nitroacetophenones, which were available, with benzaldehyde in alcoholic NaOH solution.

11. 3-o-Nitrophenyl-1,5-diphenyl-pyrazoline

o-Nitrophenyl styryl ketone:-

3·5 g. Benzaldehyde and 5·5 g. o-nitroacetophenone yielded, in alcoholic solution, with addition of NaOH (Engler and Dorant: B.28,2498; 1895) 6·2 g. (74% th.) o-nitrophenyl styryl ketone. Yellow needles from EtOH, m.p. 124°C.

Preparation of Pyrazoline:-

5 g. o-Nitrophenyl styryl ketone and 2·2 g. phenylhydrazine in 15c.c. glacial AcOH were boiled 1 h. The pyrazoline was precipitated with water and recrystallised from EtOH. Red needles, m.p. 128° - 130°C. Yield 4·2g. of recrystallised product (62% th.).

The pyrazoline yielded no aniline on reduction with Na/Hg.

On treating the nitrophenyl styryl ketone with phenylhydrazine in cold alcoholic solution, an oil was obtained which did not give Knorr's reaction. This was probably the phenylhydrazone, but it could not be obtained in crystalline form. On boiling with AcOH it gave the above pyrazoline and, on reduction with Na/Hg, it gave aniline. The m- and p- isomers gave similar oily products.

Knorr's reaction: Blue.

Estimation of Nitrogen:-

0·1268 g. gave 14·2c.c. N_2 at 16°C. and 722 mm., measured over 40% KOH.

$$N = 14{\cdot}2 \times \frac{273}{289} \times \frac{712}{760} \times \frac{0{\cdot}126}{0{\cdot}1268} = 12{\cdot}53\%$$

(Theory for $C_{21}H_{17}O_2N_3$ = 12·25%)

---

12. 3-m-Nitrophenyl-1.5-diphenyl-pyrazoline

m-Nitrophenyl styryl ketone:-

3·5 g. Ph·CH:O and 5·5 g. m-nitroacetophenone in 25c.c. EtOH + 5c.c. 10% NaOH yielded, after 7 days, 5·1 g. (61% th.) m-nitrophenyl styryl ketone, red needles from EtOH, m.p. 137° - 140°C.

Preparation of Pyrazoline:-

2·5 g. m-Nitrophenyl styryl ketone and 1·1 g. phenylhydrazine were boiled in 15c.c. glacial AcOH for 1 h. The pyrazoline was precipitated with water and recrystallised from EtOH. Orange-yellow needles, m.p. 131°C. Yield 2·6 g. (76% th.). The pyrazoline yielded no aniline on reduction with Na/Hg.

Knorr's reaction: Blue.

Estimation of Nitrogen:-

0·1405 g. gave 14·7c.c. N_2 at 17°C. and 774 mm., measured over 40% KOH.

$$N = 14{\cdot}7 \times \frac{273}{290} \times \frac{764}{760} \times \frac{0{\cdot}126}{0{\cdot}1405} = 12{\cdot}47\%$$

(Theory for $C_{21}H_{17}O_2N_3$ = 12·25%.)

---

13. 3-p-Nitrophenyl-1.5-diphenyl-pyrazoline

p-Nitrophenyl styryl ketone:-

3·5 g. Ph·CH:O and 5·5 g. p-nitroacetophenone in 30c.c. EtOH + 5c.c. 10% NaOH yielded, after 48 h., 5·5 g. (65% th.) p-nitrophenyl styryl ketone. Yellow crystals, from EtOH, m.p. 128° - 130°C.

Preparation of Pyrazoline:-

2·5 g. p-Nitrophenyl styryl ketone and 1·1 g. phenylhydrazine, boiled for 1 h. with 15c.c. glacial AcOH yielded, after precipitation with water and crystallisation from EtOH, 2·5 g. red needles, i.e. 73·5% th., m.p. 185° - 187°C.

The pyrazoline yielded no aniline on reduction with Na/Hg.

Knorr's reaction: Blue.

Estimation of Nitrogen:-

0·1216 g. gave 12·9c.c. N_2 at 17°C. and 748 mm., measured over 40% KOH.

$$N = 12{\cdot}9 \times \frac{273}{290} \times \frac{738}{760} \times \frac{0{\cdot}126}{0{\cdot}1216} = 12{\cdot}2\ \%$$

(Theory for $C_{21}H_{17}O_2N_3$ = 12·25%.)

---

14. 3-p-Aminophenyl-1.5-diphenyl-pyrazoline

p-Aminophenyl styryl ketone:-

7·5 g. p-Aminoacetophenone and 11 g. Ph·CH:O (2 mols.) were dissolved in 30c.c. EtOH and 5c.c. 10% NaOH added (M. Scholtz and L. Hüber: B.37,390-397; 1904). After 3 mins., a canary-yellow precipitate of dibenzylideneaminoacetophenone, m.p. 143° - 144°C.,

separated (See p.8):-

$2Ph{\cdot}CHO + Me{\cdot}CO{\cdot}C_6H_4{\cdot}NH_2 = Ph{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}N{:}CH{\cdot}Ph + 2H_2O.$

The dibenzylidene compound was dissolved in large excess of hot dil. HCl. On cooling, colourless needles of the hydrochloride of $Ph{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_4{\cdot}NH_2$ separated. On warming with water, the hydrochloride was decomposed, with liberation of the base.

Preparation of Pyrazoline:-

2·23 g. p-Aminophenyl styryl ketone and 1·1 g. phenylhydrazine were boiled in 10c.c. glacial AcOH for 1 h. The pyrazoline was precipitated with water and recrystallised from alcohol. It was obtained in white needles, which turned brown in air, m.p. 115°C. (with decomposition). Yield 2·2 g. (71% th.).

The pyrazoline yielded no aniline on reduction with Na/Hg.

Knorr's reaction: Blue.

Estimation of Nitrogen:-

0·0963 g. gave 10·8c.c. N_2 at 15°C. and 778 mm., measured over 40% KOH.

$$N = 10{\cdot}8 \times \frac{273}{288} \times \frac{769}{760} \times \frac{0{\cdot}126}{0{\cdot}0963} = 13{\cdot}53\%.$$

(Theory for $C_{21}H_{19}N_3$ = 13·42%.)

---

15. 3-Thienyl-1,5-diphenyl-pyrazoline

Thienyl styryl ketone:-

5 g. $Ph{\cdot}CH{:}O$ and 6 g. acetothienone (prepared by the action of AcCl on thiophene in presence of

PCl_5 -- Steinkopf: Ann.413,347;1917) in 10c.c. 75% EtOH + 5c.c. 10% NaOH yielded a crop of pale yellow crystals over-night. Colourless needles, after recrystallisation from EtOH, m.p. 85°C. Yield 7·2 g. (85% th.).

Preparation of Pyrazoline:-

6·4 g. Thienyl styryl ketone and 4·4 g. phenylhydrazine were boiled ½ h. in 10c.c. glacial AcOH. The pyrazoline separated as yellow crystals on cooling. Recrystallised from EtOH, it formed yellow needles, m.p. 133°C. Yield 7·5 g. (68·5% th.).

The phenylhydrazone could not be isolated.

The pyrazoline yielded no aniline on reduction with Na/Hg.

Knorr's reaction: Green.

Estimation of Carbon and Hydrogen:-

0·1016 g. gave 0·0279 g. CO_2 and 0·0488 g. H_2O.

$$C = 0{\cdot}0279 \times \frac{3}{11} \times \frac{100}{0{\cdot}1016} = 74{\cdot}91\%.$$

$$H = 0{\cdot}0488 \times \frac{1}{9} \times \frac{100}{0{\cdot}1016} = 5{\cdot}34\%.$$

(Theory for $C_{19}H_{16}N_2S$ = 74·95% C, and 5·30% H.)

Estimation of Nitrogen:-

0·0973 g. gave 8·2c.c. N_2 at 18°C. and 735 mm., measured over 40% KOH.

$$N = 8{\cdot}2 \times \frac{273}{291} \times \frac{726}{760} \times \frac{0{\cdot}126}{0{\cdot}0973} = 9{\cdot}52\% \text{ (Th. = 9·21\%.)}.$$

Estimation of Sulphur:-

1·8536 g. gave 1·4330 g. $BaSO_4$.

$$S = 1{\cdot}4330 \times 0{\cdot}1373 \times \frac{100}{1{\cdot}8536} = 10{\cdot}62\% \text{ (Th. = 10·54\%)}.$$

16. 3-Styryl-1,5-diphenyl-pyrazoline (Straus: B.51,1457-77;1918.)

