

### Summary

The effect of ascorbic acid and dihydroxymaleic acid on the autoxidation of various organic developing agents is investigated. In two experiments, stannous ion and hydrazine are added to hydroquinone solutions.

A retardation is observed in most cases. This is explained on the assumption that the autoxidation of the developing agents is catalyzed by their quinonoid oxidation products, and that the added reducing agents eliminate these quinonoid products.

The quinones are assumed to catalyze the autoxidations by virtue of their reaction with the

developing agents in which highly reactive semi-quinones are formed. Most likely the latter are also reduced by the inhibitors.

In some cases, the reducing agents accelerate the autoxidation of the developing agents. The acceleration is caused by the formation of semi-quinones in the reduction of the quinones. This interpretation is supported by experiments in which  $\psi$ -cumoquinone accelerates the autoxidation of ascorbic acid to an extent which cannot be explained by a reduction of the  $\psi$ -cumoquinone to the  $\psi$ -cumohydroquinone and autoxidation of the latter.

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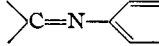
[COMMUNICATION No. 930 FROM THE EASTMAN KODAK LABORATORIES]

## Investigation of Pyrazole Compounds. IV.<sup>1</sup> The Acylation of 3-Phenyl-5-pyrazolone and 3-Anilino-5-pyrazolone

BY A. WEISSBERGER AND H. D. PORTER

The acyl derivatives of 1-phenyl-3-amino-5-pyrazolone were described in the first paper of this series<sup>2</sup> where the constitution of the parent compound was established. The present paper deals with the acylation of 3-phenyl-5-pyrazolone,<sup>3</sup> and 3-anilino-5-pyrazolone.<sup>1,4</sup> The determination of the positions of the acyl groups was again assisted by color tests, in which the substance under investigation is heated with *p*-nitrosodimethylaniline,<sup>1</sup> or oxidized in the presence of *p*-aminodimethylaniline.<sup>5</sup>

A modification of the latter test, which uses the silver halide of a photographic film as the oxidizing agent, was most helpful. Originated by Fischer and Siegrist,<sup>6</sup> it has become the basis for several successful color photographic processes,<sup>7</sup> and is frequently used in color photographic research. The compound is dissolved in carbonate, an unsymmetrically dialkylated developing agent of the *p*-phenylenediamine class, *e. g.*, *p*-aminodimethylaniline, is added, and a strip of exposed photographic film is immersed in the solution. The *p*-phenylenediamine derivative reduces the

silver halide of the emulsion and the compound under test, if it is of suitable constitution, couples with the oxidized developing agent to form a dye with a  $\text{>C=N-}$    $\text{-N(CH}_3)_2$  group.<sup>8</sup> The film is washed, silver and excess silver halide are removed with a photographic reducer and thio-sulfate, and a clear film is obtained. If a dye is formed, it gives information by its existence, color<sup>6</sup> and location, on the nature of the parent compound. The dye may be deposited throughout the emulsion layer of the film, at the emulsion surface only, or it may be found in the developer solution. If the molecular weight of the dye is low and the solubility in the alkaline developer high, the dye formed in the emulsion layer may bleed entirely or in part into the developing solution. On the other hand, coupling compounds which, because of their low rate of diffusion, do not penetrate into the gelatin, react only with that oxidized developing agent which diffuses out of the emulsion. These compounds form dyes on the surface of the film or as a precipitate in the liquid. In carrying out the film-strip test, a blank should be made to distinguish the dye formed as described above from colored oxidation and condensation products formed by the developing agent in the absence of couplers.

(1) Investigation of Pyrazole Compounds, III, *THIS JOURNAL*, **65**, 732 (1943).

(2) Weissberger and Porter, *ibid.*, **64**, 2133 (1942).

(3) Curtius, *J. prakt. Chem.*, **50**, 515 (1894).

(4) Worrall, *THIS JOURNAL*, **44**, 1551 (1922).

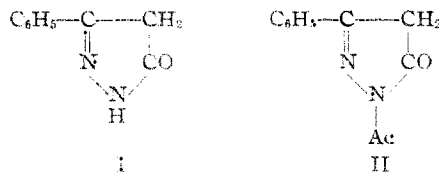
(5) Weissberger and Porter, *ibid.*, **65**, 52 (1943).

(6) Fischer and Siegrist, *Phot. Korr.*, **51**, 19 (1914).

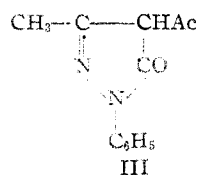
(7) Davies, *Phot. J.*, **76**, 248 (1936); Forrest and Wing, *J. Soc. Mot. Pict. Eng.*, **29**, 248 (1937); Mees, *J. Frankl. Inst.*, **233**, 50 (1942).

(8) Mees, "The Theory of the Photographic Process," The Macmillan Co., New York, N. Y., 1942, p. 393.

