on top of the salt in the flask so that it did not have an opportunity to react rapidly on the whole of the salt, acetyl chloride was formed, and appeared in the distillate with the anhydride.

The crude anhydride obtained was slightly colored, and boiled between 130°-138°. The yield was about 82% of the theoretical, calculated from the oxychloride. On further distillation with a little sodium acetate, it gave a water-white product, boiling at 138°, free from chlorine or oxychlorides of silicon, and giving the usual reactions for acetic anhydride, such as the formation of acetanilide with aniline (m. p. 112°), and of amyl acetate with amyl alcohol. On evaporation with water in a weighed platinum crucible, no weighable residue was left, showing absence of any silicon compound.

The oxychloride boiling at 198°-202° gave similar results. A mixture of the oxychlorides boiling between 140°-190° also reacted with sodium acetate, giving acetic anhydride, as did also a mixture of the oxychlorides boiling above 200°.

With sodium propionate and propionic, anhydride was likewise obtained, the yield, however, being only 60% of the theoretical. Sodium butyrate gave only a small yield of anhydride, which was darkly colored, showing considerable decomposition. The reaction in this case did not work as smoothly as in the previous ones.

From the above results it is established that the action of these oxychlorides on sodium salts of fatty acids is similar to that of the oxychlorides of carbon, sulphur and phosphorus, resulting in the formation of anhydrides, sodium chloride and silica.

The writer is indebted to Mr. B. L. Pfeifer for his help in carrying on parts of this work.

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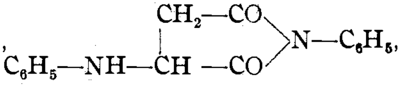
THE REACTIONS OF CERTAIN FUMAROID AND MALEINOID COMPOUNDS WITH AROMATIC AMINES.[1]

BY W. H. WARREN AND M. R. GROSE.

Received September 16, 1912.

Interest in the behavior of fumaric and maleic acids with aniline is due, in a measure, to the reaction itself, the result of which is quite different from that expected, but especially to the possibility it offers of further insight into the nature of the relationship of these two isomers. From analogy we should expect each acid to form its anilide but the reaction departs from the usual course and yields one and the same product, namely, phenylaminosuccinphenylimide,



$$\begin{array}{l}\mathrm{CH_2—CO} \\ \quad | \qquad\qquad\qquad > \mathrm{N—C_6H_5}, \\ \mathrm{C_6H_5—NH—CH—CO}\end{array}$$

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[1] Read before Section IV on Organic Chemistry of the Eighth International Congress of Applied Chemistry, Washington and New York. September 4-13, 1912.

a crystallin compound melting at 210–211°. Perkin[1] first prepared this derivative of succinimide by evaporating an aqueous solution of aniline maleate, but did not determin its structure. Upon treating aniline fumarate in the same manner, he found that no reaction took place. Repeating Perkin's experiments, Michael[2] prepared and analyzed the compound from aniline maleate and naturally assumed, since the analytical results agreed with those calculated for maleinanilide, that he had obtained that compound, though aside from the analysis he had no basis for such a conclusion. Anschütz and Wirtz[3] subsequently proved Perkin's compound to be phenylaminosuccinphenylimide and not maleinanilide. They further found that they could prepare this compound from malic acid as well as from several maleinoid bodies but did not extend the reaction to fumaroid bodies.

We first obtained Perkin's compound by heating monomethyl fumarate and aniline on the water bath. At a slightly higher temperature, dimethyl and diethyl fumarate gave the same result, and at 140–150° the yield from fumaric acid itself was nearly quantitative. Tingle and Bates[4] had already obtained the latter result at 160–170°.

Perkin's compound results from two different reactions, the first leading to the formation of an imido ring from the action of aniline on the carboxyl groups and the second involving the addition of aniline at the double bond. The question arises as to the sequence of these reactions. Since distillation of acid aniline malate gives Perkin's compound and maleinanil, and since aniline at 100° easily converts the latter into the former, we may regard maleinanil as an intermediate product, that is to say, its presence indicates that the imido ring is formed first. On the other hand, if addition were the first reaction, we should expect phenylaminosuccinic acid to accompany Perkin's compound, but its absence lends support to the former alternative. Assuming that the imido ring is formed first, we find the explanation easy for maleinoid compounds but, as fumaric acid can form neither anhydride nor anil, we must assume conversion of the fumaroid to the maleinoid form before the imido ring is possible. The reaction of addition, as far as we know, might take place equally well with maleinoid or fumaroid compounds, though, of course, one configuration might permit what the other would not.

In our study of the reactions leading to Perkin's compound, we have undertaken to determin what aromatic amines react with maleinoid and fumaroid compounds in the manner described, and what is the sequence of the reactions involved. Thus far, we have found that an unsubstituted

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[1] *Ber.*, 14, 2577 (1881).

[2] *Ibid.*, 19, 1372 (1886).

[3] *Ann.*, 239, 137 (1887).

