ON THE REACTIONS OF THE FORMAMIDINE DERIVATIVES.

[SECOND PAPER.]

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In a previous paper[1] it has been pointed out that the substituted formamidines show a peculiar reactivity toward compounds containing methylene hydrogen, such as acetoacetic ester, acetylacetone, etc. At a temperature of 115° or above, the following reaction occurs:

$$RNHCH : NR + H_2CXY = RNHCH : CXY + RNH_2,$$

thus forming the free amine and a substituted aminomethylene derivative. In case the methylene compound contains a carbethoxy group, a secondary reaction may take place, giving a substituted acid amide as follows:

$$RNHCH : CXCOOEt + RNH_2 = EtOH + RNHCH : CXCONHR.$$

The completeness of this secondary reaction is conditioned largely by the temperature and the nature of the reacting methylene derivative. Thus with malonic ester the amide formation is practically complete, with acetoacetic ester 50 to 80 per cent. of the amine reacts with the carbethoxy group, while with cyanacetic ester no amide formation occurs.

The ease of the primary reaction, that is, the replacement of the H_2 of the $:CH_2$ by the group $:CHNHR$, seems to be affected by the positive or negative nature of the molecule. Thus benzyl cyanide and desoxybenzoin react with greater difficulty than the more negative malonic or acetoacetic ester and the more positive methylpyrazolone fails to combine with diphenylformamidine, while methylphenyl- and diphenylpyrazolone do so with ease.

The following paper is a more extended study of this interesting reaction and, while incomplete, is published at this time owing to the departure of one of the authors. The investigation is being continued in this laboratory and will be extended to other compounds containing methylene hydrogen, such as the isoxolones, etc.:

Formamidines and Malonic Ester.—Di-α-naphthylformamidine is easily prepared in good yield by heating molecular quantities of α-naphthylamine and orthoformic ester on the water bath for several hours. The *α-naphthalide of ethyl α-naphthalidomethylenemalonate*, $\alpha\text{-}C_{10}H_7NHCH : C(COOEt)CONHC_{10}H_7\text{-}\alpha$, was formed when 15 g. of the formamidine and 10 g. malonic ester were heated at 150° for three hours. The product was purified by washing with cold alcohol and then crystallizing from benzene and glacial acetic acid. It forms yellow needles difficultly soluble in the usual organic solvents and melts at 162°. Analysis:

Calculated for $C_{29}H_{22}O_3N_2$:	N, 6.83.
Found:	N, 6.57, 6.65.

[1] *Ber.*, **35**, 2496.

Monobromo Derivative.—Two grams of the above compound were dissolved in chloroform and one molecule of bromine added. This was absorbed instantly and was followed by a slow evolution of hydrobromic acid. The heavy yellow solid that separated was crystallized from glacial acetic acid. It then melted at 227° and gave results on analysis that showed the formation of a *monobromide*, $C_{26}H_{21}O_3N_2Br$.

Calculated: N, 5.74.
Found: N, 5.99.

An analogous result to the formation of a monobromo compound has been noted in the case of ethyl anilidomethylenecyanacetate.[1] With the expectation of forming the dinaphthalide, the α-naphthalide of ethyl α-naphthalidomethylenemalonate was heated at 220° with an excess of α-naphthylamine but the difficultly soluble yellow powder that resulted melted at 285° and gave figures on analysis that indicated the formation of di-α-naphthylurea.

Di-β-naphthylformamidine and malonic ester react easily at 150° to give the *β-naphthalide of ethyl β-naphthalidomethylenemalonate.* This compound, which is only slightly soluble in boiling alcohol, crystallizes from acetic acid in fine yellow needles melting at 172°. Analysis:

Calculated for $C_{26}H_{22}O_3N_2$: N, 6.38.
Found: N, 6.72.

Further evidence of the reactivity of the methylene hydrogen is shown by the fact that malonanilide and di-β-naphthylformamidine, when heated, combine with the formation of β-naphthylamine and *β-naphthalidomethylenemalonanilide*,

$$C_{10}H_7NHCH : C(CONHPh)_2,$$

a compound difficultly soluble in alcohol and acetic acid, crystallizing in light yellow needles, melting at 289°. Analysis:

Calculated for $C_{26}H_{21}O_2N_3$: N, 10.31.
Found: N, 10.22.