This pyrazoline was first reported as the phenylhydrazone of dibenzylideneacetone by Minnuni (Gazz.Chim.Ital.29,II.,398;1899). It was recognised as the pyrazoline by Straus (loc. cit.).

Preparation of Pyrazoline:-

2·34 g. Dibenzylideneacetone and 1·1 g. phenylhydrazine in 10c.c. glacial AcOH were boiled for ½ h. The pyrazoline was precipitated with water and crystallised from MeOH. Colourless needles, m.p. 151°C. (Straus, loc. cit., gives 153°C.).

The phenylhydrazone of dibenzylideneacetone is not isolable.

Knorr's reaction: Green.

---

17. 3-tert.-Butyl-1,5-diphenyl-pyrazoline (Auwers and Voss: B.42,4411;1909).

Tertiary-butyl styryl ketone (benzalpinacoline), colourless needles, m.p. 41°C., was prepared by condensation of Ph·CH:O and pinacoline in aqueous-alcoholic NaOH solution at ordinary temperature (Vorländer and Kalkow: B.30,2269;1897 and Org. Syn. V.,15).

Preparation of Pyrazoline:-

4·7 g. Benzalpinacoline and 2·7 g. phenylhydrazine in 10c.c. glacial AcOH were boiled for ½ h. The pyrazoline crystallised on cooling and, recrystallised from EtOH, was obtained as colourless needles, m.p. 107°C. (v. A. and V., loc. cit., 108° - 108·5°C.). Yield 5·3 g. (76% th.).

Knorr's reaction: Magenta.

The phenylhydrazone of benzylidenepinacoline is not isolable, the pyrazoline separating from cold alcoholic solution directly (K. v. Auwers and H. Voss: B,42,4411;1909).

---

18. 1-Phenyl-3-tert.-butyl-5-p-tolyl-pyrazoline

p-Methylstyryl tert.-butyl ketone:-

6 g. p-Toluic aldehyde and 5 g. pinacoline, in 20c.c. 75% EtOH, + 5c.c. 10% NaOH, gave after 7 days, pale yellow crystals of p-methylstyryl tert.-butyl ketone, m.p. 83°C. Yield 8·7 g. (87% th.).

Analysis:-

0·1871 g. gave 0·1503 g. H_2O and 0·5692 g. CO_2.

$$H = 0{\cdot}1503 \times \frac{1}{9} \times \frac{100}{0{\cdot}1871} = 8{\cdot}93\%;$$

$$C = 0{\cdot}5692 \times \frac{3}{11} \times \frac{100}{0{\cdot}1871} = 82{\cdot}97\%.$$

(Theory for $C_{14}H_{18}O$ = 8·91% H and 83·17% C.)

Preparation of Pyrazoline:-

4·9 g. p-Methylstyryl tert.-butyl ketone and 2·2 g. phenylhydrazine, boiled for ½ h. with 15c.c. glacial AcOH, gave on dilution with water an oil which was induced to crystallise by trituration with MeOH. Recrystallised from 75% EtOH, the pyrazoline formed golden-yellow needles, m.p. 129°C. Yield 3·7 g. (63% th.).

Estimation of Nitrogen:-

0·1025 g. gave 8·6c.c. N_2 at 17°C. and 762 mm., measured over 40% KOH.

$$N = 8{\cdot}6 \times \frac{273}{290} \times \frac{752}{760} \times \frac{0{\cdot}126}{0{\cdot}1025} = 9{\cdot}84\%$$

(Theory for $C_{20}H_{24}N_2$ = 9·59%.)

The pyrazoline gave no aniline on reduction with Na/Hg.

The phenylhydrazone was not isolable.

Knorr's reaction: Magenta.

---

19. 5-p-Tolyl-1,3-diphenyl-pyrazoline

p-Methylstyryl phenyl ketone

12·5 g. p-Toluic aldehyde and 12 g. acetophenone were condensed in 50c.c. 75% EtOH, with addition of 10c.c. 10% NaOH. Pale yellow crystals separated after 1 h. Recrystallised from ligroin, the ketone melted at 96°C. (Hanzlík and Bianchi: B. 32,2283;1899 give 96·5°C.). Yield 18·3 g. (82·5% th.).

Preparation of Pyrazoline:-

4·5 g. p-Methylstyryl phenyl ketone and 2·2 g. phenylhydrazine were boiled in 10c.c. glacial AcOH for ½ h. On cooling, the pyrazoline crystallised. Colourless needles, from alcohol, m.p. 129°C. Yield 4·9 g. (79% th.).

The pyrazoline gave no aniline on reduction with Na/Hg. The phenylhydrazone was not isolable.

Knorr's reaction: Blue-green.

Estimation of Nitrogen:-

0·1469 g. gave 11·5c.c. N_2 at 17°C. and 756 mm., measured over 40% KOH.

$$N = 11{\cdot}5 \times \frac{273}{290} \times \frac{747}{760} \times \frac{0{\cdot}126}{0{\cdot}1469} = 9{\cdot}14\%$$

(Theory for $C_{22}H_{20}N_2$ = 8·98%.)

---

20. Product Obtained from Cinnamylideneaceto-phenone Phenylhydrazone

Cinnamylideneacetophenone, golden-yellow needles, m.p. 102°C., was prepared by condensing cinnamic aldehyde and acetophenone in alcoholic NaOH solution (Scholtz: B.28,1730;1895).

The phenylhydrazone (v. Auwers and Voss: B.42,4411;1909), yellow needles, m.p. 156° - 158°C., was prepared by condensing the ketone with phenylhydrazine in cold alcoholic solution.

On boiling the phenylhydrazone with glacial AcOH for 1 h., and allowing to cool, a crop of colourless crystals separated, m.p. 123° - 124°C., after crystallisation from EtOH. This compound is not a pyrazoline (See p. 10 of this thesis).

On applying Knorr's test, in the usual way, an intense blue-green colour is obtained.

---

21. Product Obtained from Cinnamylidenepinacoline Phenylhydrazone

Cinnamylidenepinacoline was supplied by Professor Boon.

4·3 g. Cinnamylidenepinacoline and 2·2 g. phenylhydrazine were boiled in 20c.c. glacial AcOH for ½ h. On cooling, colourless crystals separated. Precipitation was completed by addition of water, and the product recrystallised from EtOH. Colourless needles, m.p. 141°C. Yield of purified product 4·5 g. (75% th.).

This product is probably, like the preceding compound, anomalous (See p.10 of this thesis).

Knorr's reaction: Magenta.

Estimation of Nitrogen:-

0·1107 g. gave 8·85c.c. N_2 at 18°C. and 778 mm., measured over 40% KOH.

$$N = 8{\cdot}85 \times \frac{273}{291} \times \frac{768}{760} \times \frac{0{\cdot}126}{0{\cdot}1107} = 9{\cdot}55\%$$

(Theory for $C_{21}H_{24}N_2$ = 9·21%.)

---

22. 5-o-Hydroxyphenyl-1,3-diphenyl-pyrazoline

(K. v. Auwers and H. Voss: B.42,4411;1909.)

o-Hydroxystyryl phenyl ketone (salicalacetophenone), yellow plates, m.p. 154°C., with decomposition, was prepared by condensing salicylaldehyde and acetophenone in aqueous-alcoholic NaOH solution (Harries and Büsse: B.29,378;1896).

Preparation of Pyrazoline:-

11·2 g. Salicalacetophenone and 5·4 g. phenylhydrazine, boiled for ½ h. in 20c.c. glacial AcOH, gave crystals of the pyrazoline on cooling. Recrystallised from EtOH, the pyrazoline formed greenish-white needles, m.p. 155°C. Yield 12·2 g. (78% th.). (K. v. A. and H. V., loc cit. give the m.p. as 136°C.; this is probably a misprint for 156°C.).

The phenylhydrazone is not isolable.

The pyrazoline yields no aniline on reduction with Na/Hg.

Knorr's reaction: Magenta.

---

23. 5-p-Hydroxyphenyl-1,3-diphenyl-pyrazoline

p-Hydroxystyryl phenyl ketone, m.p. 182°C., was prepared by condensing p-hydroxybenzaldehyde and acetophenone in alcoholic NaOH solution, recrystallising from 30% EtOH (Bablich and v. Kostanecki: B.

29,236;1896). The condensation takes place very rapidly, a 90% yield being obtained in 5 minutes.

Preparation of Pyrazoline:-

Quantities and conditions exactly as in the case of the ortho isomer. Yield of recrystallised product (75% EtOH) 12·7 g. (81% th.). Colourless crystals, m.p. 146°C.

The hydrazone was not isolable and the pyrazoline gave no aniline on reduction with Na/Hg.