THIS JOURNAL, 31, 1235 (1909).

amine like β-naphthylamine and amines containing methyl or ethoxy as substituents act like aniline. It is probable that diamines form the imido ring with one amino group, while the other adds at the double bond, thus forming a bridged succinimido ring. On the other hand, halogen or carboxyl as substituents entirely inhibit the reaction. As regards sequence of the reactions, the evidence points to the dependence of addition at the double bond upon previous formation of the imido ring.

Experimental.

I. Structural Characteristics of Reacting Amines.

Of the products aniline can form from maleinoid and fumaroid compounds, Perkin's compound is the type most easily obtained. Since other aromatic amines might form different types, we kept in mind the following possibilities in order of likelihood:

1. Saturated compounds due to imido ring formation and addition at the double bond (type of Perkin's compound).
2. Unsaturated compounds due to imido ring formation alone (type of maleinanil).
3. Saturated compounds due to addition at the double bond (type of phenylaminosuccinic acid), including monanilides and dianilides of such acids.
4. Unsaturated compounds of the type of maleinanilide and fumaranilide.

Analysis will usually establish the type, but such isomers as Perkin's compound and the dianilides of maleic and fumaric acids cannot be distinguished in this way. The former type, however, as a secondary amine forms a nitrosamine, the preparation and analysis of which settle the question of structure. Consequently, we have relied upon these nitrosamines to prove the type of compound formed. Compounds of the third type can also form nitrosamines, but analysis, or their acidic properties, will eliminate them as possibilities.

We were led to investigate this subject by an experiment in which monomethyl fumarate and aniline were heated on the water bath. We expected to prepare the anilide of this mono-ester but obtained Perkin's compound, no matter in what proportion we used the reacting substances. As this ester of fumaric acid has not been described, we include it here.

Monomethyl Fumarate, $C_5H_6O_4$, $CH_3O—CO—CH=CH—COOH$.—A 5% solution of potassium hydroxide in absolute methyl alcohol, containing half the quantity of alkali required for complete saponification, was slowly added to 25 grams of dimethyl fumarate in 250 cc. of absolute methyl alcohol. The ester was dissolved without rise of temperature. Twelve hours later methyl alcohol was distilled off and the residue, after extraction with ether, was acidified with hydrochloric acid. The crystallin precipitate was collected on a filter plate and the filtrate extracted with ether, which gave an additional yield of substance. We obtained about 15 grams of ester melting at 143°. Crystallized from alcohol, it gave the following results on analysis:

Subst., 0.1907; CO_2, 0.3212; and H_2O, 0.0861.
Calculated for $C_5H_6O_4$: C, 46.15; H, 4.62.
Found: C, 45.95; H, 5.05.

Crystallized from alcohol, monomethyl fumarate forms flattened prisms with obliquely truncated ends. It is somewhat more soluble in hot than in cold water; easily soluble in alcohol or ether; and sparingly soluble in cold chloroform, benzene or carbon disulfide. Saponification of this ester gave fumaric acid and esterification, the dimethyl ester.

Phenylaminosuccinphenylimide, $C_{16}H_{14}O_2N_2$, $C_6H_5-NH-C_4H_3O_2=N-C_6H_5$.—We obtained Perkin's compound from the following fumaroid bodies under the conditions stated:

1. Aniline (2 mols.) and monomethyl fumarate (1 mol.) at 100°.
2. Aniline (2 mols.) and dimethyl or diethyl fumarate (1 mol.) at about 125°.
3. Aniline (2 mols.) and fumaric acid (1 mol.) at 140–150°.

Crystallized from alcohol, or better from glacial acetic acid, it melted at 210–211° and gave the correct results on analysis.

From alcohol this compound is white but from glacial acetic acid its color varies from a faint to a pronounced yellow. This appearance of color either has not been previously observed, or has been considered as having no significance. Had we noticed it in this compound alone, we should probably have passed it by; but, as even more striking instances of the same thing have appeared in the case of other similarly constituted compounds, we have thought it worth mentioning.

First we thought the color might be due to impurity but we could detect no difference by analysis. The white modification, recrystallized from glacial acetic acid, acquired a decidedly yellow color and finally became reddish yellow after several hours contact with the boiling solvent. Thus far, we have found no differences in melting point or crystallin form of these modifications, but have not thoroughly examined them, as the matter does not directly concern our present subject. Orndorff and Pratt[1] have recently described a color change of phthaloxime from white to yellow, which in some respects is like our case. They regard the hydroxyl group as a factor, since the change was caused to some extent by boiling methyl alcohol, water and ethyl alcohol, but *most readily by glacial acetic acid.* They could discover no differences in the melting point or solubility and would have failed to detect the isomerism but for the difference in color.

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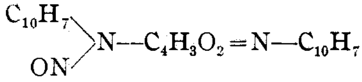
[1] *Am. Chem. J.*, **47**, 89 (1912).

