[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 190.]

RESEARCHES ON QUINAZOLINES (TWENTY-SEVENTH PAPER). THE SYNTHESIS OF 3-AMINOARYL-4-QUINAZOLONES FROM ACYLANTHRANILS AND AROMATIC DIAMINES.

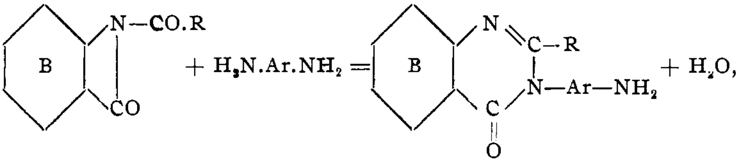
BY MARSTON TAYLOR BOGERT, ROSS AIKEN GORTNER AND CARL GUSTAVE AMEND.

Received March 11, 1911.

In continuation of our study of the synthesis of quinazolines from acylanthranils and primary amines[1] we have investigated also the behavior of the aromatic diamines with various acylanthranils, and the present paper records some of the results.

It has been shown by Klaber[2] that when acetanthranils condense with primary aliphatic diamines the reaction is a complicated one, resulting in the formation of at least three distinct products, but no appreciable amount of the aminoalkylquinazolone. We were, therefore, somewhat surprized to discover that when aromatic primary diamines are condensed with acylanthranils under proper conditions, not only is the reaction a remarkably smooth and simple one, but the desired aminoarylquinazolone is often produced in practically theoretical yield. The condensation can be effected either by gently fusing the two together (best), or by heating a mixture of the two in a suitable solvent.

The reaction by which these new bases are formed may be represented as follows:



in which B is a simple or substituted benzene nucleus, R a simple or substituted alphyl or aryl radical, and Ar a simple or substituted aromatic radical.

The condensation thus depends upon the presence of at least one primary amino group, while the other aromatic amino group may be primary, secondary or tertiary.

The ease and rapidity with which these new amine bases may be obtained in high yield and purity opens up a most extensive field and one into which we have as yet made but a few hasty trips.

The aminoarylquinazolones carrying a primary amino group show in general the following properties: They are crystallin or pulverulent

---

[1] Anschütz, Schmidt and Greiffenberg, *Ber.*, 35, 3480 (1902); Bogert, *et al.*, THIS JOURNAL, 27, 649, 1305, 1327 (1905); 28, 94, 884, 1449 (1906); 29, 82, 517, 729 (1907); 30, 807 (1908); 31, 943, 1071 (1909); 32, 119, 1297, 1654 (1910).

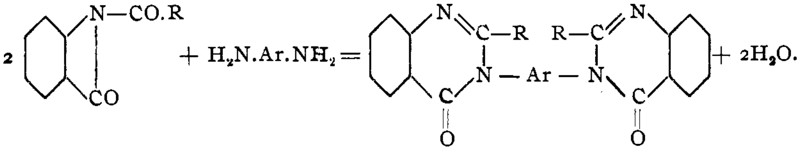
[2] Dissert., Columbia University, 1907, pp. 34, *et seq.*

solids of definit melting or decomposing points; very slightly soluble in water or in dilute aqueous solutions of the caustic alkalies; soluble in dilute hydrochloric or sulfuric acids, and more or less soluble in ninety-five per cent. alcohol. By careful purification, they can generally be obtained practically colorless, but on standing, or more rapidly on heating, they gradually darken.

When the primary amino groups are eliminated from these aminoarylquinazolones, the compounds thus obtained are not decomposed as to the nucleus when boiled with a twenty per cent. aqueous or alcoholic sodium hydroxide solution, but when fused with caustic alkali give aniline or substituted anilines. Many of these new bases are remarkably triboelectric. Diazotized in the usual way, they yield diazo or tetraazo salts which unite with suitable couplers to form valuable azo dyestuffs, some of which will be described in a subsequent paper.

The following diamines were used in our experiments: *o*-, *m*- and *p*-phenylenediamines, 2,4- and 2,5-diaminotoluene, benzidine, *o*-tolidine (3,3′-dimethyl-4,4′-diaminodiphenyl), ethoxybenzidine (3-ethoxy-4,4′-diaminodiphenyl) and dianisidine (3,3′-dimethoxy-4,4′-diaminodiphenyl). All of these condensed smoothly to aminoaryl quinazolones except the *o*-phenylene diamine. We have also condensed with acylanthranils di- and poly-amines containing but one primary amino group. The substances thus produced contain no diazotizable amino group, but can be used as couplers in the preparation of azo dyestuffs, or as starting points for the production of other classes of dyes.