The *m-toluide of ethyl m-toluidomethylenemalonate* from di-*m*-tolylformamidine and malonic ester is deposited from alcohol in light yellow needles melting at 95°. Analysis:

Calculated for $C_{20}H_{22}O_3N_2$: N, 8.28.
Found: N, 8.20.

o-Phenetidine and orthoformic ester failed to react at the temperature of the water bath, but when heated in an oil bath at 140° gave a good yield of *methenyldi-o-phenetidine*, which crystallized from ligroin in white needles melting at 81°. Analysis:

Calculated for $C_{17}H_{20}O_2N_2$: N, 9.85.
Found: N, 9.81.

The new amidine is easily soluble in alcohol and this solution, when treated with chloroplatinic acid, deposits on evaporation red crystals of the *chloroplatinate* which melt at 178°. Analysis of the salt dried at 100°:

Calculated for $(C_{17}H_{20}O_2N_2)_2H_2PtCl_6$: Pt, 19.94.
Found: Pt, 19.95.

The above amidine and malonic ester give, at 130°, a product which melts at 110° and is moderately soluble in alcohol, from which it separates in white needles. This proved to be *o-ethoxyanilide* of *ethyl-o-ethoxyanilidomethylenemalonate.* Analysis:

Calculated for $C_{22}H_{26}O_5N_2$: N, 7.03.
Found: N, 7.00.

Derivatives of Ethyl Acetoacetate.—*Acetoaceto-p-bromanilide* is formed when aceto-

[1] *Ber.*, **35**, 2510.

acetic ester and *p*-bromaniline are heated at 135° for several hours. The oily product, which solidified on standing, was recrystallized from a mixture of ligroin and benzene, in which it is difficultly soluble. From this solvent or from hot water it separates in thin leaflets that melt at 137.5°. Analysis:

Calculated for $C_{10}H_{10}O_2NBr$: N, 5.47.
Found: N, 5.32.

As this melting point, 137.5°, is practically the same as that of the product obtained by Knorr[1] by the action of bromine on acetoacetanilide to which is assigned the formula $CH_3COCHBrCONHPh$, with a melting point of 138°, Knorr's compound was made and was found to melt at 137.5°, but a mixture of this with acetoaceto-*p*-bromanilide melted at 117°, thus showing them to be different substances.

Anilidomethyleneacetoaceto-p-bromanilide was readily obtained on heating diphenylformamidine and acetoaceto-*p*-bromanilide at 125°. It forms fine, slightly yellowish crystals from alcohol, which melt at 158°. Analysis:

Calculated for $C_{17}H_{15}O_2N_2Br$: N, 7.80.
Found: N, 7.97.

The isomeric *p-bromanilidomethyleneacetoacetanilide* melts at 171°.

When di-*p*-bromdiphenylformamidine m. 170°, which is easily prepared from *p*-bromaniline and orthoformic ester at 100°, and acetoacetic ester are heated at 125°, the reaction product contains *p*-bromaniline and a solid moderately soluble in hot alcohol and acetic acid, which crystallizes in white needles melting at 190°, the *p-bromanilidomethyleneacetoaceto-p-bromanilide*. Analysis:

Calculated for $C_{17}H_{14}O_2N_2Br_2$: N, 6.39.
Found: N, 6.72.

There is also formed the *ethyl-p-bromanilidomethyleneacetoacetate*, $CH_3COC:(CHNHC_6H_4Br)COOEt$, white needles easily soluble in alcohol and melting at 107°. Analysis:

Calculated: N, 4.48.
Found: N, 4.76.

From acetoacetanilide and di-*p*-tolylformamidine can be obtained *p-toluidomethyleneacetoacetanilide*, white needles, difficultly soluble in hot alcohol, which melt at 142°. Analysis:

Calculated for $C_{18}H_{18}O_2N_2$: N, 9.52.
Found: N, 9.87.

Di-ψ-cumylformamidine and acetoacetic ester give the following, when heated at 125°: Pseudocumidine; the *ψ-cumidomethyleneacetoaceto-ψ-cumidide*, white crystals from glacial acetic acid melting at 183°. Analysis:

Calculated for $C_{28}H_{28}O_2N_2$: N, 7.69.
Found: N, 7.78.

Ethyl-ψ-cumidomethyleneacetoacetate, white clumps, very soluble in alcohol, m. 98°. Analysis:

Calculated for $C_{16}H_{21}O_3N_2$: N, 5.09.
Found: N, 5.39.