Naphthylamines.—The two naphthylamines differ from aniline only in the structure of the ring. We tried the action of both on fumaric acid but only the *beta* compound gave a satisfactory result. It acted essentially like aniline.

β-Naphthylaminosuccin-β-naphthylimide, $C_{24}H_{18}O_2N_2$, or $C_{10}H_7-NH-C_4H_3O_2=N-C_{10}H_7$.—Five grams of fumaric acid (1 mol.) and 12.5 grams of β-naphthylamine (2 mols.) were heated several hours in an oil bath. The reaction mixture became pasty and finally set to a hard, yellowish mass. After treatment with ether and sodium carbonate solution to remove unaltered substance, the product crystallized from glacial acetic acid in fine yellow needles which melted at 250–252° and gave the following result on analysis:

Subst., 0.194; N, 13.2 cc.; 23°; 763.7 mm.
Calculated for $C_{24}H_{18}O_2N_2$: N. 7.65. Found: N, 7.71.

The yield of this compound is good. It dissolves best in acetone but is sparingly soluble in such solvents as alcohol, glacial acetic acid, and benzene and practically insoluble in ether or ligroin. It crystallized nearly white from acetone or alcohol but yellow from glacial acetic acid. After several crystallizations from acetone, it melted with decomposition at 250–255°, and its analysis agreed with that of the yellow modification. As far as melting point and composition are concerned, the two forms do not differ. As an additional test, a hot saturated solution of the substance, that had been crystallized from acetone and analyzed, was boiled for 10 hours under a return condenser. The solution gradually became red and as it cooled crystallization took place. Recrystallization of this product from acetone showed no difference except that of color.



The Nitroso Derivative, $\begin{matrix}C_{10}H_7\\ON\end{matrix}\!\!>N-C_4H_3O_2=N-C_{10}H_7$, was prepared by covering 2 grams of the preceding compound with glacial acetic acid, adding sodium nitrite and diluting the solution with water at the end of the reaction. The product, crystallized from acetone, began to darken at 200°, melted approximately at 260° and gave the following result on analysis:

Subst., 0.2005; N, 18.6 cc.; 19.5°; 750.3 mm.
Calculated for $C_{24}H_{17}O_3N_3$: N, 10.63. Found: N, 10.50.

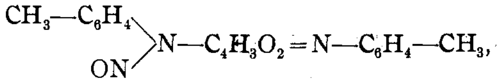
This compound crystallized from acetone in rhombic crystals. It is slightly soluble in hot alcohol or benzene; moderately soluble in hot chloroform; and insoluble in ether or ligroin.

Methyl as Substituent.—The action of the three toluidines and of one xylidine on fumaric acid showed that neither presence of methyl groups nor their position has any noticeable influence on the reaction.

o-Tolylaminosuccin-o-tolylimide, $C_{18}H_{18}O_2N_2$ or $CH_3—C_6H_4—NH—C_4H_3O_2=N—C_6H_4—CH_3$.—Five grams of fumaric acid (1 mol.) and 9 grams of *o*-toluidine (2 mols.) were heated in an oil bath. At 120° the reaction took place quickly and apparently was over in a few minutes. The viscous product, treated with hydrochloric acid and then with sodium carbonate solution, became granular and crystallized from alcohol in fine white needles which melted at 112–113°, and gave the following result on analysis:

Subst., 0.2061; N, 17.7 cc.; 21°; 751.3 mm.
Calculated for $C_{18}H_{18}O_2N_2$: N, 9.53. Found: N, 9.66.

The yield of this compound is good. It is soluble in alcohol, acetone, chloroform, benzene, and glacial acetic acid, but nearly insoluble in ether or ligroin.

The Nitroso Derivative,  $\left.\begin{array}{l}CH_3—C_6H_4\\ ON\end{array}\right>N—C_4H_3O_2=N—C_6H_4—CH_3$, prepared as previously described and crystallized from very dilute alcohol, melted at 85°, and gave the following result on analysis:

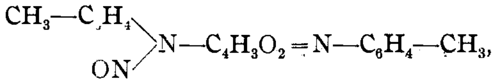
Subst., 0.2238; N, 25.4 cc.; 21°; 751.9 mm.
Calculated for $C_{18}H_{17}O_3N_3$: N, 13.00. Found: N, 12.78.

This compound does not form well-defined crystals. It dissolves easily in alcohol, chloroform, ether, benzene, acetone and glacial acetic acid, but is practically insoluble in ligroin.

m-Tolylaminosuccin-m-tolylimide, $C_{18}H_{18}O_2N_2$ or $CH_3—C_6H_4—NH—C_4H_3O_2=N—C_6H_4—CH_3$.—Fumaric acid and *m*-toluidine react in the manner just described for *o*-toluidine. The product crystallized from alcohol in fine white needles which melted at 130°, and gave the following result on analysis:

Subst., 0.1914; N, 16.1 cc.; 21°; 742 mm.
Calculated for $C_{18}H_{18}O_2N_2$: N, 9.52. Found: N, 9.35.