The acylanthranils employed were acetanthranil,[1] 5-bromoacetanthranil,[2] 5-nitroacetanthranil,[3] 4- and 5-acetaminoacetanthranils,[4] benzoylanthranil,[5] and *m*- and *p*-nitrobenzoylanthranils. The acetanthranils were prepared by boiling the corresponding anthranilic acids, or their acetyl derivatives, with excess of acetic anhydride, while the benzoylanthranils were obtained by boiling the corresponding benzoylanthranilic acids with excess of acetic anhydride. The benzoylanthranils apparently do not yield aminoarylquinazolones under the same conditions as the acetanthranils, but rather diquinazolonyl compounds:



---

[1] Bogert and Seil, This Journal, 29, 529 (1907).

[2] Bogert and Hand, *Ibid.*, 27, 1484 (1905).

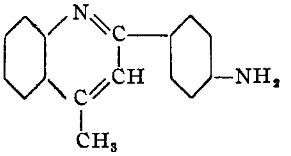
[3] Bogert and Cook, *Ibid.*, 28, 1451 (1906).

[4] Bogert, Amend and Chambers, *Ibid.*, 32, 1297 (1910).

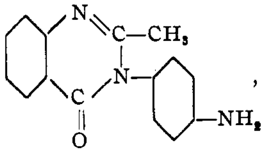
[5] Friedländer and Wleügel, *Ber.*, 16, 2229 (1883).

Our experience has been to show that this diquinazolonyl formation occurs to a very limited extent, or not at all, with acetanthranil even when the latter is used in large excess. With the benzoylanthranils, however, as just stated, the chief product appears to be the diquinazolonyl, with little or no aminoarylquinazolone. Diquinazolonyls thus formed are readily isolated by virtue of their sparing solubility in the ordinary solvents.

A comparison of the formulas of these new amino compounds and flavaniline shows a rough similarity in structure



(Flavaniline base)



(2-Methyl-3-*p*-aminophenyl-4-quinazolone)

but on testing the above quinazolone compound, it was found when pure to be without tinctorial power.

Experimental.

I. Preparation of the Acylanthranils.

Acetanthranil is readily and rapidly prepared in large yield (80–90 per cent. of the theory) by the following simple process: Three parts of acetic anhydride are heated to 120–30° and one part finely pulverized anthranilic acid gradually added. The acetic acid formed as the by-product on the addition of the anthranilic acid immediately distils over (the temperature of the solution being kept above the boiling point of the acetic acid but below that of its anhydride), and the strength of the anhydride is thus maintained. After all the anthranilic acid has been added, the distillation is continued until the volume of the solution is reduced to about two-thirds or one-half its original bulk. On cooling, the acetanthranil generally crystallizes out at once. In case crystallization does not follow immediately upon cooling, it can be induced very easily by scratching the sides of the containing vessel or by seeding. In a properly arranged apparatus, the anthranilic acid can be added in a steady stream and (using 500 g. anthranilic acid) in 15–30 mins. the operation is usually completed and the crystallized acetanthranil obtained. As thus produced, and dried in absence of moisture, the acetanthranil is practically pure. In a moist atmosphere it rapidly hydrolyzes and must then be recrystallized from acetic anhydride once more.

5-Bromoacetanthranil,[1] *5-nitroacetanthranil*[2] and *4-* and *5-acetaminoacetanthranils*[3] were prepared as already described in the literature.

---

[1] Bogert and Hand, *Loc. cit.*

[2] Bogert and Cook, *Ibid.*

[3] Bogert, Amend and Chambers, *Ibid.*

Benzoylanthranil[1] is easily obtained by boiling benzoylanthranilic acid with excess of acetic anhydride. It is not readily hydrolyzed by hot water, but boiling with dilute hydrochloric acid changes it to benzoylanthranilic acid. In the literature, the melting point of this anthranil is given as 122–3°. By recrystallization from acetic anhydride, we have raised its melting point to 124.5° (cor.).

m-Nitrobenzoylanthranilic acid, $(1)HOOC.C_6H_4(2)NHCOC_6H_4NO_2$ (*m*-).—An aqueous solution of sodium anthranilate was treated with the calculated amount of *m*-nitrobenzoyl chloride and the precipitated *m*-nitrobenzoylanthranilic acid purified by crystallization from alcohol.