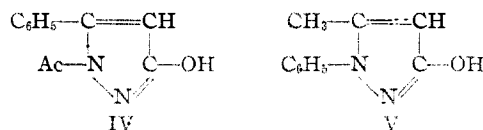
3-Phenyl-5-pyrazolone, I, on heating on the steam-bath with acetic anhydride forms, according to the literature,<sup>3,9</sup> 1-acetyl-3-phenyl-5-pyrazolone, II, melting at 121°. We found that II



melts at 127–128°, and that the lower m. p. reported in the literature is caused by the presence of up to 20% of another monoacetyl compound melting at 150°. Structure II is confirmed for the compound melting at 127°. This is soluble in carbonate, excluding O-acetylation, and is hydrolyzed to I by caustic alkali. Inasmuch as 1-phenyl-3-methyl-4-acetyl-5-pyrazolone, III, is



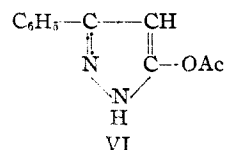
stable to caustic alkali,<sup>10</sup> the hydrolysis excludes C-acetylation in position 4. With these properties, the compound melting at 127° might still be 1-acetyl-3-hydroxy-5-phenyl-pyrazole, IV, the carbonate solubility being analogous to that of 1-phenyl-3-hydroxy-5-methyl-pyrazole, V.<sup>11</sup> However, the compound melting at 127°



readily forms a magenta dye, not only with *p*-aminodimethylaniline in the film-strip test, but also with *p*-nitrosodimethylaniline. With a compound of structure IV, the dye formation would involve a deacetylation, and this is unlikely to occur in the condensation with *p*-nitrosodimethylaniline.

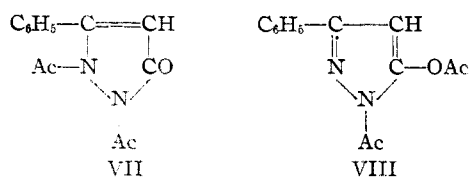
The monoacetyl compound melting at 150° is best prepared by acetylation of I in pyridine. It is insoluble in carbonate and readily hydrolyzes to I with caustic alkali. It is, therefore, 3-phenyl-5-acetoxypyrazole, VI. In agreement with this structure and with the general behavior of O-acetyl as compared with N-acetyl deriva-

tives, VI is more readily hydrolyzed by alkali than II.



When II is heated in pyridine, it rearranges completely to form VI. In this reaction, an acetyl group wanders from nitrogen to oxygen, a migration which has been observed in a few cases<sup>12</sup> only. The rearrangement explains why VI rather than II is formed when I is acetylated in pyridine. The reverse rearrangement, of VI to II, was not observed in pyridine. However, on heating in acetic acid, not only VI is formed from II, but the reverse migration also takes place. Since the acetyl group is present in the solvent, the reaction in acetic acid is probably not a migration in the strict sense but rather an exchange reaction with the solvent which proceeds with isomerization.

Acetylation of II or of VI gives the diacetyl derivative of m. p. 84° which was obtained by von Rothenburg on acetylation of I and was formulated as 1,2-diacetyl-3-phenyl-5-pyrazolone,<sup>9</sup> VII. In view of the formation from II and VI, the diacetyl compound is more likely to be 1-acetyl-3-phenyl-5-acetoxypyrazolone, VIII. This struc-



ture is confirmed by the deacetylation of von Rothenburg's compound to II and to VI, with alcoholic piperidine and with water-containing acetic acid, respectively. Formula VII could only be maintained if during the acetylation and the deacetylation there occurred reversible migrations of acetyl, consistent with the yields obtained. This is not the case, particularly in view of the fact that no rearrangement of VI was found in pyridine.

Besides VIII, a new diacetyl derivative melting at 75° can be isolated in small yield when I is boiled with acetic anhydride. By the same treatment, VIII itself is rearranged to the new compound. Like VIII, this is insoluble in carbonate.

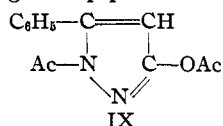
(9) von Rothenburg, *J. prakt. Chem.*, **52**, 31 (1895).

(10) Stoltz, *ibid.*, **55**, 145 (1897).

(11) Mayer, *Ber.*, **36**, 717 (1903).

(12) C. W. Porter, "Molecular Rearrangements," The Chemical Catalog Company, Inc., New York, N. Y., 1928.

Acetylation on carbon is excluded by the hydrolysis to I, leaving as possible formulas, VII and that of a 1-acetyl-3-acetoxy-5-phenylpyrazole, IX. On heating with piperidine, the new diacetyl

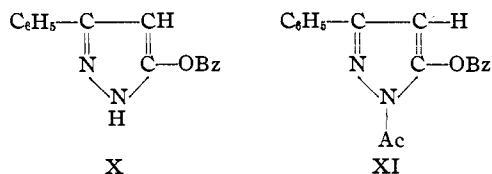


compound yields a new monoacetyl derivative melting at  $144^\circ$ . The latter is soluble in carbonate, hydrolyzed to I in alkali, and forms a dye neither with *p*-nitrosodimethylaniline nor in the film-strip test. Thus, it has the properties which, as discussed above, are to be expected of IV; this structure is therefore assigned to the monoacetyl derivative melting at  $144^\circ$ . No migration of acetyl from nitrogen to oxygen—similar to the change of II to VI—was observed with IV in pyridine. However, from a solution of IV in acetic acid, VI could be isolated after heating. It is probably formed by an exchange reaction with the solvent. The formation of IV by partial deacetylation of the compound melting at  $75^\circ$  agrees as well with formula VII as with formula IX.