The yield of this compound is good. Except in ether or ligroin, in which it is only slightly soluble, it dissolves readily in all ordinary solvents.

The Nitroso Derivative,  $\left.\begin{array}{l}CH_3—C_6H_4\\ ON\end{array}\right>N—C_4H_3O_2=N—C_6H_4—CH_3$, was prepared in the usual manner. It crystallized from alcohol in white plates which melted at 120° and gave the following result on analysis:

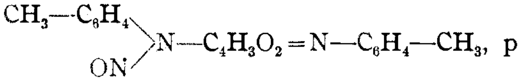
Subst., 0.2101; N, 24.2 cc.; 23°; 755.1 mm.
Calculated for $C_{18}H_{17}O_3N_3$: N, 13.00. Found: N, 12.90.

This compound is readily soluble in alcohol, chloroform, benzene, acetone, and glacial acetic acid but only slightly soluble in ether.

p-Tolylaminosuccin-p-tolylimide, $C_{18}H_{18}O_2N_2$, or $CH_3—C_6H_4—NH—C_4H_3O_2=N—C_6H_4—CH_3$.—Five grams of fumaric acid (1 mol.) and 9 grams of *p*-toluidine (2 mols.) were heated in an oil bath for 3 hours at 150°. The product, crystallized from alcohol, melted at 209–211°, and gave the following result on analysis:

Subst., 0.2033; N, 17.1 cc.; 18.5°; 749 mm.
Calculated for $C_{18}H_{1}\ O_2N_2$: N, 9.52. Found: N, 9.55.

The yield of this compound is good. Though sparingly soluble in alcohol, it crystallizes from this solvent in needles. It is moderately soluble in cold benzene or glacial acetic acid but practically insoluble in ether or ligroin. Recrystallization from glacial acetic acid of the white crystals from alcohol gives a product having a pronounced yellow color. The two modifications, however, show no differences in melting point or crystallin form.

The Nitroso Derivative,  $\genfrac{}{}{0pt}{}{CH_3—C_6H_4}{ON}\!>\!N—C_4H_3O_2=N—C_6H_4—CH_3$, prepared in the usual way and crystallized from alcohol, melted at 169–170°, and gave the following result on analysis:

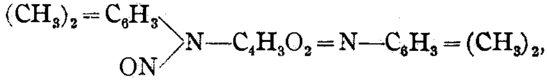
Subst., 0.1773; N, 20.6 cc.; 19°; 748.6 mm.
Calculated for $C_{18}H_{17}O_3N_3$: N, 13.00. Found: N, 13.15.

This nitrosamine crystallizes from hot alcohol, in which it is moderately soluble, in clusters of white needles. It is readily soluble in glacial acetic acid, benzene or chloroform, but practically insoluble in ether.

2,4-Dimethylphenylaminosuccin-2,4-dimethylphenylimide, $C_{20}H_{22}O_2N_2$, or $(CH_3)_2=C_6H_3—NH—C_4H_3O_2=N—C_6H_3=(CH_3)_2$.—Five grams of fumaric acid (1 mol.) and 10.5 grams (2 mols.) of xylidine ($NH_2 : CH_3 : CH_3 = 1 : 2 : 4$), boiling at 210–211°, were heated for 4 hours in an oil bath at 160.° The final product was a viscous mass. It crystallized from alcohol in clusters of slightly yellow needles which melted at 132–133°, and gave the following result on analysis:

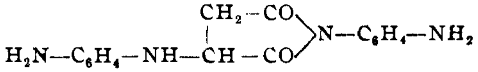
Subst., 0.2048; N, 16.1 cc.; 21°; 754.3 mm.
Calculated for $C_{20}H_{22}O_2N_2$: N, 8.70. Found: N, 8.87.

The yield of this compound is good. It is sparingly soluble in ether or ligroin, but dissolves readily in chloroform, benzene, or glacial acetic acid.

The Nitroso Derivative,  $\genfrac{}{}{0pt}{}{(CH_3)_2=C_6H_3}{ON}\!>\!N—C_4H_3O_2=N—C_6H_3=(CH_3)_2$, prepared as usual, was precipitated yellowish white on diluting the acid solution. Because of its low melting point and extreme solubility, it was dissolved in very dilute alcohol and obtained in indistinct crystals having a yellow color. Its melting point lies between 80 and 90° but is not sharply defined. Upon analysis it gave the following result:

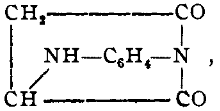
Subst., 0.1924; N, 19.7 cc.; 21°; 752 mm.
Calculated for $C_{20}H_{21}O_3N_3$: N, 11.96. Found: N, 11.53.