Knorr's reaction: Blue.

Estimation of Nitrogen:-

0·1612 g. gave 12·4c.c. N_2 at 18°C. and 774 mm., measured over 40% KOH.

$$N = 12{\cdot}4 \times \frac{273}{291} \times \frac{763}{760} \times \frac{0{\cdot}126}{0.1612} = 9{\cdot}14\%.$$

(Theory for $C_{21}H_{18}ON_2$ = 8·92%.)

---

24. 5-o-Methoxyphenyl-1,3-diphenyl-pyrazoline

This pyrazoline was prepared by methylation of 5-o-hydroxyphenyl-1,3-diphenyl-pyrazoline (No. 22 of this series) as follows:-

To 3·1 g. of the hydroxy-pyrazoline, dissolved in 100c.c. 10% NaOH, 15c.c. Me_2SO_4 were added. The mixture was vigorously shaken for ½ h., and then warmed on the water-bath for 15 min. The alkaline reaction-mixture was extracted with ether, and the ethereal extract evaporated. The residue of methoxy-pyrazoline was recrystallised from EtOH. Golden-yellow needles, m.p. 121°C. Yield 2·2 g. (67% th.).

The pyrazoline yielded no aniline on reduction with Na/Hg. As the pyrazoline was not prepared by the usual method, no opportunity presented itself

for the investigation of the stability, or otherwise, of the phenylhydrazone.

Knorr's reaction: Magenta.

Estimation of Nitrogen:-

0·1723 g. gave 13·1c.c. N_2 at 18°C. and 743 mm., measured over 40% KOH.

$$N = 13{\cdot}1 \times \frac{273}{291} \times \frac{732}{760} \times \frac{0{\cdot}126}{0{\cdot}1723} = 8{\cdot}66\%.$$

(Theory for $C_{22}H_{20}ON_2$ = 8·54%.)

---

25. 5-m-Methoxyphenyl-1.3-diphenyl-pyrazoline

(H.Baur and P.Vogel: J.Pr.Ch.88,329-342;1913.)

m-Methoxybenzalacetophenone, m.p. 65°C., was prepared by condensation of m-methoxybenzaldehyde with acetophenone in aqueous-alcoholic NaOH solution.

Preparation of Pyrazoline:-

2·4 g. m-Methoxybenzalacetophenone and 1·1 g. phenylhydrazine were boiled for ½ hour in 10 c.c. glacial AcOH. The pyrazoline was precipitated with water and recrystallised from ether. Pale greenish-yellow needles, m.p. 96°C. (B. and V., loc. cit., give 98°C.). Yield 2·6 g. (79% th.).

Knorr's reaction: Green.

---

26. 5-p-Methoxyphenyl-1.3-diphenyl-pyrazoline

p-Methoxystyryl phenyl ketone (anisalacetophenone) was prepared by condensing anisaldehyde with acetophenone in alcoholic NaOMe solution (Pond and Schoffstall: Am.Soc.22,666;1899). M.p. 77°C.

Preparation of Pyrazoline:-

4·8 g. Anisalacetophenone and 2·2 g. phenylhydrazine were boiled for ½ h. with 20c.c. glacial AcOH. The pyrazoline crystallised on cooling. After recrystallisation from EtOH, it was obtained as colourless needles, m.p. 121°C. Yield of pure product 4·8 g. (73% th.).

An attempt to isolate the phenylhydrazone was unsuccessful.

Knorr's reaction: Blue.

Estimation of Nitrogen:-

0·1946 g. gave 14·9c.c. N_2 at 16°C. and 742 mm., measured over 40% KOH.

$$N = 14{\cdot}9 \times \frac{273}{289} \times \frac{732}{760} \times \frac{0{\cdot}126}{0{\cdot}1946} = 8{\cdot}78\%.$$

(Theory for $C_{22}H_{20}ON_2$ = 8·54%.)

---

27. 3-Methyl-1,5-diphenyl-pyrazoline (K. v. Auwers and H. Voss: B.42,4411;1909.)

The phenylhydrazone of benzalacetone is isolable, m.p. 157°C. (A. and V., loc. cit.).

Preparation of Pyrazoline:-

7·3 g. Benzalacetone and 5·4 g. phenylhydrazine were boiled for ½ h. in 20c.c. glacial AcOH. The pyrazoline crystallised on cooling. Recrystallised from EtOH, it formed pale yellow needles, m.p. 115°C. (A. and V., loc. cit., 115° - 116°C.). Yield 9·5 g. 80% th.).

Knorr's reaction: Magenta.

---

28. 1-Phenyl-3-methyl-5-o-hydroxyphenyl-pyrazoline

(Harries: B.24,3182;1891. Auwers and Müller: B.41,4230;1908. Auwers and Voss: B.42,4411;1909.)

o-Hydroxystyryl methyl ketone (salicalacetone), m.p. 139°C., was prepared by condensing salicylic aldehyde with acetone in aqueous NaOH solution (Harries: loc. cit.)

The phenylhydrazone of salicalacetone is isolable (Auwers and Voss: loc. cit.); yellow needles, m.p. 158° - 159°C.

Preparation of Pyrazoline:-

3·2 g. Salicalacetone and 2·2 g. phenylhydrazine were boiled for 1 h. with 15c.c. glacial AcOH. The pyrazoline crystallised on cooling and was recrystallised from EtOH. Colourless needles, m.p. 150°C. (A. and M., loc. cit., give 147° - 148°C.).

Knorr's reaction: Magenta.

---

29. 1,3-Diphenyl-5-(3,4-dimethoxyphenyl)-pyrazoline

Veratralacetophenone:-

5·5 g. Veratraldehyde and 4 g. acetophenone were dissolved in 25c.c. absolute EtOH, and 3c.c. 10% NaOH added. Golden yellow needles had separated after 24 h. Recrystallised from 75% EtOH, the ketone formed pale yellow needles, m.p. 93°C. Yield 5·8 g. (65% th.).

Estimation of Carbon and Hydrogen:-

0·1403 g. 0·0560 g. H_2O and 0·2920 g. CO_2.

$$H = 0{\cdot}0560 \times \frac{1}{9} \times \frac{100}{0{\cdot}1043} = 5{\cdot}96\%;$$

$$C = 0{\cdot}2920 \times \frac{3}{11} \times \frac{100}{0{\cdot}1043} = 76{\cdot}36\%.$$

(Theory for $C_{17}H_{10}O_3$ = 5·97% H and 76·12% C.)

Preparation of Pyrazoline:-

8 g. Veratralacetophenone and 3·3 g. phenylhydrazine in 40c.c. glacial AcOH were boiled 1 h. On diluting, after cooling, with water the pyrazoline separated as an oil which coagulated on shaking. It was recrystallised from EtOH. Colourless needles, m.p. 136°C. Yield 8·4 g. (84% th.).

An attempt to isolate the phenylhydrazone was unsuccessful.

The pyrazoline gave no aniline on reduction with Na/Hg.

Knorr's reaction: Blue.

Estimation of Nitrogen:-

0·1415 g. gave 9·55c.c. N_2 at 17°C. and 771 mm., measured over 40% KOH.

$$N = 9{\cdot}55 \times \frac{273}{290} \times \frac{761}{760} \times \frac{0{\cdot}126}{0{\cdot}1415} = 8{\cdot}01\%$$

(Theory for $C_{23}H_{22}O_2N_2$ = 7·82%.)

---

30. 1-Phenyl-3-tert.-butyl-5-(3,4-dimethoxyphenyl)-pyrazoline

3,4-Dimethoxystyryl tert.-butyl ketone (veratralpinacoline):-

4·2 g. Veratraldehyde and 2·5 g. pinacoline in 20c.c. EtOH + 3c.c. 10% NaOH gave, after standing 10 days, a fibrous mass of lustrous yellow needles. Recrystallised from alcohol, the ketone melted at 112°C. Yield 4·2 g. (67% th.).

Estimation of Carbon and Hydrogen:-

0·1137 g. gave 0·0805 g. H_2O and 0·3031 g. CO_2.

$$H = 0{\cdot}0805 \times \frac{1}{9} \times \frac{100}{0{\cdot}1137} = 7{\cdot}87\%$$

$$C = 0{\cdot}3021 \times \frac{3}{11} \times \frac{100}{0{\cdot}1137} = 72{\cdot}45\%;$$

(Theory for $C_{15}H_{20}O_3$ = 8·07% H and 72·58% C.)

Preparation of Pyrazoline:-

2·5 g. Veratralpinacoline and 1·1 g. phenylhydrazine were boiled in 15c.c. glacial AcOH for 1 h. The pyrazoline was precipitated with water and recrystallised from EtOH. Colourless needles, m.p. 101°C. Yield 2·5 g. (73·5% th.).