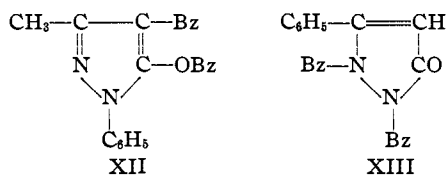
With water-containing acetic acid, *i. e.*, the conditions under which VIII is deacetylated to VI, the diacetyl derivative melting at  $75^\circ$  also yields VI. Provided that no migration of acetyl occurs in this deacetylation, the diacetyl compound is IX. Then, in the formation of IX from VIII, an acetyl group would wander from nitrogen 1 to nitrogen 2. This type of migration was studied by von Auwers and Dietrich,<sup>13</sup> and, in agreement with the results of these authors, the acetyl group would wander to that nitrogen atom which, in view of the groups attached to it, is the more basic one. With structure VII for the diacetyl derivative melting at  $75^\circ$ , the formation of this compound from VIII would involve the migration of acetyl from oxygen to nitrogen in position 2, and the deacetylation to VI would imply the reverse migration. Although the possibility of the latter migration is demonstrated by the formation of VI from IV, one is inclined to prefer formula IX over VII on account of the less complex relation to VI. This preference is enhanced by evidence to be presented in discussing the acetylation of 3-anilino-5-pyrazolone. We therefore assume for the diacetyl compound melting at  $75^\circ$  formula IX, although VII cannot be dismissed entirely.

(13) von Auwers and Dietrich, *J. prakt. Chem.*, **139**, 65 (1934).

The benzylation of I, with one mole of benzoyl chloride in pyridine, gives a monobenzoyl derivative, which is insoluble in aqueous alkali and regenerates the parent compound with alcoholic piperidine. It is, therefore, 3-phenyl-5-benzoyloxy-pyrazole, X. When this is acetylated, the product formed can be debenzoylated with piperidine to II, and is therefore 1-acetyl-3-phenyl-5-benzoyloxy-pyrazole, XI.



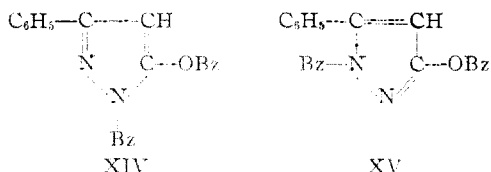
In order to benzoylate X further, it was treated with benzoyl chloride in pyridine or in toluene. In both cases, a dibenzoyl derivative of m. p.  $117^\circ$  was obtained. When toluene was used, this was accompanied by a dibenzoyl derivative of m. p.  $181^\circ$ . Both compounds are insoluble in aqueous alkali, but regenerate I with alcoholic sodium hydroxide. Since 1-phenyl-3-methyl-4-benzoyl-5-benzoyloxy-pyrazole, XII, on treatment with caustic alkali loses only that benzoyl group which is attached to oxygen,<sup>14</sup> the regeneration of I excludes attachment of a benzoyl group to carbon. Attempts to obtain information on the structure of the dibenzoyl derivatives by partial debenzoylation with piperidine failed. With the lower melting compound, only I was isolated besides the starting material. The pure materials recovered accounted for only a small part of the reactant. The higher-melting compound, after the same treatment, was recovered almost quantitatively.



With hydrogen chloride in dioxane, both compounds are debenzoylated to X, and therefore neither is likely to be 1,2-dibenzoyl-3-phenyl-5-pyrazolone, XIII, a structure which would be analogous to von Rothenburg's formula for his diacetyl compound. Formula XIII would be possible only if, with hydrogen chloride in dioxane, a benzoyl group wandered from nitrogen to oxygen and the reverse migration occurred in

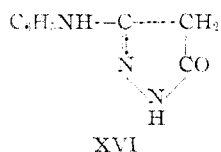
(14) Michaelis and Engelhardt, *Ber.*, **41**, 2668 (1908).

the benzoylation of X. By the process of elimination, therefore, one of the dibenzoyl derivatives must be 1-benzoyl-3-phenyl-5-benzoyloxy-pyrazolone, XIV, and the other 1-benzoyl-3-benzoyloxy-5-phenylpyrazole XV. Inasmuch as

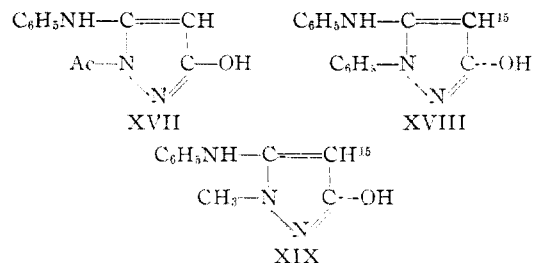


the lower-melting compound is obtained under conditions similar to those yielding VIII, while the higher-melting one is formed under conditions similar to those yielding IX, *i. e.*, in an acid medium, and XIV and XV correspond to VIII and IX, respectively, we assign to the dibenzoyl derivative melting at 117° formula XIV, and to that melting at 184° formula XV.

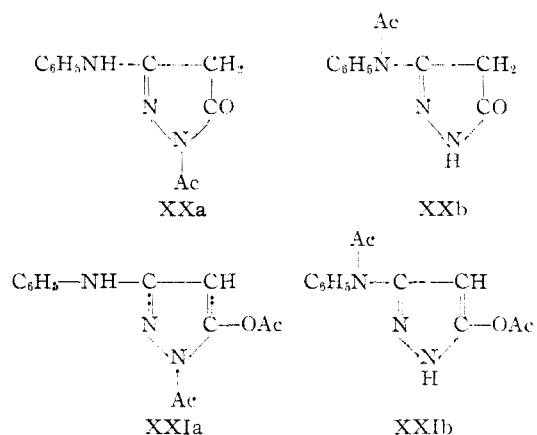
3-Anilino-5-pyrazolone XVI,<sup>14</sup> heated on the steam-bath for five minutes with excess acetic anhydride or with one equivalent of the anhydride in pyridine, gives a monoacetyl derivative of m. p. 207° dec., which is soluble in carbonate, excluding O-acetylation in position 5, and is hydrolyzed to XVI by caustic alkali, excluding