Calculated for $C_{14}H_{10}O_5N_2$: N, 9.79.
Found: N, 9.84.

The pure compound crystallizes from alcohol in colorless prisms, melting at 233.5° (cor.), which are very slightly soluble in water.

p-Nitrobenzoylanthranilic acid, prepared in a similar manner from sodium anthranilate and *p*-nitrobenzoyl chloride, crystallizes from alcohol in small, nearly colorless needles, melting at 235.5° (cor.). It is more soluble in alcohol than the meta compound and explodes when heated suddenly.

Calculated for $C_{14}H_{10}O_5N_2$: N, 9.79.
Found: N, 9.80.

m-Nitrobenzoylanthranil, $\overline{CO.C_6H_4.N}COC_6H_4NO_2$(*m*-), was prepared by boiling *m*-nitrobenzoylanthranilic acid with excess of acetic anhydride and recrystallizing the crude product from fresh acetic anhydride. It forms small colorless, or cream-colored, needles, melting at 167–8° (cor.). It is hydrolyzed by hot dilute hydrochloric acid, but not readily by boiling water.

Calculated for $C_{14}H_8O_4N_2$: N, 10.44.
Found: N, 10.53.

p-Nitrobenzoylanthranil, prepared in a similar manner, crystallizes from acetic anhydride in light yellow needles, melting at 207° (cor.), hydrolyzed by hot dilute hydrochloric acid, but not readily by boiling water.

Calculated for $C_{14}H_8O_4N_2$: N, 10.44.
Found: N, 10.45.

II. Condensations with Acetanthranil.

2-Methyl-3-m-aminophenyl-4-quinazolone, $CH_3\overline{C : N.C_6H_4.CO.N}C_6H_4NH_2$-(*m*-).—Two grams *m*-phenylenediamine hydrochloride in aqueous solution were treated with the calculated amount of sodium hydroxide, and a gram and a half of acetanthranil added to the solution. The anthranil

---

[1] Friedländer and Wleügel, *Loc. cit.*; Anschütz and Schmidt, *Ber.*, **35**, 4373 (1902); Heller, *Ibid.*, **36**, 2766 (1903); Bamberger, *et al.*, *Ibid.*, **36**, 822 (1903), and **42**, 1649 (1909); Heller and Fiesselmann, *Ann.*, **324**, 134 (1902).

dissolved instantly. The solution was evaporated to dryness, the residue extracted with 95 per cent. alcohol and the alcoholic solution concentrated to crystallization. Yield, 0.5 g. The crystals obtained were recrystallized from dilute alcohol, dried at 110° and analyzed:

Calculated for $C_{15}H_{13}ON_3$: C, 71.71; H, 5.18; N, 16.73.
Found: C, 71.77; H, 5.26; N, 16.75.

A better method for the preparation of the above substance is the following: An equimolecular mixture of acetanthranil and *m*-phenylenediamine is heated to fusion and kept at the temperature of initial fusion for about five minutes. The product is finely pulverized, washed thoroughly with dilute sodium hydroxide solution, then with water, is redissolved in dilute hydrochloric acid, the solution filtered, the filtrate reprecipitated with sodium hydroxide, the precipitate washed thoroughly with water and dried. It is then usually sufficiently pure for the preparation of azo dyes. If desired, it can be further purified, as noted above, by recrystallization from dilute alcohol. Yield, 70–80 per cent. of the theory.

Carefully purified and dried over alkali *in vacuo*, it can be obtained practically colorless. As usually prepared, it forms crystals resembling wheat beards in shape and color. It melts at 210° (cor.), is very slightly soluble in water, but easily soluble in 95 per cent. alcohol or in dilute hydrochloric acid.

In one experiment, an aqueous solution of *m*-phenylenediamine was treated with acetanthranil and the product crystallized from alcohol as usual. The quinazolone was thus obtained in crystals, but on diluting the mother-liquor a different substance separated. This other compound was recrystallized from dilute alcohol, and then melted at 158° (cor.). It contained 10.22 per cent. nitrogen, while the amide intermediate in the quinazolone condensation contains 15.61 per cent. nitrogen. It was not identified.