An attempt to isolate the phenylhydrazone was unsuccessful.

The pyrazoline gave no aniline on reduction with Na/Hg.

Knorr's reaction: Magenta.

Estimation of Nitrogen:-

0·1519 g. gave 10·7c.c. N_2 at 15°C. and 770mm., measured over 40% KOH.

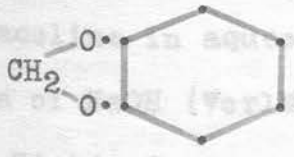
$$N = 10{\cdot}7 \times \frac{273}{288} \times \frac{762}{760} \times \frac{0{\cdot}126}{0{\cdot}1519} = 8{\cdot}42\%.$$

(Theory for $C_{21}H_{26}O_2N_2$ = 8·28%.)

---

31. 1-Phenyl-3-tert.-butyl-5-(methylene-3,4-dihydroxyphenyl)-pyrazoline

Piperonylidenepinacoline:



a colourless, crystalline solid, m.p. 101°C., was supplied by Professor Boon for the preparation of the pyrazoline.

Preparation of Pyrazoline:-

2·3 g. Piperonylidenepinacoline and 1·1 g. phenylhydrazine were dissolved in 20c.c. EtOH, with addition of 1c.c. AcOH. Knorr's reaction was given almost immediately (magenta) by a drop of the reaction-mixture. The phenylhydrazone could not be isolated, the pyrazoline crystallising on standing.

To ensure complete pyrazoline formation, the alcohol was displaced by adding 20c.c. AcOH and heating for 1 h., allowing the alcohol to escape. The pyrazoline crystallised on cooling. It was recrystallised from AcOH and dried over KOH. Colourless needles, m.p. 112°C. Yield 2·7 g. (84% th.).

The pyrazoline gave no aniline on reduction with Na/Hg.

Estimation of Nitrogen:-

0·1132 g. gave 8·3c.c. N_2 at 17°C. and 774mm., measured over 40% KOH.

$$N = 8{\cdot}3 \times \frac{273}{290} \times \frac{764}{760} \times \frac{0{\cdot}126}{0{\cdot}1132} = 8{\cdot}74\%.$$

(Theory for $C_{20}H_{22}O_2N_2$ = 8·70%.)

---

32. 1-Phenyl-3-tert.-butyl-5-p-methoxyphenyl-pyrazoline

Anisalpinacoline (p-methoxystyryl tert.-butyl-ketone) was prepared by condensation of anisaldehyde and pinacoline in aqueous-alcoholic solution, with addition of NaOH (Vorländer: Ann.341,34;1905).

Yield of recrystallised anisalpinacoline, m.p. 34°C., from 4 g. anisaldehyde and 3 g. pinacoline was 5·2 g. (80% th.).

Preparation of Pyrazoline:-

2·2 g. Anisalpinacoline and 1·1 g. phenylhydrazine were boiled for ½ h. in 10c.c. glacial AcOH. The pyrazoline, precipitated with water and recrystallised from 50% AcOH, formed colourless crystals, m.p. 117°C. Yield 2·1 g. (68% th.).

An attempt to isolate the phenylhydrazone was unsuccessful.

The pyrazoline yielded no aniline on reduction with Na/Hg.

Knorr's reaction: Magenta.

Estimation of Nitrogen:-

0·1213 g. gave 9·45c.c. N_2 at 17°C. and 775 mm., measured over 40% KOH.

$$N = 9·45 \times \frac{273}{290} \times \frac{765}{760} \times \frac{0·126}{0·1213} = 9·28\%.$$

(Theory for $C_{20}H_{24}ON_2$ = 9·09%.)

---

33. 1,3-Diphenyl-5-o-nitrophenyl-pyrazoline

o-Nitrostyryl phenyl ketone (o-nitrobenzalacetophenone) was prepared from o-nitrobenzaldehyde and acetophenone in alcoholic NaOH solution (Sorge: B,35,1067;1902). Yellow needles from alcohol, m.p. 122°C. (S., loc. cit., 124°C.).

Preparation of Pyrazoline:-

2·5 g. Nitrobenzalacetophenone and 1 g. phenylhydrazine were boiled for ½ h. with 10c.c. glacial AcOH. The pyrazoline crystallised on cooling and was recrystallised from EtOH. Red needles, m.p. 138°C. Yield 2·9 g. (86% th.).

Isolation of Phenylhydrazone:-

When the same quantities of ketone and phenylhydrazine as were used above for the preparation of the pyrazoline were dissolved in 10c.c. cold absolute EtOH, and allowed to stand over-night, with addition of 1c.c. AcOH, a crop of blood-red crystals, m.p. 115° - 120°C., was obtained. These crystals responded to Knorr's reaction, as did the pyrazoline, to give a blue colour. It was, therefore, concluded that the phenylhydrazone was contaminated with pyrazoline.

On reduction with Na/Hg, the phenylhydrazone gave aniline, but the pyrazoline gave none.

On boiling the phenylhydrazone for ½ h. with AcOH, it was converted into the pyrazoline.

Estimation of Nitrogen in Pyrazoline:-

0·1207 g. gave 12·8c.c. N_2 at 15°C. and 764 mm., measured over 40% KOH.

$$N = 12{\cdot}8 \times \frac{273}{288} \times \frac{753}{760} \times \frac{0{\cdot}126}{0{\cdot}1207} = 12{\cdot}58\%.$$

(Theory for $C_{21}H_{17}O_2N_3$ = 12·24%.)

---

34. 1.3-Diphenyl-5-m-nitrophenyl-pyrazoline

m-Nitrostyryl phenyl ketone (m-nitrobenzalacetophenone), yellow needles, m.p. 145°C., was prepared by condensing m-nitrobenzaldehyde with acetophenone in alcoholic solution, in presence of NaOH (Sorge: B.35,1068;1902).

Preparation of Phenylhydrazone:-

2·5 g. m-Nitrobenzalacetophenone and 1·1 g. phenylhydrazine, dissolved in 10c.c. cold absolute EtOH, with addition of 1c.c. AcOH, gave over-night

a crop of reddish-yellow crystals which, after washing with EtOH and drying, melted at 102°C. These crystals did not respond to Knorr's test, but gave aniline on reduction.

Preparation of Pyrazoline:-

The phenylhydrazone, on boiling for ½ h. with AcOH, gave on cooling a crop of yellow needles. Canary yellow needles, from EtOH, m.p. 122° - 123°C. Yield 90% th.

The pyrazoline gave no aniline on reduction with Na/Hg.

Knorr's reaction: Green.

Estimation of Nitrogen:-

0·1016 g. gave 10·7c.c. N_2 at 16°C. and 757 mm.,

$$N = 10{\cdot}7 \times \frac{273}{289} \times \frac{747}{760} \times \frac{0{\cdot}126}{0{\cdot}1016} = 12{\cdot}33\%.$$

(Theory for $C_{21}H_{17}O_2N_3$ = 12·24%.)

---

35. 1,3-Diphenyl-5-p-nitrophenyl-pyrazoline

p-Nitrostyryl phenyl ketone (p-nitrobenzal-acetophenone), yellow needles from EtOH, m.p. 162°C., was prepared by condensing p-nitrobenzaldehyde with acetophenone in alcoholic NaOH solution (Sorge: B.35, 1068;1902 gives m.p. 164°C.).

The ketone was treated with phenylhydrazine in cold alcoholic solution, with addition of a small amount of AcOH, as in the case of the o- and m- isomers. Yellow crystals separated over-night; but these melted at 68° - 70°C. (M.p. of pyrazoline is 73° - 75°C.) and gave the same reaction (blue) as the pyrazoline with H_2SO_4 and $NaNO_2$. The phenyl-

hydrazone, therefore, either changes completely into the pyrazoline in the cold, or has practically the same m.p. as the pyrazoline when contaminated with the pyrazoline.

Preparation of Pyrazoline:-

The red crystals obtained above were boiled for ½ h. with glacial AcOH, after which a crop of crystals similar in appearance was obtained, m.p. 73° - 75°C.

No aniline was obtained on reducing either the pyrazoline, or the crystalline product prior to boiling with AcOH, with Na/Hg.

Knorr's reaction: Blue.

Estimation of Nitrogen:-

0·1002 g. gave 10·8c.c. N_2 at 17°C. and 750 mm., measured over 40% KOH.

$$N = 10{\cdot}8 \times \frac{273}{290} \times \frac{740}{760} \times \frac{0{\cdot}126}{0{\cdot}1002} = 12{\cdot}44\%.$$

(Theory for $C_{21}H_{17}O_2N_3$ = 12·24%.)