Action of Diamines.—We studied the behavior of fumaric acid with *p*-phenylenediamine and benzidine, but obtained rather unsatisfactory results. A reaction undoubtedly took place with both diamines but the products were very insoluble and therefore could not be purified with certainty. If the reaction were analogous to those with monamines, *p*-phenylenediamine would give a compound of the type



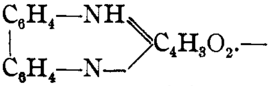
$$\begin{matrix} & CH_2-CO \\ & | \\ H_2N-C_6H_4-NH- & CH-CO \end{matrix} \!\!> N-C_6H_4-NH_2$$

which we should expect to have basic properties. The product was very indifferent toward acids. On the other hand, the action of one molecule of diamine on one molecule of fumaric acid might form a bridged succinimido ring of the type



which as near as we can judge is what takes place.

Semibenzidaminosuccinsemibenzidimide, $C_{16}H_{12}O_2N_2$ or



$$\begin{matrix} C_6H_4-NH \\ | \\ C_6H_4-N- \end{matrix} \!\!> C_4H_3O_2$$

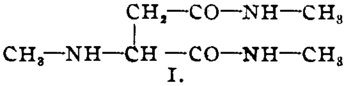
.—Four grams of fumaric acid (1 mol.) and 12.6 grams of benzidine (2 mols.) were heated in an oil bath for several hours at 150–160°. We recovered about half the diamine from the brownish yellow product. This we took to mean that the two substances had reacted molecule for molecule. The compound did not melt below 300°. As it was insoluble in all ordinary solvents, we prepared the material for analysis by treating it with acid and alkali to remove any unaltered substance and obtained the following result:

Subst., 0.3468; N, 34 cc.; 21°; 731 mm.

Calculated for $C_{16}H_{12}O_2N_2$: N, 10.61. Found: N, 10.68.

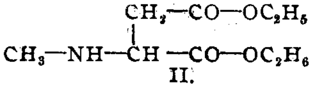
This compound is very resistant to chemical action. Boiling hydrochloric acid dissolves it slightly but otherwise seems to have no effect. Nitric acid produces a reddish solution; and hot sulfuric acid dissolves it with slight color. Boiling alkalies cause no change.

Action of Amines having the Amino Group in the Side Chain.—The amino group in the side chain imparts an aliphatic rather than an aromatic character to the amine. Therefore, it was not possible to predict with certainty how benzylamine would act, since aliphatic and aromatic amines differ in their behavior with maleinoid and fumaroid compounds. Körner and Menozzi,[1] for example, obtained two products by the action of alcoholic methylamine on diethyl fumarate or maleate, namely, (I) methylaminosuccinmethyldiamide and (II) diethylmethylaminosuccinate:



$$\begin{matrix} & CH_2-CO-NH-CH_3 \\ & | \\ CH_3-NH- & CH-CO-NH-CH_3 \end{matrix}$$

I.



$$\begin{matrix} & CH_2-CO-OC_2H_5 \\ & | \\ CH_3-NH- & CH-CO-OC_2H_5 \end{matrix}$$

II.

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[1] *Gaz. chim. ital.*, 19, 422.

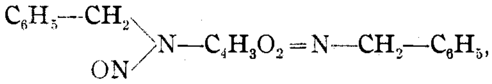
In both there was addition of the amine at the double bond but no formation of the succinimido ring. Benzylamine, however, behaves like the other aromatic amines.

Benzylaminosuccinbenzylimide, $C_{18}H_{18}O_2N_2$ or $C_6H_5—CH_2—NH—C_4H_3O_2=N—CH_2—C_6H_5$.—Benzylamine converts fumaric acid or its ethyl ester into this compound. Nine grams of diethyl fumarate (1 mol.) and 11 grams of benzyl amine (2 mols.) were heated in an oil bath under a return condenser for several hours at 150°. The liquid product upon standing changed to a crystallin mass. After treatment with ether to remove unaltered substance, the compound, crystallized from alcohol, melted at 205°, and gave the following result on analysis:

Subst., 0.1960; N, 16.8 cc.; 21.5°; 744.2 mm.

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

The yield of this compound is good. It crystallizes from alcohol in fine, white needles and is freely soluble in hot benzene, glacial acetic acid or chloroform, but practically insoluble in ether or ligroin. It tastes decidedly bitter, though not intensely so.

The Nitroso Derivative,  $\left.\begin{array}{r}C_6H_5—CH_2\\ ON\end{array}\right>N—C_4H_3O_2=N—CH_2—C_6H_5$, prepared in the usual way, crystallized from alcohol in fine white needles, which melted at 156°, and gave the following result on analysis:

Subst., 0.1732; N, 20.2 cc.; 21°; 757.6 mm.

Calculated for $C_{18}H_{17}O_3N_3$: N, 13.00. Found: N, 13.16.

This compound dissolves freely in alcohol, glacial acetic acid or acetone; difficultly in chloroform or benzene; and is practically insoluble in ether.

Influence of other Substituents than Methyl.—Although the methyl group does not have a retarding influence, certain other substituents entirely inhibit the action of the amine. Thus, for example, there was no reaction between fumaric acid and tribromoaniline (1 : 2 : 4 : 6) or *p*-bromoaniline. The same is true of the carboxyl group, since the methyl ester of *p*-aminobenzoic acid gave a negative result. On the other hand, the influence of the hydroxyl group is favorable, since the ethyl ether of *p*-aminophenol permits the reaction to take place. We have as yet made no experiments with other substituents.