Two grams of the 2-methyl-3-*m*-aminophenyl-4-quinazolone were dissolved in 4 cc. water and 1.5 g. concentrated sulfuric acid, 10 cc. more water added, the solution cooled to 0° and diazotized with the calculated amount of sodium nitrite using starch paper as indicator. The resultant diazo solution was warmed for an hour on the water bath. Nitrogen was evolved and the solution turned dark red. It was heated to boiling, filtered boiling hot, and the filtrate neutralized. On cooling, a yellow amorphous mass separated, slightly soluble in water, soluble in caustic alkalies to a deep red solution, and also dissolving in acids. It could not be crystallized or purified and was not further investigated. In addition to the above, a small amount of an insoluble substance was formed in the reaction.

2-Methyl-3-p-aminophenyl-4-quinazolone. — *p*-Phenylenediamine hydrochloride was dissolved in water, a slight excess of potassium hydroxide added, and then slightly less than the calculated amount of acetanthranil. On warming the solution, the quinazolone separated in plates of a faint pinkish gray cast, melting at 220° (cor.). Yield, two grams from two grams anthranil. By fusing together the free diamine and the acetanthranil, as described above for the meta compound, a much larger yield (80–90 per cent. of the theory) can be secured.

Calculated for $C_{15}H_{13}ON_3$: N, 16.73.
Found: N, 16.82.

The compound is very slightly soluble in water or in dilute caustic alkalies, easily soluble in 95 per cent. alcohol or in dilute hydrochloric acid. From alcohol, it often separates as a gray powder. Freshly precipitated from acid solution and dried carefully *in vacuo* over alkali, it can be obtained practically colorless.

3,3'-p-Phenylene-bis-(2-methyl-4-quinazolone),

$CH_3C : N.C_6H_4.CO.N(1)C_6H_4(4)N.CO.C_6H_4.N : CCH_3$.— A small amount of this diquinazolonyl was found in one of the above *p*-phenylenediamine condensations. It was easily separated from the *p*-aminophenylquinazolone as it is much less soluble in alcohol. It crystallized from a large volume of hot alcohol in colorless, microscopic crystals, melting above 300°.

Calculated for $C_{24}H_{18}O_2N_4$: N, 14.20.
Found: N, 14.17.

It is insoluble in water and dissolves in alcohol with difficulty. In other experiments, *p*-phenylenediamine was fused with excess of acetanthranil without the formation of any appreciable amount of the diquinazolonyl compound.

2-Methyl-3-m-aminotolyl-4-quinazolone,

$CH_3C : N.C_6H_4.CO.NC_6H_3(NH_2)(m\text{-})CH_3(o\text{-}, \text{ or } p\text{-})$.— An equimolecular mixture of acetanthranil and 2,4-diaminotoluene was gradually heated on the sand bath until the mass boiled. When cool the glassy melt was pulverized, dissolved in dilute hydrochloric acid, the solution filtered, and the filtrate precipitated by potassium hydroxide. The sticky precipitate slowly hardened. It was then powdered, washed thoroughly with water, and crystallized from dilute alcohol. Minute colorless needles were thus obtained, melting at 131.4° (cor.).

Calculated for $C_{16}H_{15}ON_3$: N, 15.8.
Found: N, 15.7.

Acetanthranilic m-aminotoluidide,

$(1)CH_3CONHC_6H_4(2)CONHC_6H_3(NH_2)(m\text{-})CH_3(o\text{-}, \text{ or } p\text{-})$.— In another experiment, an equimolecular mixture of 2,4-diaminotoluene and acetanthranil was gently fused, the product washed with dilute potassium hydroxide solution, dissolved in dilute hydrochloric acid, filtered, the filtrate reprecipitated by alkali, the precipitate washed and recrystallized from alcohol. Stellate groups of colorless needles resulted, melting at 137–8° (cor.), insoluble in water, but easily soluble in alcohol.

Calculated for $C_{16}H_{17}O_2N_3$: N, 14.84.
Found: N, 14.68.

We have not determined the position of the methyl group in this or the foregoing compound, so that we do not know which of the two amino groups took part in the condensation.

2-Methyl-3-p-aminotolyl-4-quinazolone,

$CH_3C : N.C_6H_4.CONC_6H_3(NH_2)(p\text{-})CH_3(o\text{-}, \text{ or } m\text{-})$,

was prepared in a manner entirely similar to that employed for the *m*-aminotolyl compound, using 2,5- instead of 2,4-diaminotoluene, the diamine being first carefully purified by recrystallization from ethyl acetate.

Calculated for $C_{16}H_{15}ON_3$: N, 15.8.
Found: N, 15.9.