C-acetylation in position 4. It turns the green solution of *p*-nitrosodimethylaniline to deep red, indicating the formation of a magenta dye. The latter is also formed in the film-strip test. When the dye was prepared in a pure state, it was found to contain the acetyl group. This confirms the assumption that the latter is not attached in position 4 or to the oxygen in position 5. The acetyl group must therefore be attached to one of the three nitrogen atoms. By analogy with IV, 1-acetyl-3-hydroxy-5-anilino-pyrazole, XVII, would be soluble in carbonate and hydrolyzed to XVI by alkali. However, it would not react with *p*-nitrosodimethylaniline or form a pure magenta dye when oxidized in the presence of *p*-aminodimethylaniline, because the corresponding phenyl derivative XVIII<sup>9</sup> and methyl derivative XIX,<sup>1</sup> do not react with *p*-nitrosodimethylaniline, and give only a weak bluish magenta<sup>1</sup> in the film-strip test. This leaves for the monoacetyl derivative the structure of 1-



acetyl-3-anilino-5-pyrazolone, XXa, or 3-N-acetylanilino-5-pyrazolone, XXb.

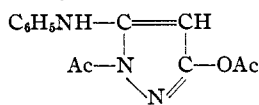


If the heating of XVI with excess acetic anhydride on the steam-bath is continued for one-half hour, a diacetyl derivative of m. p. 131° is obtained. This is also formed by acetylation of the acetyl derivative melting at 207°, XXa or b. With one mole of piperidine, or with water-containing acetic acid, the monoacetyl derivative melting at 207° is regenerated from the new compound. The diacetyl derivative (m. p. 131°) is insoluble in carbonate, showing that one acetyl group is attached to oxygen in position 5. Hence, it is either 1-acetyl-3-anilino-5-acetoxypyrazole, XXIa, or 3-N-acetylanilino-5-acetoxypyrazole, XXIb.

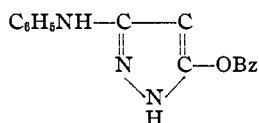
Besides this compound, there is formed a small amount of a substance melting at 107° which is obtained in a better yield by boiling XVI in acetic anhydride. The compound melting at 107°, according to analysis and because of its insolubility in carbonate and hydrolysis to XVI, is, like the compound melting at 131°, a diacetyl derivative of XVI with one acetyl group attached to oxygen and none attached to carbon. In contrast to the compound melting at 131°, it yields, on partial deacetylation with piperidine,

(15) In a preceding paper<sup>9</sup> this compound was formulated as a pyrazolone anil. The tautomeric formula of an anilino-pyrazole is preferred in the present paper for reasons of comprehensibility.

a monoacetyl derivative melting at 203°, which does not form a dye with *p*-nitrosodimethylaniline or in the film-strip test. It was mentioned earlier that a monoacetyl derivative of structure XVII should be soluble in carbonate, hydrolyzed by alkali to XVI, and unable to form a dye of pure magenta color in our tests. The monoacetyl derivative melting at 203° has these properties, dye formation being completely absent with *p*-nitrosodimethylaniline and in the film-strip test. It is, therefore, assigned the structure XVII. The inability to form a dye is reminiscent of the same behavior of IV. From a comparison of IV and XVII, it may be suggested that for XVII this lack indicates the prevalence of the anilino structure over the formally possible anil form, since a dye would be derived from the latter. Since the diacetyl compound (m. p. 107°) is obviously the O-acetyl derivative of the compound XVII, melting at 203°, it is 1-acetyl-3-acetoxy-5-anilino-pyrazole XXII.



XXII



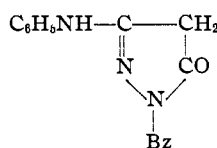
XXIII

The nature of the reactions leading to XXII is revealed by the fact that this compound is also obtained by boiling the diacetyl compound, XXIa or b, melting at 131°, in acetic acid. The formulas show that this preparation involves the migration of an acetyl group to nitrogen 2. The analogy with the rearrangements of acylpyrazoles<sup>13</sup> is obvious if the diacetyl derivative melting at 131° is XXIa. It would not hold if it had the structure XXIb. The former structure is, therefore, the more probable. Moreover, no rearrangement was observed when the monoacetyl compound, XXa or b, melting at 207°, was boiled in acetic acid. The difference in the behavior of the monoacetyl compound and the corresponding diacetyl compound would be difficult to explain with the formulas XXb and XXIb. With formulas XXa and XXIa, the difference is readily understood because XXIa has the structure of a pyrazole, while XXa is a pyrazolone. Hence, we assign to the monoacetyl compound melting at 207° structure XXa, and to the diacetyl compound melting at 131° structure XXIa.

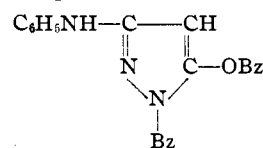
Formula XXII is analogous to formula IX, and the preparation of XXII is similar to that of the diacetyl derivative of I melting at 75°. These

analogies support formula IX for the latter compound in preference to VII. A formula analogous to VII is excluded with the derivative of XVI, because such a formula would represent an alkali-soluble product.