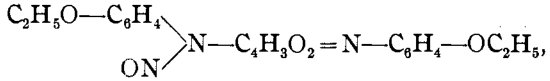
p-Ethoxyphenylaminosuccin-p-ethoxyphenylimide, $C_{20}H_{22}O_4N_2$ or $C_2H_5O—C_6H_4—NH—C_4H_3O_2=N—C_6H_4—OC_2H_5$.—Five grams of fumaric acid (1 mol.) and 12.5 grams of *p*-phenetidine were heated for several hours in an oil bath at 150°. The product, a thick viscous mass, crystallized from alcohol in very fine needles which melted at 204–205°, and gave the following result on analysis:

Subst., 0.1779; N, 12.9 cc.; 21°; 744 mm.

Calculated for $C_{20}H_{22}O_4N_2$: N, 7.91. Found: N, 8.08.

The yield of this compound is good. It dissolves freely in hot glacial acetic acid or chloroform; somewhat in hot benzene; but only slightly in ether or ligroin.

The Nitroso Derivative,



$$\begin{matrix} C_2H_5O-C_6H_4 \\ ON \end{matrix}\!\!>N-C_4H_3O_2=N-C_6H_4-OC_2H_5,$$

crystallizes from alcohol in short, thick, yellow needles which melted at 133–134°, and gave the following result on analysis:

Subst., 0.2087; N, 20.2 cc.; 20°; 754.3 mm.

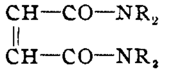
Calculated for $C_{20}H_{21}O_5N_3$: N, 10.94. Found: N, 10.99.

This nitrosamine is freely soluble in hot alcohol, chloroform, or benzene but not appreciably in ether or ligroin.

II. Sequence of the Reactions.

At present, we are inclined to think that primary amines first form an imido ring with fumaroid or maleinoid compounds and then add at the double bond. Acid aniline malate, for example, forms maleinanil (imido ring) and phenylaminosuccinphenylimide (imido ring and addition) on distillation. Anschütz and Wirtz[1] have shown that maleinanil adds aniline at 100°; and we have shown that it behaves in the same way with methyl aniline. Evidently, addition is easy but we are not yet ready to say whether it is due to the imido ring, or to the maleinoid configuration, or to both causes.

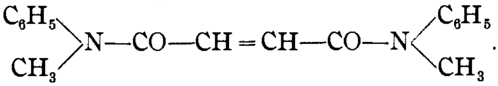
Secondary amines cannot form the imido ring but give compounds of the following type:



$$\begin{matrix} CH-CO-NR_2 \\ \| \\ CH-CO-NR_2 \end{matrix}$$

Methyl aniline and diphenylamine form such compounds with fumaric acid or fumaryl chloride, and there can be no question about their fumaroid configuration. Methyl aniline forms one and the same compound with fumaric acid, fumaryl chloride or maleic anhydride. Here we must assume conversion of a maleinoid into a fumaroid compound by the secondary amine. On the other hand, we must assume conversion of a fumaroid into a maleinoid compound, when aniline forms phenylaminosuccinphenylimide from fumaric acid. The fumaroid compounds formed by secondary amines are wholly incapable of adding a primary amine. Whether this means that fumaroid compounds in general will not permit addition, or that it cannot take place because there is no imido ring, remains unanswered. These relationships are surely perplexing, but their explanation may add much to our knowledge of fumaric and maleic acids.

Fumarmethylanilide, $C_{18}H_{18}O_2N_2$ or



$$\begin{matrix} C_6H_5 \\ CH_3 \end{matrix}\!\!>N-CO-CH=CH-CO-N\!\!<\!\!\begin{matrix} C_6H_5 \\ CH_3 \end{matrix}$$

.—Five grams of fumaric acid

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[1] *Ann.*, **239**, 137 (1887).

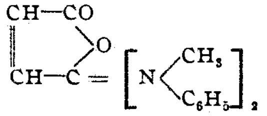
(1 mol.) and 15 grams of methyl aniline (3 mols.) were heated for several hours in an oil bath under a return condenser. We used three molecules of the secondary amine to permit formation of the anilide and addition at the double bond. The latter reaction did not take place, for we recovered nearly one-third of the amine. Crystallized from alcohol, this compound melted at 187–188°. Maleic anhydride gave the same compound with methyl aniline. It gave the following results on analysis:

Subst., 0.2013; CO_2, 0.5440; H_2O, 0.1162.
Subst., 0.2110; N, 17.8 cc.; 24°; 762.2 mm.

Calculated for $C_{18}H_{18}O_2N_2$:	C, 73.47; H, 6.12; N, 9.52.
Found:	C, 73.70; H, 6.46; N, 9.44.