---

36. 1-Phenyl-3-tert.-butyl-5-p-nitrophenyl-pyrazoline

p-Nitrostyryl tert.-butyl ketone (p-nitrobenzalpinacoline):-

5 g. p-Nitrobenzaldehyde and 3·5 g. pinacoline, dissolved in 100c.c. EtOH gave, on standing 3 days, a crop of yellow crystals. M.p., after recrystallisation from EtOH, 127°C. Yield 5·3 g. (69% th.).

Preparation of Phenylhydrazone:-

3·25 g. p-Nitrobenzalpinacoline and 1·25 g.

phenylhydrazine were dissolved in 40c.c. EtOH, and 1·25c.c. AcOH added. After standing 2 h., scarlet needles had separated. Washed with cold EtOH, these melted at 178° - 180°C. This was, presumably, the phenylhydrazone; but Knorr's reaction was given strongly. Aniline was obtained on reduction with Na/Hg.

Preparation of Pyrazoline:-

When the crystals obtained in the cold were boiled ½ h. with AcOH, yellow crystals separated on cooling. Recrystallised from 50% AcOH; golden-yellow needles, m.p. 152°C.

The pyrazoline gave no aniline on reduction.

Knorr's test: Magenta.

Estimation of Nitrogen:-

0·0972 g. gave 10·9c.c. N_2 at 18°C. and 776 mm., measured over 40% KOH.

$$N = 10{\cdot}9 \times \frac{273}{291} \times \frac{765}{760} \times \frac{0{\cdot}126}{0{\cdot}0972} = 13{\cdot}34\%.$$

(Theory for $C_{19}H_{21}O_2N_3$ = 13·00%.).

---

37. 1-Phenyl-3-thienyl-5-o-methoxyphenyl-pyrazoline

o-Methoxystyryl thienyl ketone (o-methoxybenzal-acetothienone) was prepared by condensing 6·8 g. o-methoxybenzaldehyde and 6·3 g. acetothienone in 10c.c. 75% EtOH + 1c.c. 10% NaOH. An oil separated overnight and crystallised after 5 days. The reddish crystals were recrystallised from EtOH, separating as yellow needles, m.p. 64°C. Yield 8·4 g. (69% th.).

Preparation of Pyrazoline:-

4·9 g. o-Methoxybenzalacetothienone and 2·2 g. phenylhydrazine were dissolved in 15c.c. absolute EtOH and 2·2c.c. AcOH added. After 5 days, a yellow oil separated; this oil gave an intense green with H_2SO_4 and $NaNO_2$. The oil could not be induced to crystallise; it was, therefore boiled for 1 h. with 15c.c. AcOH. Yellow crystals separated on cooling and were recrystallised from 75% EtOH. M.p. 148°C. Yield (lemon-yellow needles) 5·6 g. (84% th.).

The pyrazoline gave no aniline on reduction with Na/Hg and showed an intense green colour on treatment with H_2SO_4 and $NaNO_2$.

Estimation of Carbon and Hydrogen:-

0·1478 g. gave 0·3876 g. CO_2 and 0·0720 g. H_2O.

$$C = 0{\cdot}3876 \times \frac{3}{11} \times \frac{100}{0.1478} = 71{\cdot}51\%;$$

$$H = 0{\cdot}0720 \times \frac{1}{9} \times \frac{100}{0{\cdot}1478} = 5{\cdot}42\%.$$

Estimation of Nitrogen:-

0·0852 g. gave 6·35c.c. N_2 at 15°C. and 750 mm., measured over 40% KOH.

$$N = 6{\cdot}35 \times \frac{273}{288} \times \frac{741}{760} \times \frac{0{\cdot}126}{0{\cdot}0852} = 8{\cdot}67\%.$$

Estimation of Sulphur:-

1·1711 g. gave 0·8069 g. $BaSO_4$.

$$S = 0{\cdot}8069 \times 0{\cdot}1373 \times \frac{100}{1{\cdot}1711} = 9{\cdot}46\%.$$

(Theory for $C_{20}H_{18}ON_2S$:- C = 71·82%, H = 5·43%, N = 8·38%, S = 9·46%.)

STUDY OF FLUORESCENCE OF FOREGOING PYRAZOLINES IN VARIOUS SOLVENTS ON EXPOSURE TO ULTRAVIOLET RAYS

The majority of the pyrazolines under observation fluoresce in the solid state on exposure to ultraviolet rays, but the intensity of fluorescence is to a considerable extent dependent on the state of division of the solid compound. It is, therefore, essential to conduct observations on the substance in solution if anything in the nature of accurate comparison of either tint or intensity be aimed at.

It was found to be convenient to prepare for examination 1/100th molar solutions, by dissolving the centigram-molecular weight (approximately 3 cgms, in most cases) of the pyrazoline in 10c.c. solvent. When alcohol was employed, the sparing solubility of a few of the compounds in this solvent made it impossible to attain the desired concentration of solution. In these few cases, observation was conducted on the warm saturated solution. This procedure was preferred to that of reducing the concentration throughout the series, as the fluorescence of many of the more faintly luminous compounds could not then be observed. This course of action was justified, moreover, by the fact that fluorescence is apparently independent of temperature within the working range.

The solutions were examined in test-tubes which were subjected to preliminary investigation by ultraviolet rays in order to make certain that the glass itself was in no case fluorescent.

It was a comparatively easy matter to

classify the solutions according to colour and intensity of fluorescence. A very convenient method of recording the results, and one which lends itself to subsequent comparative consideration, is that employed on pages 50, 59 and 63. The pyrazolines are represented by their serial numbers, see Table I. (facing p. 7). Those which show indistinguishable fluorescences are placed in horizontal juxtaposition; those which exhibit the same colour of fluorescence, but differ in intensity, are arranged in vertical columns in order (reading from top to bottom) of diminishing intensity.

The author attempted to determine spectroscopically the wave-length of the emitted fluorescent light. It was found, however, that in every case a continuous spectrum was obtained. This difficulty was, no doubt, occasioned by the fact that a monochromatic source of ultraviolet radiation was not available.

The classification of the pyrazolines according to colour and intensity of fluorescence, however, furnished much interesting information with regard to the interrelationship of fluorescence and chemical constitution in this group of compounds.

Table II. (p. 49) indicates the colours of the alcoholic solutions of the various pyrazolines and the nature of the fluorescence, if any, in ordinary daylight.

Table III. (p. 50) shows the results obtained on exposure of the alcoholic solutions to ultraviolet rays.

TABLE II.

		Solvent: Alcohol	
	Colour of Solution	Fluorescence in Daylight	Remarks
1.	straw	nil	
2.	colourless	pale blue	
3.	straw	nil	
4.	straw	nil	
5.	pale straw	nil	supersatd. in cold
6.	straw	nil	
7.	straw	nil	
8.	colourless	very faint blue	supersatd. in cold
9.	colourless	nil	supersatd. in cold
10.	pale straw	very faint blue	
11.	golden-yellow	nil	
12.	golden-yellow	nil	supersatd. in cold
13.	reddish-yellow	nil	supersatd. in cold
14.	deep straw	nil	
15.	greenish-yellow	faint green	
16.	yellowish-green	green	supersatd. in cold
17.	colourless	nil	supersatd. in cold
18.	colourless	nil	
19.	colourless	pale blue	
20.	colourless	pale blue	
21.	colourless	nil	
22.	colourless	faint green	
23.	colourless	faint blue	
24.	yellowish-green	faint green	
25.	straw	nil	
26.	colourless	faint blue	
27.	colourless	nil	
28.	colourless	faint blue-green	
29.	colourless	pale blue	
30.	colourless	very faint blue	
31.	colourless	nil	
32.	colourless	nil	
33.	golden-yellow	nil	supersatd. in cold
34.	pale yellow	nil	supersatd. in cold
35.	reddish-orange	nil	
36.	pale straw	nil	
37.	colourless	faint green	

TABLE III.

FLUORESCENCE IN ALCOHOLIC SOLUTION IN ULTRAVIOLET RAYS

	9	Deep "Royal" blue, without opalescence.
Light "Electric" blue, decreasing in intensity in direction of arrow. ↓	8	
	2,19,20,23,25,26,29	Light "Electric" blue (opalescent) of uniform tint and intensity.
	14	
	10	
	30	
	31	
	21	
	32	
	17,18	
	11,12,13	Very faint -- gradation impossible.
Green, decreasing in intensity in direction of arrow. ↓	16	Bright yellowish-green.
	22,24	Yellowish-green.
	15,37	Bluish-green.
	28	
	27	Very faint bluish-green.
	1	
	3,4,5,6,7,33,34,35,36	No fluorescence.