Di-*o*-anisylformamidine was made by Rüggeberg[2] by heating the amine and orthoformic ester in a sealed tube at 160°. It can be prepared more simply by heating the components in an oil bath at 140° and crystallizing the product from a mixture of benzene and ligroin. It then melts at 105°. The amidine and acetoacetic ester react

[1] *Ann.*, **236**, 79.
[2] Dissertation, Freiburg, 1904.

at 150° to give *ethyl-o-methoxyanilidomethyleneacetoacetate*, needle-shaped crystals from alcohol, melting at 112°. Analysis:

Calculated for $C_{14}H_{17}O_4N$: N, 5.32.
Found: N, 5.40.

Under like conditions methenyldi-*p*-phenetidine and acetoacetic ester yield the *p-ethoxyanilidomethyleneacetoaceto-p-ethoxyanilide*, fine yellow crystals, easily soluble in alcohol, which melts at 138°. Analysis:

Calculated for $C_{21}H_{24}O_4N_2$: N, 7.82.
Found: N, 7.70.

With acetoacetic ester, di-α-naphthylformamidine yields two products. The first, which consists of fine yellow needles, difficultly soluble in hot alcohol, melts at 167–8° and proved to be *α-naphthalidomethyleneacetoaceto-α-naphthalide*. Analysis:

Calculated for $C_{25}H_{20}O_2N_2$: N, 7.37.
Found: N, 7.56.

The second is ethyl *a-naphthalidomethyleneacetoacetate*, a compound which melts at 92° and is very soluble in alcohol and moderately soluble in ligroin. Analysis:

Calculated for $C_{17}H_{17}O_3N$: N, 4.94.
Found: N, 5.46.

When the naphthalide (m. 167°) was dissolved in chloroform and bromine (1 mol.) added, the halogen was instantly absorbed with the formation of a *dibromide* which separated as a heavy yellow powder almost insoluble in boiling acetic acid. It melts at 226°. Analysis:

Calculated for $C_{25}H_{20}O_2N_2Br_2$: N, 5.18.
Found: N, 5.22.

In general, the bromine is loosely bound in these methylene derivatives, as is shown by their tendency to form monobromo compounds, and to even lose all of the bromine on recrystallization. This latter happened in an effort to make a bromide from the corresponding *m*-xylyl derivative.

From di-β-naphthylformamidine and acetoacetic ester was obtained *β-naphthalidomethyleneacetoaceto-β-naphthalide*, light yellow granules from glacial acetic acid melting at 184°. Analysis:

Calculated for $C_{25}H_{20}O_2N_2$: N, 7.37.
Found: N, 7.50.

Ethyl-β-naphthalidomethyleneacetoacetate, white clumps from ligroin, very soluble in alcohol, m. 95°. Analysis:

Calculated for $C_{17}H_{17}O_3N$: N, 4.94.
Found: N, 5.09.

Derivatives of Ethyl Cyanacetate.—The formamidines and cyanacetic ester react smoothly at 125° to yield an amine and the aminomethylene derivative. The carbethoxy group remains intact, no secondary reaction occurring at this temperature. The following compounds have been obtained:

Ethyl-ψ-cumidomethylenecyanacetate, $C_6H_2Me_3NHCH:C(CN)COOEt$, white needles from acetic acid melting at 196°. Analysis:

Calculated for $C_{15}H_{18}N_2O_2$: N, 10.85.
Found: N, 11.00.

Ethyl-α-naphthalidomethylenecyanacetate, slightly yellow needles from alcohol melting at 146°. Analysis:

Calculated for $C_{16}H_{14}O_2N_2$: N, 10.55.
Found: N, 10.72.

Ethyl-β-naphthalidomethylenecyanacetate, brownish yellow needles from alcohol which melt at 152°. Analysis:

Calculated for $C_{16}H_{14}O_2N_2$: N, 10.55.
Found: N, 10.58.

Derivatives of Benzyl Cyanide.—*m-Toluidomethylenebenzylcyanide*, $m\text{-}C_7H_7NHCH : C(CN)C_6H_5$, is formed when benzyl cyanide and di-*m*-tolylformamidine are heated at 160–80°. From alcohol or ligroin the new compound crystallizes in silver-gray leaves that melt at 126°. Analysis:

Calculated for $C_{16}H_{14}N_2$: N, 12.00.
Found: N, 12.26.