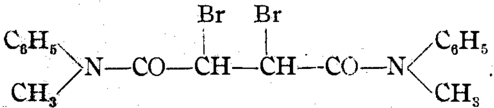
This compound crystallizes from alcohol in fine, white needles. It is freely soluble in glacial acetic acid or chloroform; moderately in benzene or acetone; slightly in ether; and insoluble in ligroin.

By the action of methyl aniline on phthalylaspartic acid Piutti[1] obtained a compound, having the same percentage composition and melting point, which he called methylphenylaminefumaride and assigned the structure:



By the action of methyl aniline on fumaryl chloride, using both substances in ether solution, we obtained a compound which melted at 187–188° and was identical in every respect with Piutti's compound and with what we have called fumarmethylanilide. Consequently, the question of its structure rests upon that of fumaryl chloride. If the latter is unsymmetrical, Piutti's formula is correct; but, since the symmetrical formula is usually accepted, we have regarded our compound as fumarmethylanilide.

Dibromosuccinmethylanilide, $C_{18}H_{18}O_2N_2Br_2$ or



$$\begin{matrix} C_6H_5 \\ CH_3 \end{matrix}\!\!>N-CO-\overset{Br}{\overset{|}{C}}H-\overset{Br}{\overset{|}{C}}H-CO-N\!\!<\!\begin{matrix} C_6H_5 \\ CH_3 \end{matrix}$$

.—For the further identification of fumarmethylanilide, it was treated with bromine in chloroform solution and converted into dibromosuccinmethylanilide. Crystallized from alcohol, this compound melted at 214° and gave the following result on analysis:

Subst., 0.1810; AgBr, 0.1512.
Calculated for $C_{18}H_{18}O_2N_2Br_2$: Br, 35.24. Found: Br, 35.55.

This compound crystallizes in short, hexagonal prisms from alcohol in which it is sparingly soluble. It is moderately soluble in hot chloro-

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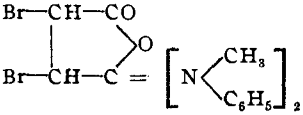
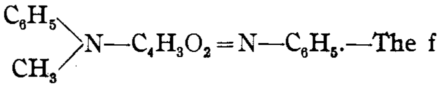
[1] *Gaz. chim. ital.*, 16, 24 (1886).

form. Except for its higher melting point, this compound is identical with Piutti's dibromomethylphenylaminefumaride which he prepared by the action of bromine on methylphenylaminefumaride and gave the structure



Because of its relation to fumarmethylanilide and fumaryl chloride, we have called this compound dibromosuccinmethylanilide.

Methylphenylaminosuccinphenylimide, $C_{17}H_{16}O_2N_2$ or



$\begin{matrix} C_6H_5 \\ CH_3 \end{matrix} \!\!> N{-}C_4H_3O_2{=}N{-}C_6H_5$.—The failure of fumarmethylanilide to add methyl aniline is not because the latter is a secondary amine, since it also refuses to add aniline even when heated with this primary amine at its boiling point. Moreover, maleinanil adds methyl aniline as easily as it does aniline.

One gram of maleinanil (1 mol.) and 0.61 gram of methyl aniline (1 mol.) were heated together at 100° for 2 hours. The product crystallized from alcohol in long needles which melted at 173°, and gave the following result on analysis:

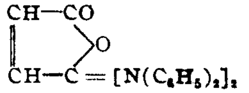
Subst., 0.2190; N, 19.7 cc.; 20°; 754.8 mm.
Calculated for $C_{17}H_{16}O_2N_2$: N, 10.00. Found: N, 10.22.

Fumartetraphenylamide, $C_{28}H_{22}O_2N_2$ or $(C_6H_5)_2N{-}CO{-}CH{=}CH{-}CO{-}N(C_6H_5)_2$.—A solution of 3.3 grams of fumaryl chloride (1 mol.) in anhydrous ether was slowly added to an ether solution of 12.5 grams of diphenylamine (4 mols.). The precipitate, treated with sodium carbonate solution, then with ether and crystallized from glacial acetic acid, melted at 272–273°, and gave the following result on analysis:

Subst., 0.2013; N, 12.5 cc.; 21°; 748.9 mm.
Calculated for $C_{28}H_{22}O_2N_2$: N, 6.70. Found: N, 6.96.

This compound is moderately soluble in hot glacial acetic acid from which it crystallizes in fine, white needles; readily soluble in hot chloroform; slightly soluble in hot alcohol or acetone; and insoluble in ether or ligroin.

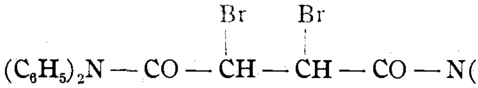
Piutti obtained from diphenylamine and fumaric or maleic acid a compound melting at 275–276°, which he gave the name diphenylaminefumarid and the structure



Without doubt, this compound is identical with that just described and should be called fumartetraphenylamide because of its relation to fumaryl chloride.