Heated with benzoic anhydride in pyridine, XVI forms a monobenzoyl derivative, which, with piperidine in alcohol, is debenzoylated to the parent compound. Because of its insolubility in aqueous alkali, it is assigned the structure of 3-anilino-5-benzoyloxy-pyrazole, XXIII. The same compound is obtained, in better yield, with two moles of benzoyl chloride and one mole of water in pyridine at room temperature, probably through the formation of benzoic anhydride.<sup>16</sup> If the reaction mixture is heated in the absence of water and the latter added subsequently with some additional heating, another monobenzoyl derivative is obtained. This is soluble in alkali and easily forms a magenta dye with *p*-nitrosodimethylaniline and in the film-strip test. It closely resembles, in these properties, the monoacetyl derivative XXa and is therefore considered to be 1-benzoyl-3-anilino-5-pyrazolone, XXIV. When XVI is heated with benzoyl chloride in dioxane, a dibenzoyl derivative results which is insoluble in carbonate. It is considered to be 1-benzoyl-3-anilino-5-benzoyloxy-pyrazole, XXV. Presumably this is also formed as an intermediate in the above preparation of XXIV.



XXIV



XXV

### Experimental

**1-Acetyl-3-phenyl-5-pyrazolone, II.**—(1)<sup>8</sup> A mixture of 2.5 g. of 3-phenyl-5-pyrazolone, I,<sup>3</sup> and 5 ml. of acetic anhydride was heated on the steam-bath for two minutes with stirring, cooled, and filtered. The residue was rinsed with cold 50% ethanol and recrystallized from methanol (15 ml.), 2 g. (66%) of fine white flakes; m. p. 127–128°.

*Anal.* Calcd. for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>: N, 13.85. Found: N, 13.90.

(2)<sup>9</sup> A mixture of 1 g. of 3-phenyl-5-pyrazolone, I,<sup>3</sup> 0.6 ml. of acetic anhydride, and 4 ml. of acetic acid was heated on the steam-bath for two minutes. The product which crystallized out was recrystallized from methanol, 0.75 g. (62%) of II. From the acetic acid filtrate was obtained by dilution with 1 ml. of water and recrystallization, 0.2 g. (17%) of VI.<sup>17</sup>

(16) Ipatieff and Friedman, *THIS JOURNAL*, **61**, 686 (1939).

(17) Identified by m. p. and mixed m. p.

II<sup>17</sup> was also obtained, in 67 and 25% yield, respectively, by adding one equivalent of piperidine to a boiling absolute ethanol (4 ml./g.) solution of 1-acetyl-3-phenyl-5-acetoxypyrazole, VIII, or of 1-acetyl-3-phenyl-5-benzoyloxy-pyrazole, XI, refluxing for fifteen minutes and cooling.

On standing in 2% sodium hydroxide solution at room temperature for one hour, II was hydrolyzed to 3-phenyl-5-pyrazolone, I.<sup>17</sup>

**1-Acetyl-3-hydroxy-5-phenylpyrazole, IV**, was prepared from 1-acetyl-3-acetoxy-5-phenylpyrazole, IX, (0.75 g.) following the procedure for the preparation of II from VIII. The crude product (75%) was twice recrystallized slowly from benzene, 0.15 g. (25%) of fine white needles; m. p. 144-146°.

*Anal.* Calcd. for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>: N, 13.85. Found: N, 13.77.

IV was unchanged by heating for half an hour in pyridine on the steam-bath.

**3-Phenyl-5-acetoxypyrazole, VI**.—To a suspension of 4 g. of 3-phenyl-5-pyrazolone, I,<sup>3</sup> in 10 ml. of pyridine on the steam-bath was added 2.5 g. of acetic anhydride, dropwise with stirring. The solution was heated fifteen minutes longer, cooled, and diluted with water (10 ml.) until just cloudy. Crystallization was induced by scratching, the mixture cooled, and filtered to yield 2.2 g. (44%) of white granules; m. p. 150-152°, unchanged after recrystallization from methanol.

*Anal.* Calcd. for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>: N, 13.85. Found: N, 13.84.

When 2 g. of acetyl chloride was used in place of the acetic anhydride and the reaction run at room temperature, VI<sup>17</sup> (40%) was also obtained.

On shaking with 2% sodium hydroxide, VI dissolved in about ten minutes to give, on acidification, 3-phenyl-5-pyrazolone, I.<sup>17</sup>

VI<sup>17</sup> was formed by partial hydrolysis of 1-acetyl-3-phenyl-5-acetoxypyrazole, VIII, and of 1-acetyl-3-acetoxy-5-phenylpyrazole, IX. When the solutions of these compounds in 66% acetic acid (6 ml./g.) were refluxed for ten minutes, VI crystallized after cooling in 25% yield. It was formed by a rearrangement of 1-acetyl-3-phenyl-5-pyrazolone, II, subjected to the conditions just stated. From the reaction separated crystals (30% of the weight of II) which consisted of about equal parts of VI<sup>17</sup> and of 3-phenyl-5-pyrazolone, I,<sup>17</sup> the former being extracted with benzene. When VI<sup>17</sup> itself was subjected to these conditions, 25% of it was recovered. VI<sup>17</sup> was also formed (isolated in 10% yield) by a rearrangement of II and of 1-acetyl-3-hydroxy-5-phenylpyrazole, IV, on heating in glacial acetic acid (3 ml./g.) for half an hour. When VI itself was subjected to this treatment, II<sup>17</sup> was isolated in 10% yield.

By a rearrangement, VI<sup>17</sup> was also obtained on heating II in pyridine on the steam-bath for half an hour. However, no change in the m. p. of VI<sup>17</sup> was effected by the same treatment.

**1-Acetyl-3-phenyl-5-acetoxypyrazole, VIII**, was prepared, by heating with excess acetic anhydride (2 ml./g.) on the steam-bath for half an hour, from 3-phenyl-5-pyrazolone, I,<sup>3</sup> (yield 60%),<sup>9</sup> from 1-acetyl-3-phenyl-5-pyrazolone, II, (yield 50%) and from 3-phenyl-5-acetoxypyrazole, VI (yield 60%). VIII<sup>17</sup> was further obtained (45%) when

0.6 g. of acetyl chloride was added to a cold solution of 1 g. of VI, in 5 ml. of pyridine; the mixture was stirred at room temperature for twenty-four hours, decomposed in ice-water and the residue recrystallized from methanol.