NOTE:- Compounds whose fluorescences are indistinguishable in tint and intensity appear in the same horizontal row.

DISCUSSION OF FLUORESCENCE IN ALCOHOLIC SOLUTION

No. 2 of the series (1.3.5-triphenyl-pyrazoline), on account of the identity of its three substituent groups, constitutes a convenient standard of comparison for the other members. In daylight, it shows a distinct blue fluorescence which is intensified, on exposure to ultraviolet rays, to a brilliant "Electric" blue, the solution appearing opaque or opalescent.

The members of the series whose fluorescence could not be distinguished, either in tint or intensity, from that of triphenyl-pyrazoline are here tabulated, employing the same system as in Table I. (facing p. 7).

	III.	V.
2.	phenyl	phenyl
19.	phenyl	p-tolyl
20.	anomalous	
23.	phenyl	p-hydroxyphenyl
26.	phenyl	p-methoxyphenyl
25.	phenyl	m-methoxyphenyl
29.	phenyl	3.4-dimethoxyphenyl

No. 19 (1.3-diphenyl-5-p-tolyl-pyrazoline) shows, as might have been anticipated, that replacement of phenyl by tolyl in position 5 has no appreciable effect on fluorescence.

That hydroxyl (See No. 23), introduced in the para position in the nucleus in position 5, has no effect is interesting in view of the fact that the

same group in the ortho position (No. 22) modifies the colour of fluorescence to a yellowish-green.

The methyl ethers of the 5-o- and -p-hydroxyphenyl-pyrazolines show the same fluorescent behaviour as the parent hydroxy-compounds, viz.: blue for the p-methoxy-compound (No. 25) and yellowish-green for the o-methoxy-compound (No. 24).

Introduction of methoxyl in the meta position in the benzene nucleus in position 5 does not alter fluorescence in any way. Owing to failure to induce m-hydroxybenzaldehyde to condense with acetophenone, 5-m-hydroxyphenyl-1,5-diphenyl-pyrazoline was not available for comparison.

No. 29 of the series (1,3-diphenyl-5-3,4-dimethoxyphenyl-pyrazoline), containing two methoxyl groups in the nucleus in position 5, shows no deviation from the parent type; but the symmetrically substituted 3-trimethoxyphenyl-1,5-diphenyl-pyrazoline (No. 9) is unique in exhibiting a deep "Royal" blue fluorescence, without a trace of opalescence.

The members of the series which show the same colour of fluorescence as triphenylpyrazoline, but less intensely, are tabulated below, in order of decreasing intensity (from top to bottom):

	III.	V.
2.	phenyl	phenyl
14.	p-aminophenyl	phenyl
10.	o-ethoxyphenyl	phenyl
30.	tert.-butyl	3,4-dimethoxyphenyl

(Continued on p. 53)

(Table continued from previous page.)

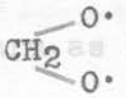
31.	tert.-butyl	methylene-3.4-dioxyphenyl
21.	anomalous	
32.	tert.-butyl	p-methoxyphenyl
17.	tert.-butyl	phenyl
18.	tert.-butyl	p-tolyl
11.	o-nitrophenyl	phenyl
12.	m-nitrophenyl	phenyl
13.	p-nitrophenyl	phenyl

In No. 14 (3-p-aminophenyl-1.5-diphenyl-pyrazoline) the intensity of fluorescence is almost equal to that of triphenyl-pyrazoline itself.

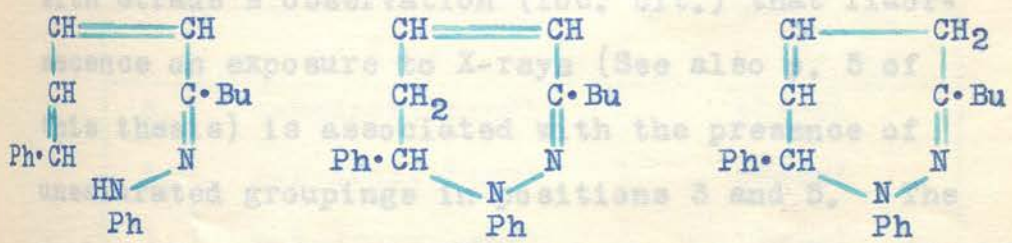
3-o-Ethoxyphenyl-1.5-diphenyl-pyrazoline (No. 10) is unexpectedly fluorescent, as the corresponding hydroxy-pyrazoline (N. 3) shows no fluorescence at all.

No. 17 (3-tert.-butyl-1.5-diphenyl-pyrazoline) and No. 18 (1-phenyl-3-tert.-butyl-5-p-tolyl-pyrazoline) are the least fluorescent of this group, with the exception of Nos. 11, 12 and 13, whose fluorescence is very faint indeed. It is not surprising that they show no difference in tint or intensity.

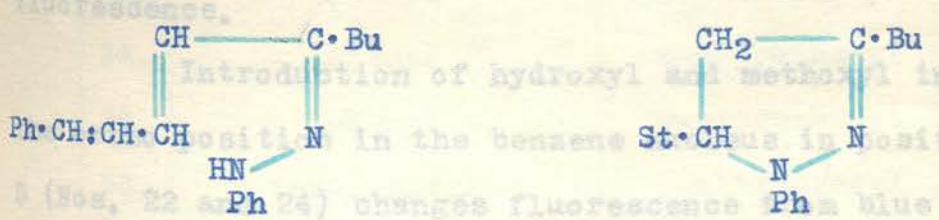
The fluorescence of Nos. 30, 31 and 32, which all contain the tertiary butyl group in position 3, is slightly intensified, as compared with Nos. 17 and 18, by the introduction of methoxyl or the methylenedioxy group:



It is of interest that the anomalous compound derived from cinnamylideneacetophenone phenylhydrazone (No. 20; see Table on p. 51.) shows a brilliant blue fluorescence, indistinguishable from that of triphenyl-pyrazoline. This is in conformity with Straus's view (B.51,1547;1918) that this compound is not 5-styryl-1.3-diphenyl-pyrazoline, since the introduction of styryl in position 5 would probably change the colour of fluorescence from blue to green (Cf. No. 15). It is noteworthy that the compound produced from the phenylhydrazone of cinnamylidenepinacoline (No. 21) shows a blue fluorescence and is, therefore, probably anomalous also. If such be the case, ring-closure will follow the course:



rather than:



(St = styryl; Bu = tert.-butyl.)

The members of the series which show a greenish fluorescence are as follow:-

	III.	V.
16.	styryl	phenyl
22.	phenyl	o-hydroxyphenyl
24.	phenyl	o-methoxyphenyl
15.	thienyl	phenyl
37.	thienyl	o-methoxyphenyl
27.	methyl	phenyl
28.	methyl	o-hydroxyphenyl
1.	----	phenyl

Consideration of this group reveals that removal of phenyl from position 3 changes the colour of fluorescence from blue, in triphenyl-pyrazoline, to an extremely faint bluish-green in 1,5-diphenyl-pyrazoline. This is quite in keeping with Straus's observation (loc. cit.) that fluorescence on exposure to X-rays (See also p. 5 of this thesis) is associated with the presence of unsaturated groupings in positions 3 and 5. The analogy is further justified by the fact that (No.16) 3-styryl-1.5-diphenyl-pyrazoline and (No.15) 3-thienyl-1.5-diphenyl-pyrazoline both exhibit a brilliant green fluorescence.

Introduction of hydroxyl and methoxyl in the ortho position in the benzene nucleus in position 5 (Nos. 22 and 24) changes fluorescence from blue in triphenyl-pyrazoline, to yellowish-green.

Replacement of phenyl by thienyl in position 3 has the effect of changing fluorescence from bright blue, in triphenyl-pyrazoline, to rather faint bluish-green in 3-thienyl-1.5-diphenyl-pyrazoline (No. 15).

The effect of thienyl, as compared with phenyl, is again illustrated by a comparison of No. 24 (1-phenyl-3-thienyl-5-o-methoxyphenyl-pyrazoline), which shows a distinctly bluish-green fluorescence, with No. 37 (1.3-diphenyl-5-o-methoxy-phenyl-pyrazoline), which exhibits a pure yellowish-green fluorescence.

Replacement of phenyl in position 3 by the saturated aliphatic methyl group almost destroys fluorescence in No. 27 (1.5-diphenyl-3-methyl-pyrazol-ine) and in No. 28 (1-phenyl-3-methyl-5-o-hydroxy-phenyl-pyrazoline).