Like fumarmethylaniline, fumartetraphenylamide will not add aniline even when heated with this amine at its boiling point. Since maleinanil easily adds aniline or methyl aniline at 100°, we compared its behavior in this respect with diphenylamine and found a decided difference. Maleinanil and diphenylamine were heated together at 100° and the former was recovered unchanged. All secondary amines, therefore, are not able to add themselves to this maleinoid compound. We shall show later that diphenylamine differs from methyl aniline also in its behavior with maleic anhydride.

Dibromosuccintetraphenylamide, $C_{28}H_{22}O_2N_2Br_2$ or



$(C_6H_5)_2N-CO-\overset{\overset{Br}{|}}{C}H-\overset{\overset{Br}{|}}{C}H-CO-N(C_6H_5)_2$.—Fumartetraphenylamide gradually adds bromine in chloroform solution. The product, crystallized from glacial acetic acid, melted at 231°, and gave the following result on analysis:

Subst., 0.1965; N, 8.4 cc.; 25.5°; 751.3 mm.
Calculated for $C_{28}H_{22}O_2N_2Br_2$: N, 4.84. Found: N, 4.70.

Dibromosuccintetraphenylamide is sparingly soluble in hot glacial acetic acid, and crystallizes in fine, white needles. It is also sparingly soluble in hot chloroform; slightly in hot alcohol or acetone; and insoluble in ligroin or ether.

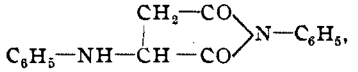
Diphenylmaleinaminic Acid, $C_{16}H_{13}O_3N$ or $(C_6H_5)_2N-CO-CH=CH-COOH$.—From methyl aniline and fumaric or maleic acid Piutti prepared methylphenylfumaraminic acid, but we could obtain only fumarmethylanilide from the same amine and fumaric acid or maleic anhydride. To compare the behavior of diphenylamine with that of methyl aniline, we heated 3 grams of maleic anhydride (1 mol.) and 10 grams of diphenylamine (2 mols.) at 100°. The mixture was liquid at first and later solidified to a mass of crystals. We recovered half the amine and did not succeed in changing the reaction by increasing the temperature. After crystallization from alcohol, the product melted at 130°, and gave the following result on analysis:

Subst., 0.2107; N, 10.2 cc.; 22°; 751.4 mm.
Calculated for $C_{16}H_{13}O_3N$: N, 5.24. Found: N, 5.42.

This compound crystallized from alcohol in radiating needles. Its ready solubility in sodium carbonate solution is evidence of its acidic character. Though not certain of the maleinoid character of this compound, we have regarded it as such because of its formation from maleic anhydride at a comparatively low temperature, but it may prove to have the fumaroid configuration.

Summary.

Aniline and fumaric or maleic acid form phenylaminosuccinphenylimide,



$$\begin{array}{l} \quad\quad\quad\quad\quad CH_2-CO \\ \quad\quad\quad\quad\quad\ | \quad\quad\quad\quad > N-C_6H_5, \\ C_6H_5-NH-CH-CO \end{array}$$

in the production of which two reactions are concerned, namely, one leading to the formation of the imido ring and the other involving addition of the amine. A further study of these reactions has led to the following results:

1. Other primary amines, such as β-naphthylamine, the three toluidines, xylidine, benzidine, benzylamine and *p*-phenetidine, resemble aniline in their behavior with fumaric acid; whereas tribromoaniline, *p*-bromoaniline and methyl- *p*-aminobenzoate fail to react.

2. The indications are that these two reactions take place in sequence and are not concurrent, since the addition of amines seems to be dependent on the imido ring. But for the present we cannot decide whether addition is due to the imido ring, to maleinoid configuration, or to both causes, until we have examined maleinoid compounds containing no imido ring. It is quite evident, however, that most fumaroid compounds cannot add amines.

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THE PREPARATION AND DECOMPOSITION OF BENZYLMONOCHLORO- AND BENZYLDICHLOROAMINES.

BY RASIK LAL DATTA.

Received September 14, 1912.

The interaction of both aliphatic and aromatic amines was studied in brief in a paper to the Chemical Society,[1] when it was shown that dichlorocarbamide is essentially a chlorinating agent, behaving analogously to hypochlorous acid. The products of the interaction of dichlorourea with amines are both monochloro and dichloro derivatives with the primary ones and monochloro with the secondary ones. The chlorination proceeds quietly without the least amount of hydrolysis with the higher members, while, with the lower members the chlorination is accompanied by brisk hydrolysis resulting in the evolution of gases. The reaction was specially studied with benzylamine, which according to the proportions of dichlorourea gave both benzyl monochloro- and benzyldichloroamines.

The original method of obtaining these chloroamines depends upon the action of sodium or calcium hypochlorite on amines.[2] In fact this was the only method known and the present method is next to it in simplicity,

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[1] *J. Chem. Soc.*, 101, 166 (1912).

[2] Berg, *Compt. rend.*, 116, 327 (1893).