On stirring at room temperature with 2% sodium hydroxide, VIII dissolved within one-half hour. The solution gave on acidification 3-phenyl-5-pyrazolone, I.<sup>17</sup>

**1-Acetyl-3-acetoxy-5-phenyl-5-pyrazole, IX**.—(1) A solution of 25 g. of 3-phenyl-5-pyrazolone, I,<sup>3</sup> in 50 ml. of acetic anhydride was refluxed for six hours, cooled and 20 g. of ice added. The crystalline mass formed on scratching was filtered, rinsed with 20 ml. of 50% ethanol, and recrystallized from methanol, warming only to 45° and letting cool to room temperature undisturbed, to give 11.5 g. (31.5%) of VIII.<sup>17</sup> The filtrate, on cooling, gave 12 g. of mixed crystals (m. p. 55-62°) which were recrystallized from 120 ml. of "heptane" (Eastman Kodak Co.), cooling slowly in a hot cupboard at 40° to give IX. With small additional amounts obtained by the same procedure from the various filtrates, the total yield was 5.3 g. (14.5%) of long, colorless prisms; m. p. 75-76°. Rapid recrystallization from "heptane" gave white needles; m. p. 75-76°.

*Anal.* Calcd. for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>: N, 11.48. Found: N, 11.32.

(2) A solution of 7 g. of 1-acetyl-3-phenyl-5-acetoxypyrazole, VIII, in a mixture of 9.6 ml. of acetic anhydride and 0.4 ml. of acetic acid was refluxed for three hours. Worked up as in procedure (1), 2.1 g. (30%) of unchanged VIII<sup>17</sup> and 0.9 g. (13%) of IX resulted.<sup>17</sup>

When IX was shaken with 2% sodium hydroxide in 30% ethanol for ten minutes, the solution, after filtering from the undissolved material, gave on acidification and concentration 3-phenyl-5-pyrazolone, I.<sup>17</sup>

**3-Phenyl-5-benzoyloxy-pyrazole, X**.—To a solution of 10 g. of 3-phenyl-5-pyrazolone, I,<sup>3</sup> in 50 ml. of pyridine heated on the steam-bath was added 8.9 g. of benzoyl chloride, dropwise with stirring. After five minutes the solution was cooled to room temperature and diluted with water (30 ml.) until just cloudy. Crystallization was induced by scratching, the mixture cooled under the tap, filtered, and rinsed with 95% ethanol, 11 g. (67%), m. p. 169-171°; recrystallized from 95% ethanol, feathery, white crystals; m. p. 170-171°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: N, 10.6. Found: N, 10.5.

X<sup>17</sup> (16%) was also obtained when dry hydrogen chloride was bubbled for three hours through a hot dioxane solution of 1-benzoyl-3-phenyl-5-benzoyloxy-pyrazole, XIV, or of 1-benzoyl-3-benzoyloxy-5-phenylpyrazole, XV. The solutions, after cooling, were filtered, and the product triturated with 95% ethanol.

X was debenzoylated to I<sup>17</sup> under the conditions for the formation of II from XI.

**1-Acetyl-3-phenyl-5-benzoyloxy-pyrazole, XI**.—A mixture of 1 g. of 3-phenyl-5-benzoyloxy-pyrazole, X, and 4 ml. of acetic anhydride was heated on the steam-bath for one hour, cooled and filtered, 0.7 g. (57%), m. p. 108-109°; recrystallized from methanol, fine white needles; m. p. 108-109°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>: C, 70.5; H, 4.57. Found: N, 70.53; H, 4.63.

XI<sup>17</sup> was also obtained (50%) by acetylation of X with acetyl chloride in pyridine solution.

**1-Benzoyl-3-phenyl-5-benzoyloxy-pyrazole, XIV.**—To a solution of 2.6 g. of 3-phenyl-5-benzoyloxy-pyrazole, X, in 5 ml. of pyridine heated on the steam-bath, was added 2.1 g. of benzoyl chloride, dropwise with stirring. Heating was continued for half an hour, the mixture cooled, decomposed with ice-water, filtered, and the product recrystallized from 65 ml. of 95% ethanol, 2.1 g. (58%) of short, white needles; m. p. 117–118°.

*Anal.* Calcd. for C<sub>23</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>: N, 7.6. Found: N, 7.58.

When XIV was shaken with 2% sodium hydroxide in 50% ethanol for one hour, the solution, after filtering from the undissolved material, deposited on acidification and concentration 3-phenyl-5-pyrazolone, I.<sup>17</sup> After debenzoylation with piperidine under the conditions for the formation of II from XI, only a small amount of 3-phenyl-5-pyrazolone, I,<sup>17</sup> and a small amount of unchanged XIV<sup>17</sup> were obtained in pure form.

**1-Benzoyl-3-benzoyloxy-5-phenylpyrazole, XV.**—To a solution of 2.6 g. of 3-phenyl-5-benzoyloxy-pyrazole, X, in 25 ml. of boiling toluene was added 1.4 g. of benzoyl chloride, the mixture refluxed for three hours, cooled, filtered and the product recrystallized from absolute ethanol, 0.8 g. (22%) of short white needles; m. p. 181–182°.

*Anal.* Calcd. for C<sub>23</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>: C, 74.9; H, 4.35; N, 7.6. Found: C, 74.84; H, 4.20; N, 7.41.