In conclusion, the members of the series which show no fluorescence in alcoholic solution, on exposure to ultraviolet radiation, are as follow:-

	III.	V.
3.	o-hydroxyphenyl	phenyl
4.	m-hydroxyphenyl	phenyl
5.	p-hydroxyphenyl	phenyl
6.	o-methoxyphenyl	phenyl
7.	m-methoxyphenyl	phenyl
33.	phenyl	o-nitrophenyl
34.	phenyl	m-nitrophenyl
35.	phenyl	p-nitrophenyl
36.	tert.-butyl	p-nitrophenyl

It is most interesting that the intro-duction of hydroxyl (Nos. 3, 4 and 5) and methoxyl (Nos. 6 and 7) into the benzene nucleus in position 3 completely inhibits fluorescence, whereas the similar introduction of the same groups in position

5 does not.

The introduction of the nitro group into the benzene nucleus, in either position 3 or position 5, has a very marked effect on fluorescence. In the former case (Nos. 11, 12 and 13) the three isomeric 3-nitrophenyl-1,5-diphenyl-pyrazolines are almost devoid of fluorescence in alcoholic solution. In the latter case (Nos. 33, 34 and 35) the three isomeric 5-nitrophenyl-1.3-diphenyl-pyrazolines are completely non-fluorescent.

There is also no fluorescence in the case of 1-phenyl-3-tert.-butyl-5-p-nitrophenyl-pyrazoline, as was to be expected.

This concludes the consideration and discussion of fluorescence of the series of pyrazolines under investigation on exposure to ultraviolet radiation in alcoholic solution.

In the subsequent pages, the phenomenon of fluorescence in chloroform and also in benzene solution is similarly dealt with, the results obtained being compared and contrasted with those discussed in the foregoing section of the thesis.

Table IV., p. 58, shows the colours of the chloroform solutions of the pyrazolines, and also the nature of the fluorescence, if any, in ordinary daylight.

Table V., p. 59, summarises the behaviour of the benzene solutions on ultraviolet irradiation, the same method of tabulation being employed as in the case of the alcoholic solutions (pp. 48 and 50).

TABLE IV.

Solvent: Chloroform

	Colour of Solution	Fluorescence in Daylight
1.	colourless	nil
2.	straw	faint blue
3.	colourless purple	nil
4.	colourless purple	nil
5.	colourless purple	nil
6.	colourless purple	nil
7.	colourless purple	nil
8.	colourless brown	nil
9.	colourless p. purple	nil
10.	colourless purple	pale blue
11.	orange-yellow	nil
12.	orange-yellow	nil
13.	orange-red	nil
14.	orange-red	nil
15.	straw	pale green
16.	pale yellow	brilliant green
17.	colourless	nil
18.	colourless	nil
19.	colourless	pale blue
20.	colourless	pale blue
21.	colourless	nil
22.	colourless	pale greenish-blue
23.	deep straw	blue
24.	faint straw	pale green
25.	colourless	faint purple
26.	colourless	pale blue
27.	colourless	nil
28.	colourless	pale green
29.	colourless	pale blue
30.	colourless	faint blue
31.	colourless	nil
32.	colourless	nil
33.	golden-yellow	faint blue
34.	pale straw	nil
35.	orange-yellow	nil
36.	pale straw	nil
37.	pale yellow	brilliant green

Note:- The initially colourless solutions of Nos. 3, 4, 5, 6, and 7 turned purple, that of No. 8 brown, in the course of about 30 minutes.

TABLE V.

FLUORESCENCE IN CHLOROFORM SOLUTION IN ULTRAVIOLET RAYS

9	Deep "Royal" blue, bright, without opalescence.
11,12	Extremely faint deep "Royal" blue, without opalescence.
8	Deep "Royal" blue (opalescent).
10, 14	Less intense than 8.
2,19,20,23,26,29	Intense "Electric" blue.
25	(Decreasing in intensity in direction of arrow.)
17,18,21,31	
32	
15	Bright greenish-blue.
27,30	Slightly paler than 15.
16,37	Brilliant green.
22,24,28	Slightly paler than 16 and 37.
1	Very faint.
13	Deep red.
3,4,5,6,7,33,34,35,36	No fluorescence.

DISCUSSION OF FLUORESCENCE IN CHLOROFORM SOLUTION

There is little difference in appearance between the chloroform and alcoholic solutions in ordinary daylight, as is at once apparent from a comparison of Table II. (p.49) with Table IV. (p.58). The "greens" are accentuated, however, in chloroform solution (Cp. Nos. 15, 16, 24, 28 and 37).

A comparison of Table III. (p.50) with Table V. (p.59) shows that the nature of the solvent may exercise considerable influence on both colour and intensity of fluorescence.

In chloroform solution, No. 9 (3-s-trimethoxyphenyl-1.5-diphenyl-pyrazoline) again occupies a unique position at the head of the Table; it once more shows a deep "Royal" blue fluorescence, the solution being quite transparent. No. 8 (3-p-methoxyphenyl-1.5-diphenyl-pyrazoline) shows the same deep "Royal" blue, though opalescent, in chloroform; whereas in alcohol it heads the "Electric" blue group.

In both solvents, Nos. 2, 19, 20, 23, 25, 26, 29, 17, 18, 21, 31 and 32 show "Electric" blue fluorescences, with only slight variations of relative intensity in the different solvents.

The most noteworthy differences due to the solvent, amongst the "blues," are found in Nos. 10, 11, 12 and 14, which occur in the "Electric" blue class in alcohol, but appear in the "Royal" blue group in chloroform.

The case of Nos. 11, 12 and 13 (the three isomeric 3-nitrophenyl-1.5-diphenyl-pyrazolines) is

particularly interesting. All show the very feeblest blue fluorescence in alcohol. In chloroform there is little change in the fluorescence of the o- and m- isomers (Nos. 11 and 12); the intensity is still very feeble, although the tint changes from light blue in alcohol to deep blue in chloroform. The behaviour of the p-isomer (No. 13) is very striking, however; it shows a faint, but distinct, deep red fluorescence in chloroform. The anomalous behaviour of this pyrazoline is further discussed in connection with its fluorescence in benzene solution.

The "greens," in both alcohol and chloroform, include Nos. 1, 15, 16, 22, 24, 27, 28 and 37 (See Table on p. 66), and these fluoresce with greater intensity in chloroform than in alcohol. There are no yellowish-greens in chloroform solution. No. 30 (1-phenyl-3-tert.-butyl-5-(3.4-dimethoxyphenyl)-pyrazoline), which shows a bright greenish-blue fluorescence in chloroform, exhibits a pure blue of medium intensity in alcohol.

The behaviour of the "greens" in alcohol, chloroform and benzene is shown in comparative tabular form on p. 66.

The pyrazolines which show no fluorescence in chloroform are identical with those which do not fluoresce in alcoholic solution, viz.: Nos. 3, 4, 5, 6, 7, 33, 34, 35, 36.

Table VI. (p. 62) shows the colour and fluorescence, if any, by daylight of the pyrazolines in benzene solution.

Table VII. (p. 63) shows the behaviour of the benzene solutions on ultraviolet irradiation.

TABLE VI.

Solvent: Benzene

	Colour of Solution	Fluorescence in Daylight
1.	pale straw	nil
2.	colourless	faint blue
3.	pale straw	nil
4.	pale straw	nil
5.	pale straw	nil
6.	straw	nil
7.	straw	nil
8.	colourless	faint blue
9.	colourless	nil
10.	pale straw	faint blue
11.	golden-yellow	nil
12.	golden-yellow	nil
13.	golden-yellow	brilliant yellow
14.	golden-brown	purple
15.	faint yellow	blue
16.	faint yellow	green
17.	colourless	nil
18.	colourless	nil
19.	colourless	faint purple
20.	colourless	faint purple
21.	colourless	nil
22.	colourless	greenish-blue
23.	colourless	purple
24.	pale yellow	pale green
25.	colourless	faint purple
26.	colourless	purple
27.	colourless	nil
28.	colourless	faint blue
29.	colourless	purple
30.	colourless	nil
31.	colourless	nil
32.	colourless	nil
33.	golden-yellow	nil
34.	light yellow	nil
35.	golden-yellow	nil
36.	pale straw	nil
37.	apple-green	green

TABLE VII.

FLUORESCENCE IN BENZENE SOLUTION IN ULTRAVIOLET RAYS

9,10,14	Deep "Royal" blue.
2,8,19,20,23,25,26,29	Intense "Electric" blue.
17	Sky-blue.
18,30	(Decreasing in intensity in direction
21	of arrow.)
31	
32	
16	Greenish-blue.
15,37	(Decreasing in intensity in direction
22,24,28	of arrow.)
1	
11	Very faint purplish-blue.
12	Dull, deep red.
13	Brilliant golden-yellow.
3,4,5,6,7,27,33,34,35,36	No fluorescence.