Benzyl cyanide and di-β-naphthylformamidine fail to react at 160°, but when the temperature is raised to 200° they combine, yielding the free amine and *β-naphthalidomethylenebenzylcyanide*. The new derivative, which is only slightly soluble in boiling alcohol, was purified by crystallization from glacial acetic acid, from which it separated in fine yellow needles melting at 194°. Analysis:

Calculated for $C_{19}H_{14}N_2$: N, 10.40.
Found: N, 10.69.

Di-α-naphthylformamidine and benzyl cyanide failed to react at 200°.

Desoxybenzoin, which contains the methylene grouping, unites readily at 150° with di-*a*-naphthylformamidine to yield *α-naphthalidomethylenedesoxybenzoin*, $\alpha\text{-}C_{10}H_7NHCH : C(C_6H_5)COC_6H_5$, which crystallizes from alcohol in reddish brown needles melting at 161°. Analysis:

Calculated for $C_{25}H_{19}ON$: N, 4.00.
Found: N, 4.20.

Derivatives of Acetylacetone.—Acetyl acetone reacts easily at 125° with the formamidines to give aminomethylene compounds of the type $RNHCH : C(COCH_3)_2$, of which the following have been prepared:

o-Toluidomethyleneacetylacetone, white needles from ligroin, m. 124°. Analysis:

Calculated for $C_{13}H_{15}O_2N$: N, 6.45.
Found: N, 6.47.

m-Toluidomethyleneacetylacetone, white needles, very soluble in alcohol, m. 75°. Analysis:

Calculated for $C_{13}H_{15}O_2N$: N, 6.45.
Found: N, 6.36.

o-Phenetidylmethyleneacetylacetone, colorless needles from ligroin which melt at 115–6°. Analysis:

Calculated for $C_{14}H_{17}O_3N$: N, 5.70.
Found: N, 5.95.

α-Naphthalidomethyleneacetylacetone forms bright yellow needles from alcohol, m. 144°. Analysis:

Calculated for $C_{16}H_{15}O_2N$: N, 5.50.
Found: N, 5.81.

β-Naphthalidomethyleneacetylacetone, brownish needles from alcohol, melting at 129°. Analysis:

Calculated for $C_{16}H_{15}O_2N$: N, 5.53.
Found: N, 5.80.

Pyrazolone and Pyrazole Derivatives.—In order to study the limitations of the formamidine reaction, it was thought of interest to choose a ring compound containing the methylene grouping. Such compounds present themselves in the pyrazolones formed by the action of phenyl hydrazine on acetoacetic and benzoylacetic esters, compounds which are characterized by their tautomeric behavior, of which this reaction illustrates a phase. Experiment soon showed, for instance, that methylphenylpyrazolone and the formamidines react easily and smoothly according to the following reaction:

$$\begin{array}{l} \mathrm{N = C{-}Me} \\ \mathrm{|\quad\ \ >CH_2} \\ \mathrm{PhN - CO} \end{array} + \mathrm{RN : CHNHR} \longrightarrow$$

$$\begin{array}{l} \mathrm{N = CMe} \\ \mathrm{|\quad\ \ >C = CHNHR} \\ \mathrm{PhN - CO} \end{array} + \mathrm{RNH_2},$$

yielding substituted aminomethylenepyrazolones, which, containing a chromophoric group, are all strongly colored, red or yellow compounds. Additional evidence of the correctness of the above equation is shown by the fact that a secondary product, methenyl-bis-methyphenylpyrazolone, is often formed in the reaction as follows:

$$2\begin{array}{l} \mathrm{N = CMe} \\ \mathrm{|\quad\ \ >CH_2} \\ \mathrm{PhN - CO} \end{array} + \mathrm{RN : CHNHR} \longrightarrow$$

$$\begin{array}{l} \mathrm{N = CMe} \\ \mathrm{|\quad\ \ >C = C - CH<\begin{array}{l} \mathrm{CMe = N} \\ \mathrm{|} \\ \mathrm{CO - NPh} \end{array}} \\ \mathrm{PhN - CO\quad\ \ H} \end{array} + 2\mathrm{RNH_2}.$$

This is the first instance observed in which both the RNH and the RN : group of the substituted formamidine have been replaced in reacting with the methylene hydrogen and is an additional confirmation of the interesting analogy between orthoformic ester and the formamidines. Thus Claisen has found[1] that the methylene derivatives react with orthoformic ester to give alkoxymethylene compounds of the type XYC : CHOR, which, in turn with amines, yield the amino derivatives, XYC : CHNHR. These latter, as has been shown, are formed directly from the methylene compounds $XYCH_2$ and the formamidines. Both orthoformic ester[2] and the formamidines unite directly with methylphenylpyrazolone to give methenyl-bis-methylphenylpyrazolone.