The filtrate of the reaction mixture on diluting with four volumes of petroleum ether gave 2 g. (54%) of crude 1-benzoyl-3-phenyl-5-benzoyloxy-pyrazole, XIV.<sup>17</sup>

With 2% sodium hydroxide (see XIV), XV was hydrolyzed overnight to 3-phenyl-5-pyrazolone, I.<sup>17</sup> Attempted debenzoylation with piperidine under the conditions for the formation of II from XI gave an almost quantitative recovery of XV.<sup>17</sup> After heating the reaction mixture overnight, 15% of XV<sup>17</sup> was recovered, but no other pure product could be obtained.

**1-Acetyl-3-hydroxy-5-anilinopyrazole, XVII,** was prepared from 1-acetyl-3-acetoxy-5-anilinopyrazole, XXII, (0.3 g.) following the procedure for the preparation of II from VIII. Recrystallized from absolute ethanol, 0.1 g. (40%); fine white granules; m. p. 203–205° dec.

*Anal.* Calcd. for C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub>: N, 19.3. Found: N, 18.99.

With 2% sodium hydroxide (see II), XVII was hydrolyzed to 3-anilino-5-pyrazolone, XVI.<sup>17</sup>

**1-Acetyl-3-anilino-5-pyrazolone, XXa.**—A mixture of 1 g. of 3-anilino-5-pyrazolone, XVI,<sup>1,4</sup> and 10 ml. of acetic anhydride was stirred and heated on the steam-bath for six minutes, cooled, filtered, and the product recrystallized from acetic acid, 0.8 g. (65%) of white crystalline powder; m. p. 207–209° dec.

*Anal.* Calcd. for C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub>: N, 19.3. Found: N, 19.14.

No O-acetyl product could be isolated when XVI was subjected to the conditions for the preparation of VI from I, using, for solubility reasons, three times the amount of pyridine. Instead, XXa<sup>17</sup> (50%) was obtained.

XXa<sup>17</sup> was also obtained (81%) from 1-acetyl-3-anilino-5-acetoxy-pyrazole, XXIa, following the procedure for the

preparation of II from VIII, or (15%) by boiling in glacial acetic acid for two hours.

With 2% sodium hydroxide (see II), XXIa was hydrolyzed to 3-anilino-5-pyrazolone, XVI.<sup>17</sup> It was unaffected by boiling in glacial acetic acid for two hours.

**1-Acetyl-3-anilino-5-acetoxy-pyrazole, XXIa,** was prepared like XXa, but the reaction mixture was heated for half an hour. A first crop separated on cooling of the reaction mixture. The filtrate from this was decomposed with ice water, filtered and the solid material washed with boiling ligroin to leave a second crop, recrystallized from 95% ethanol, 65% of short, white needles; m. p. 131–132°.

*Anal.* Calcd. for C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>O<sub>3</sub>: N, 16.2. Found: N, 16.05.

From XXIa under the above conditions XXIa<sup>17</sup> was obtained in a 70% yield.

**1-Acetyl-3-acetoxy-5-anilinopyrazole, XXII,** was prepared according to the procedure given for the preparation of XXIa, but the reaction mixture was refluxed for two hours. It was then cooled, decomposed with ice water, and the product recrystallized from ligroin, 35% of white, granular crystals; m. p. 108–109°.

*Anal.* Calcd. for C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>O<sub>3</sub>: N, 16.2. Found: N, 16.26.

XXII was also obtained (6%) by concentration of the ligroin washings from the preparation of XXIa, and (10%) by refluxing XXIa in glacial acetic acid for two hours. Only unchanged XXIa was recovered after refluxing in dry xylene for two hours. Under the conditions of the hydrolysis of IX, XXII was hydrolyzed to 3-anilino-5-pyrazolone, XVI.<sup>17</sup>

**3-Anilino-5-benzoyloxy-pyrazole, XXIII.**—(1) To a suspension of 5 g. of 3-anilino-5-pyrazolone, XVI,<sup>1,4</sup> in 50 ml. of pyridine and 0.5 ml. of water was added dropwise with stirring 8 g. of benzoyl chloride, at a temperature just below 45°. After standing at room temperature for half an hour, 100 ml. of water was added, the precipitated oil brought to crystallization, filtered, and digested with 30 ml. of benzene, 6 g. (75%); m. p. 146–148°. Recrystallized from 95% ethanol, white flakes; m. p. 148–150°. The melt partially re-set above the m. p.

*Anal.* Calcd. for C<sub>16</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>: N, 15.0. Found: N, 15.09.

XXIII<sup>17</sup> was also obtained (25%) by heating XVI with one equivalent of benzoic anhydride in pyridine solution, besides 28% of 1-benzoyl-3-anilino-5-benzoyloxy-pyrazole, XXV,<sup>17</sup> from which it was separated by extraction with benzene.

Under the conditions for the formation of II from XI, or for the hydrolysis of XIV to I, XXIII was debenzoylated to 3-anilino-5-pyrazolone, XVI.<sup>17</sup>

**1-Benzoyl-3-anilino-5-pyrazolone, XXIV.**—A mixture of 7.8 g. of 3-anilino-5-pyrazolone, XVI, 60 ml. of pyridine, and 12.4 g. of benzoyl chloride was heated on the steam-bath for fifteen minutes, then 0.8 ml. of water was added, and heating continued for fifteen minutes. The solution, cooled to room temperature, was diluted with water (40 ml.) until just cloudy, cooled under the tap and filtered, 7.6 g. (65%) of yellowish needles; m. p. 193–196° dec. Recrystallized from 70 ml. of acetic acid, 3 g. of fine ivory needles; m. p. 198–200° dec.; loss probably caused by debenzoylation.