. . . . . .

DISCUSSION OF FLUORESCENCE IN BENZENE SOLUTION

Comparison of Table VI. (p. 62) with Table II. (p. 49) and with Table IV. (p. 58) shows that the colour and fluorescence by daylight of the pyrazolines, when dissolved in benzene, do not differ strikingly from the same properties in alcoholic or chloroform solution, except in the case of No. 13 (3-p-nitrophenyl-1.5-diphenyl-pyrazoline).

The remarkable behaviour of this compound has already been touched upon (p. 61). Its alcoholic and chloroform solutions, though coloured, exhibit no fluorescence by daylight. On ultraviolet irradiation, the alcoholic solution shows a very faint pale blue fluorescence, whilst the chloroform solution is unique in fluorescing a deep red.

The solution of No. 13 in benzene displays a vivid yellow fluorescence, even in daylight, and its brilliance is greatly enhanced on exposure to ultraviolet rays. Similar behaviour was observed in carbon disulphide solution, but the brilliance of fluorescence in benzene was scarcely equalled.

On account of this striking behaviour of the para isomer, the fluorescent characteristics of the three 3-nitrophenyl-1.5-diphenyl-pyrazolines are here expressed in tabular form:-

(Table at top of next page.)

Fluorescence of Isomeric 3-Nitrophenyl-1,5-diphenyl-pyrazolines in Different Solvents

	Alcohol	Chloroform	Benzene
o-	very faint pale blue	very faint dark blue	very faint purplish-blue
m-	very faint pale blue	very faint dark blue	dull purplish-red
p-	very faint pale blue	deep dull red	brilliant golden-yellow

With regard to the "blues" and "greens," no remarkable divergence is apparent in benzene, as compared with alcoholic or chloroform solution.

It is worthy of mention, however, that 3-methyl-1,5-diphenyl-pyrazoline (No. 27), which shows a bright green fluorescence in chloroform, and a very faint bluish-green fluorescence in alcohol, does not fluoresce at all in benzene.

Apart from this one exception, the members which show no fluorescence are the same for the three solvents, viz.:- Nos. 3, 4, 5, 6, 7, 33, 34, 35, and 36 (See Table on p. 68).

The behaviour of the "greens" in alcohol, chloroform and benzene is summarised on the Table on the next page. Examination reveals the following facts:-

Removal of phenyl from position 3 of the molecule of 1,3,5-triphenyl-pyrazoline not only very greatly diminishes the intensity of fluorescence, but changes the colour from pure blue to a bluish-

green (in 1.5-diphenyl-pyrazoline).

Replacement of the phenyl group in position 3 by thienyl, styryl or methyl (Nos. 15, 16 and 27) also imparts a green tinge to the fluorescence.

Hydroxyl or methoxyl in the ortho position in position 5 of the triphenyl-pyrazoline molecule (Nos. 22 and 24) is also productive of a green shade of fluorescence.

In Nos. 28, 30 and 37, the occurrence of hydroxyl or methoxyl in the molecule in position 5 is again associated with a green shade of fluorescence.

With regard to the influence of the solvent, alcohol favours production of yellowish-green shades (Nos. 16, 22 and 24), which change to pure green in chloroform, and to greenish-blue in benzene.

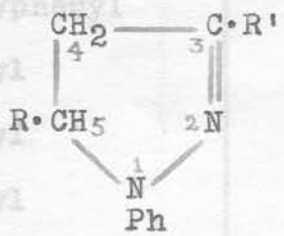
Yellowish-greens occur only in alcoholic solution, pure greens only in chloroform, and in benzene the colour is always decidedly more blue than green.

Green Fluorescence in Alcohol, Chloroform and Benzene

	III.	V.	Alcohol	Chloroform	Benzene
1.	---	phenyl	faint bluish-green	faint greenish-blue	faint greenish-blue
15.	thienyl	phenyl	bluish-green	bright green-blue	greenish-blue
16.	styryl	phenyl	bright yellowish-green	brilliant green	greenish-blue
22.	phenyl	o-hydroxyphenyl	yellowish-green	brilliant green	greenish-blue
24.	phenyl	o-methoxyphenyl	yellowish-green	brilliant green	greenish-blue
27.	methyl	phenyl	faint bluish-green	bright green-blue	nil
28.	methyl	o-hydroxyphenyl	bluish-green	brilliant green	greenish-blue
30.	tert.-butyl	3.4-dimethoxyphenyl	"Electric" blue	bright green-blue	sky-blue
37.	thienyl	o-methoxyphenyl	bluish-green	brilliant green	greenish-blue

SUMMARY

The preparation of a series of thirty-five pyrazolines and two anomalous compounds (the latter obtained from cinnamylideneacetophenone and cinnamylidenepinacoline, respectively), twenty-five of which are believed to be new, is described. These pyrazolines differ in regard to the chemical nature of the radicals R and R' in the general formula:



Most of these pyrazolines fluoresce in the solid state on exposure to ultraviolet rays. Many fluoresce in daylight when dissolved in organic solvents. Of those which exhibit no visible fluorescence in daylight, many fluoresce in ultraviolet rays; those which fluoresce in daylight do so with increased brilliance on ultraviolet irradiation.

The behaviour of the members of the series in alcoholic, chloroform and benzene solution, on exposure to ultraviolet rays, has been investigated.

With regard to the relationship of fluorescence to chemical constitution, the following generalisations apply to the group of compounds investigated:-

(1). The following nine members of

the series (indicated in the Table by the nature of the variable substituents R and R') do not fluoresce in alcoholic, chloroform or benzene solution:-

	R'	R
3.	o-hydroxyphenyl	phenyl
4.	m-hydroxyphenyl	phenyl
5.	p-hydroxyphenyl	phenyl
6.	o-methoxyphenyl	phenyl
7.	m-methoxyphenyl	phenyl
33.	phenyl	o-nitrophenyl
34.	phenyl	m-nitrophenyl
35.	phenyl	p-nitrophenyl
36.	tert.-butyl	p-nitrophenyl

(2). The following sixteen members of the series show a pure blue fluorescence (varying in tint and intensity, from member to member) in all three solvents:-

	R'	R
2.	phenyl	phenyl
8.	p-methoxyphenyl	phenyl
9.	s-trimethoxyphenyl	phenyl
10.	o-ethoxyphenyl	phenyl
14.	p-aminophenyl	phenyl
17.	tert.-butyl	phenyl
18.	tert.-butyl	p-tolyl
19.	phenyl	p-tolyl
20.	anomalous cpd. from cinnamylideneacetophenone	
21.	anomalous cpd. from cinnamylidenepinacoline	
23.	phenyl	p-hydroxyphenyl

(Continued on next page.)

25.	phenyl	m-methoxyphenyl
26.	phenyl	p-methoxyphenyl
29.	phenyl	3,4-dimethoxyphenyl
31.	tert.-butyl	methylene-3,4-dioxyphenyl
32.	tert.-butyl	p-methoxyphenyl

(3). The following seven members of the series show a green, yellowish-green or bluish-green fluorescence in all three solvents:-

	R'	R
1.	-----	phenyl
15.	thienyl	phenyl
16.	styryl	phenyl
22.	phenyl	o-hydroxyphenyl
24.	phenyl	o-methoxyphenyl
28.	methyl	o-hydroxyphenyl
37.	thienyl	o-methoxyphenyl

(4). When the place of R' (position 3) is occupied by o-, m- or p-hydroxyphenyl, fluorescence is completely inhibited. The same inhibitive action does not occur when the hydroxyphenyl group replaces R (position 5) in the general formula.

(5). When the place of R' (position 3) is occupied by o- or m-methoxyphenyl, flourescence is completely inhibited; but p-methoxyphenyl does not exert the same inhibitive influence.

(6). p-Hydroxyphenyl or p-methoxyphenyl, occupying the place of R (position 5) scarcely affects fluorescence; but the same substituents in

the ortho position change the colour of fluorescence from blue (triphenyl-pyrazoline) to yellowish-green in alcohol, green in chloroform and greenish-blue in benzene.

(7). o-, m- or p-Nitrophenyl, in place of R (position 5), completely inhibits fluorescence in all solvents. o- or m-Nitrophenyl, in place of R' (position 3), greatly diminishes the intensity of fluorescence.

(8). p-Nitrophenyl, in place of R' (position 3), also diminishes fluorescence in alcohol or chloroform, but produces a remarkably brilliant golden-yellow fluorescence in benzene solution.