Additional proof of the correctness of the above aminomethylene structure is shown in the synthesis of pyrazole rather than pyrazolone compounds by the action of phenylhydrazine on anilidomethyleneacetoacetanilide, a reaction that will be discussed later.

Methylphenylpyrazolone was heated with diphenylformamidine at 130–50°. The reaction mixture contains two products which can be separated by fractional

[1] *Ann.*, **197**, 16. *Ber.*, **26**, 2731.

[2] Claisen, *Ann.*, **297**, 378.

crystallization from alcohol and acetic acid. The more soluble compound is *1-phenyl-3-methyl-4-anilidomethylene-5-pyrazolone.* This forms bright yellow needles melting at 154°. It is soluble in concentrated sulphuric acid and is precipitated without change on the addition of water. Analysis:

Calculated for $C_{17}H_{15}ON_3$: N, 15.16.
Found : N, 15.00.

The second product consists of orange-red needles difficultly soluble in alcohol and acetic acid and melts at 180°, and proved to be *methyl-bis-methylphenylpyrazolone.* Analysis:

Calculated for $C_{21}H_{18}O_2N_4$: N, 15.64.
Found: N, 15.69.

This latter compound may result from the direct interaction of two molecules of the pyrazolone and one of the formamidine or may be formed in a secondary reaction between methylphenylpyrazolone and the aminomethylene derivative. Thus experiment showed that a quantitative yield of the methenyl-bis-pyrazolone can be obtained by heating methylphenylpyrazolone and β-naphthalidomethylenemethylphenylpyrazolone at 150°.

$$C_{10}H_8O : CHNHC_{10}H_7\text{-}\beta + C_{10}H_{10}O = \beta\text{-}C_{10}H_7NH_2 + C_{10}H_8O : CHC_{10}H_9O.$$

Under like conditions, methylphenylpyrazolone and di-β-naphthylformamidine yield *methenyl-bis-methylphenylpyrazolone* and *1-phenyl-3-methyl-4-β-naphthalidomethylene-5-pyrazolone,* yellowish brown needles from alcohol melting at 177°. Analysis:

Calculated for $C_{21}H_{17}ON_3$: N, 12.85.
Found: N, 13.02.

The corresponding *α-naphthalidomethylenemethylphenylpyrazolone* consists of deep yellow crystals that melt at 122°. Analysis:

Calculated for $C_{21}H_{17}ON_3$: N, 12.85.
Found: N, 13.28.

When boiled with alcoholic potash the pyrazolone yields a red compound melting at 174°, which is under investigation. Other pyrazolones are the following:

1-Phenyl-3-methyl-4-p-bromanilidomethylene-5-pyrazolone, dark brown needles from alcohol, m. 168°. Analysis:

Calculated for $C_{17}H_{14}ON_3Br$: N, 11.80.
Found: N, 12.2.

1-Phenyl-3-methyl-4-p-toluidomethylene-5-pyrazolone, yellow needles from alcohol, m. 164°. Analysis:

Calculated for $C_{18}H_{17}ON_3$: N, 14.44.
Found: N, 14.46.

1-phenyl-3-methyl-4-ψ-cumidomethylene-5-pyrazolone, yellow needles from alcohol, m. 171°. Analysis:

Calculated for $C_{20}H_{21}ON_3$: N, 13.16.
Found: N, 13.09.

1-Phenyl-3-methyl-4-p-ethoxyanilidomethylene-5-pyrazolone, reddish yellow crystals, m. 162°. Analysis:

Calculated for $C_{19}H_{19}ON_3$: N, 13.09.
Found: N, 12.88.

Derivatives of Diphenylpyrazolone.—1,3-Diphenylpyrazolone from benzoyl acetic ester and phenylhydrazine reacts easily with the formamidines at 125°. Thus from the pyrazolone and diphenylformamidine was obtained *1,3-diphenyl-4-anilidomethyl-*

ene-5-pyrazolone. This crystallized from glacial acetic acid in fine yellow needles melting at 140°. Analysis:

Calculated for $C_{22}H_{17}ON_3$: N, 12.39.
Found: N, 12.35.