*Anal.* Calcd. for  $C_{16}H_{12}N_2O_2$ : N, 15.0. Found: N, 14.85.

XXIV was comparatively stable to 2% sodium hydroxide. Under the conditions described for the hydrolysis of XXa, the m. p. was only lowered to 190–195° dec.

**1-Benzoyl-3-anilino-5-benzoyloxy pyrazole, XXV.**—A mixture of 5 g. of 3-anilino-5-pyrazolone, XVI,<sup>1,4</sup> and 4 g. of benzoyl chloride in 50 ml. of dioxane was stirred on the steam-bath overnight. After cooling, the solution was decanted from an oil, diluted with water (5 ml.) until cloudy, cooled, filtered, and the product recrystallized from 15 ml. of dioxane. 1 g. (13%) of short ivory needles; m. p. 132–134°.

*Anal.* Calcd. for  $C_{23}H_{17}N_3O_3$ : N, 10.97. Found: N, 10.94.

The oil formed in the reaction mixture, on trituration first with water and then methanol, gave 0.5 g. of unchanged 3-anilino-5-pyrazolone XVI.<sup>17</sup>

**Film-strip Test.**—A sample (about 0.005 g.) of the compound to be tested and an approximately equal weight of *p*-aminodimethylaniline hydrochloride are dissolved in 5 ml. of 3% sodium carbonate in a test-tube. A strip of exposed photographic film (*e. g.*, Kodalith) is immersed in the solution and the test-tube shaken occasionally until, within one to five minutes, a high density of silver is developed. The strip is then rinsed with running water for about one minute, and silver and silver halide are removed by shaking the strip in a mixture (5 ml. total) of equal parts of solutions 1 and 2, until the film is translucent. It is then washed in running water and inspected.

Solution 1: 25 g. of potassium ferricyanide, 5 g. of potassium bromide, 5 g. of sodium carbonate, water to make 1 liter. Solution 2: 200 g. of sodium thiosulfate, 5 g. of sodium carbonate, water to make 1 liter.

### Summary

The acetylation and benzylation of 3-phenyl-5-pyrazolone, I, and of 3-anilino-5-pyrazolone, XVI, were studied.

3-Phenyl-5-acetoxypyrazole, VI, 1-acetyl-3-acetoxy-5-phenylpyrazole, IX, 1-acetyl-3-hydroxy-5-phenylpyrazole, IV, 3-phenyl-5-benzoyloxy-pyrazole, X, 1-acetyl-3-phenyl-5-benzoyloxy-pyrazole, XI, 1-benzoyl-3-phenyl-5-benzoyloxy-pyrazole, XIV, 1-benzoyl-3-benzoyloxy-5-phenyl-pyrazole, XV, 1-acetyl-3-hydroxy-5-anilinopyrazole, XVII, 1-acetyl-3-anilino-5-pyrazolone, XXa, 1-acetyl-3-anilino-5-acetoxypyrazole, XXIIa, 1-acetyl-3-acetoxy-5-anilinopyrazole, XXII, 3-anilino-5-benzoyloxy-pyrazole, XX, 1-benzoyl-3-anilino-5-pyrazolone, XXIV, and 1-benzoyl-3-anilino-5-benzoyloxy-pyrazole, XXV, were prepared as new compounds and their structures established.

Pure 1-acetyl-3-phenyl-5-pyrazolone, II, melts at 127°. The compound reported in the literature as melting at 121° is contaminated with VI. The diacetyl derivative of 3-phenyl-5-pyrazolone melting at 84° is not 1,2-diacetyl-3-phenyl-5-pyrazolone, VII, but 1-acetyl-3-phenyl-5-acetoxypyrazole, VIII.

A migration of acetyl from nitrogen to oxygen was found to occur when 1-acetyl-3-phenyl-5-pyrazolone, II, was treated with pyridine, yielding 3-phenyl-5-acetoxypyrazole, VI.

A migration of acyl from position 1 to position 2 was observed with several of the above-named pyrazoles.

The formation of dyes by color development of a photographic film is described as a test.

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## A New Synthesis of the Pentacene Ring System

BY C. F. H. ALLEN AND J. W. GATES, JR.

During the last decade an increasing interest has been shown in the chemistry of the linear polynuclear hydrocarbons. The substances are colored and show an unusual activity toward reagents, whereas their quinones are the starting materials for the preparation of many derivatives. The pentacene ring system has always been formed by essentially the same type of reaction, *i. e.*, a phthalic anhydride has been condensed with an aromatic ring system, followed by ring closure. Most of the syntheses are the work of Marschalk, although the one known longest is

that of Mills,<sup>1</sup> who started with pyromellitic anhydride and benzene. Marschalk<sup>2</sup> devised improvements of a patent procedure<sup>3</sup> in which phthalic anhydride and leucoquinizarin were employed, so that this became an easier method for obtaining pentacene. He also described a less useful synthesis<sup>4</sup> from anthracene-2,3-dicarboxylic anhydride and hydroquinone.

During the course of our work with arylated

(1) Mills and Mills, *J. Chem. Soc.*, **101**, 2194 (1912).

(2) Marschalk, *Bull. soc. chim.*, [5] **4**, 1535 (1937); **5**, 156 (1938).

(3) German Patent 298,345 [*Frdl.*, **13**, 390 (1923)], ex. 6.

(4) Marschalk, *Bull. soc. chim.*, [5] **5**, 306 (1938); **6**, 1112 (1939).