Diphenylpyrazolone and di-*o*-tolylformamidine gave *1,3-diphenyl-4-o-toluidomethylene-5-pyrazolone*, yellow needles from acetic acid melting at 146°. Analysis:

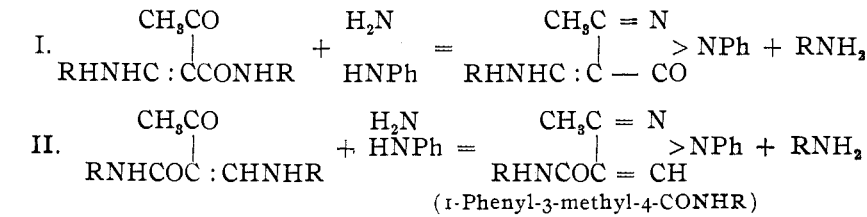
Calculated for $C_{23}H_{19}ON_3$: N, 11.89.
Found: N, 11.72.

Diphenylpyrazolone and di-β-naphthylformamidine yield *1,3-diphenyl-4-β-naphthalidomethylene-5-pyrazolone*, yellow crystals, difficultly soluble in glacial acetic acid, m. 192°. Analysis:

Calculated for $C_{26}H_{19}ON_3$: N, 10.79.
Found: N, 10.73.

Pyrazole Synthesis.—Rüggeberg[1] investigated the action of phenylhydrazine upon anilidomethylenebenzoylacetanilide and *o*-toluidomethylenebenzoylacet-*o*-toluidide and obtained compounds which he regarded as aminomethylene derivatives of diphenylpyrazolone. The two products, however, fail to agree with the properties of the anilidomethylene- and *o*-toluidomethylenediphenylpyrazolone previously described. These melt at 140° and 146°, respectively, while Rüggeberg's compounds have melting points of 155°[2] and 160°. For the purpose of more complete identification his work was repeated in the latter case. The *o*-toluidomethylenebenzoylacet-*o*-toluidide was heated for three hours in alcohol solution with phenylhydrazine. After purification there was obtained a compound crystallizing in pure white needles, melting at 165°. Rüggeberg's product was yellow and melted at 160°. Analysis, however, showed their identity. Calculated for $C_{23}H_{19}ON_3$: N, 11.89; found, 12.02 per cent. Further investigation identified this compound as the *o*-tolyl amide of 5-diphenylpyrazole-4-carboxylic acid and showed that phenylhydrazine reacted with the aminomethylene derivatives of acetoacetic and benzoylacetic esters to give a series of pyrazoles isomeric with the pyrazolones previously described.

In the formation of such a ring with phenylhydrazine, three possibilities offer themselves which can be represented as follows:



[1] Dissertation, Freiburg, 1904.

[2] This is the phenylamide of 1,5-diphenylpyrazole-4-carboxylic acid.

III. $\begin{matrix} CH_3CO \\ | \\ RHNCOC:CHNHR \end{matrix} + \begin{matrix} HNPh \\ | \\ H_2N \end{matrix} = \begin{matrix} CH_3C{-}NPh \\ \| \quad >N \\ RHNCOC{-}CH \end{matrix} + RNH_2$

(1-Phenyl-5-methyl-4-CONHR)

Equation No. I, the pyrazolone synthesis, suggested by Rüggeberg, is out of the question, since no aminomethylene derivatives are obtained. Against this also is the fact that the CONHR group is unaffected by the phenylhydrazine. Experiment has shown that anilidomethyleneacetoacetanilide and *p*-toluidomethyleneacetoacetanilide give, with phenylhydrazine, the same pyrazole with melting point 182°, which is only possible when the CONHPh group remains intact.

The formation of these pyrazole derivatives must be explained by equation II or III, the question being whether the methyl or phenyl groups are in positions 3 or 5. The direct evidence thus far obtained points to equation III as the correct formulation of the reaction and thus places them as derivatives of 1-phenyl-5-methyl or phenyl-4-carboxylic acid for the following reason. Ethyl β-naphthalidomethyleneacetoacetate was boiled with excess of phenylhydrazine in alcohol solution. After removal of the excess of phenylhydrazine, the resulting product was purified by crystallization from ligroin. It then melted at 55–6° and when saponified with alcoholic potash gave an acid melting at 167°.

This ester and acid were found to be identical with the ethyl 1-phenyl-5-methylpyrazole-4-carboxylate and corresponding acid of Claisen,[1] who made them by the action of phenylhydrazine on oxymethylene acetoacetic ester. The equation which follows,

$$\begin{matrix} CH_3CO \\ | \\ EtO_2CC:CHNHC_{10}H_7 \end{matrix} + \begin{matrix} HNC_6H_5 \\ | \\ H_2N \end{matrix} = \begin{matrix} CH_3C-NC_6H_5 \\ \| \quad >N \\ EtO_2CC-CH \end{matrix} + C_{10}H_7NH,$$

shows the mechanism of the reaction, illustrates the analogy between the grouping C : CHOR and C : CHNHR in ease of replacement and gives the proof of the structure.

The *phenylamide of 1-phenyl-5-methylpyrazole-4-carboxylic acid* is formed when anilidomethyleneacetoacetanilide is heated for two hours in alcohol solution with an excess of phenylhydrazine. The solution was then poured into water acidified with hydrochloric acid. The resulting precipitate was purified by crystallization from alcohol and benzene, from which it separates in white crystals melting at 182°. Analysis:

Calculated for $C_{17}H_{15}ON_3$: N, 15.16.
Found: N, 15.14.

As has been noted, this same pyrazole can be made by the action of phenylhydrazine on *p*-toluidomethyleneacetoacetanilide.

The *p-tolylamide of 1-phenyl-5-methylpyrazole-4-carboxylic acid* is readily obtained from *p*-toluidomethyleneacetoaceto-*p*-toluide and phenylhydrazine. It forms white needles from alcohol melting at 177°. Analysis:

[1] *Ann.*, **295**, 312.

Calculated for $C_{18}H_{16}ON_3$: N, 14.43
Found: N, 14.34.

Under like conditions, α-naphthalidomethyleneacetoacet-α-naphthalide gave the *α-naphthalide of 1-phenyl-5-methylpyrazole-4-carboxylic acid*, white needles from alcohol, melting at 168°. Analysis:

Calculated for $C_{21}H_{17}ON_3$: N, 12.85.
Found: N, 12.88.

The *β-naphthalide of 1-phenyl-5-methylpyrazole-4-carboxylic acid* crystallizes from alcohol in white needles which melt at 170°. Analysis:

Calculated for $C_{21}H_{17}ON_3$: N, 12.85.
Found: N, 12.91.

These pyrazole derivatives are all colorless compounds with melting points ten to thirty degrees higher than the corresponding isomeric colored pyrazolones.

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INTRAMOLECULAR REARRANGEMENT OF PHTHALAMIDIC ACIDS. IV.

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The previous papers on this subject by the senior author and his collaborators[1] have shown that secondary and tertiary amines, if they are not too negative, convert phthalamidic acids, $RNHCOC_6H_4CO_2H$, into imides, $C_6H_4\langle{}^{CO}_{CO}\rangle NR$, whereas primary amines, $R'NH_2$, give rise to one or more of the following products: the amidic acid, $R'NHCOC_6H_4CO_2H$, the imides, $C_6H_4\langle{}^{CO}_{CO}\rangle NR$ or $C_6H_4\langle{}^{CO}_{CO}\rangle NR'$, or the amides, $RNHCOC_6H_4CONHR'$ and $C_6H_4(CONHR')_2$. In all cases, of course, the primary product of the reaction is an ammonium salt.

In the present communication we describe the results which we have obtained by a more extended study of the above reaction. On account of the rather curious and unexpected observations described by Bishop Tingle and Rolker,[2] our attention was first directed towards the behavior of phthal-*m*-nitrophenylamidic acid, $O_2NC_6H_4NHCOC_6H_4CO_2H$, and we have investigated its interaction with a considerable number of amines of various classes. We obtained *normal salts* from butylamine, isobutylamine, isoamylamine, benzylamine, benzylethylamine and dibenzylamine; all of these salts, when heated above their melting points, evolved the amine and gave phthal-*m*-nitrophenylimide. With ammonia, di-

[1] Bishop Tingle and Cram, *Am. Chem. J.*, **37**, 596 (1907); Bishop Tingle and Lovelace, *Ibid.*, **38**, 642 (1907); Bishop Tingle and Rolker, THIS JOURNAL, **30**, 1882 (1908).

[2] *Loc. cit.*