The pure substance forms minute crystals, rather darker than those of its isomer, and melting at 169° (cor.).

2-Methyl-3-[4'-aminodiphenyl]-4-quinazolone,

$CH_3C : NC_6H_4CON(4)C_6H_4.C_6H_4NH_2(4')$.—

1.6 g. benzidine and 1.5 g. acetanthranil were gently fused together. The mass quickly set to a compact brown solid. The temperature was kept at the point of initial fusion for about five minutes. The cold melt was finely pulverized, washed with dilute potassium hydroxide solution, then with water, dissolved in dilute hydrochloric acid, the solution filtered, the filtrate precipitated with potassium hydroxide, the precipitate washed with water and dried. Yield, 2.2 g. In later experiments, the yield was raised to 90–100 per cent. of the theory.

Calculated for $C_{21}H_{17}ON_3$: N, 12.84.
Found: N, 12.70.

The substance burns with considerable difficulty. As thus obtained, the compound is generally a pale yellow or brownish powder, m. p. 282–3° (cor.), moderately soluble in 95 per cent. alcohol, very slightly soluble in water, but dissolving easily in dilute hydrochloric acid.

2-Methyl-3-[4'-aminoditolyl]-4-quinazolone,

$CH_3C:NC_6H_4CON(4)C_6H_3(3)(CH_3).C_6H_3(3')(CH_3)(4')(NH_2)$,

was prepared from *o*-tolidine and acetanthranil in essentially the same manner as the benzidine compound above. Yield, about 90 per cent.

Calculated for $C_{23}H_{21}ON_3$: N, 11.83.
Found: N, 11.69.

The pure substance is practically colorless. As usually obtained, it is a pale brownish powder, m. p. 80–1° (cor.). This drop of 200° in melting-point as compared with the benzidine compound is rather surprizing. The substance is very slightly soluble in water, but easily dissolves in 95 per cent. alcohol or in dilute hydrochloric acid.

2-Methyl-3-[4'-aminoethoxydiphenyl]-4-quinazolone,

$CH_3C : NC_6H_4CON(4)C_6H_3(3)(OC_2H_5).C_6H_4NH_2(4)'$, or

$CH_3C : NC_6H_4CON(4)C_6H_4.C_6H_3(3')(OC_2H_5)(4')(NH_2)$.—

One molecule ethoxybenzidine and slightly more than one molecule acetanthranil were fused together in an oil bath. The product was washed with boiling potassium hydroxide solution (1 : 2) and then allowed to cool. When cold it was finely pulverized, washed with water, and purified as already described for the benzidine compound. Dried over sulfuric acid and analyzed, the following figure was obtained:

Calculated for $C_{22}H_{21}O_2N_3$: N, 11.32.
Found: N, 11.31.

Brownish powder, m. p. 86–7° (cor.), very slightly soluble in water, readily soluble in 95 per cent. alcohol or in dilute hydrochloric acid. The location of the ethoxy group has not been determined definitly.

2-Methyl-3-[4'-aminodianisyl]-4-quinazolone,

$CH_3C : NC_6H_4CON(4)C_6H_3(3)(OCH_3).C_6H_3(3')(OCH_3)(4')(NH_2)$.—

An equimolecular mixture of acetanthranil and *o*-dianisidine was fused at 100°. The black melt was dissolved in alcohol and the solution diluted with water. The precipitate which separated was dissolved in dilute hydrochloric acid, the solution filtered and reprecipitated with dilute alkali. This precipitate was washed thoroughly and dried in a desiccator over sulfuric acid. Yield, 95–100 per cent.

Calculated for $C_{22}H_{21}O_2N_3$: N, 10.85.
Found: N, 11.04.

The compound is light colored and crystallin when freshly prepared, but quickly darkens. It is insoluble in water, but easily soluble in alcohol or in dilute mineral acids, giving very dark solutions. It melts at 72–3° (cor.).

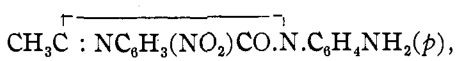
III. Condensations with Substituted Acetanthranils.

2-Methyl-6-bromo-3-p-aminodiphenyl-4-quinazolone,

$CH_3C : NC_6H_3BrCO.N.C_6H_4.C_6H_4NH_2(4')$,

prepared by heating together 5-bromoacetanthranil and benzidine, forms a light brown powder, melting at 198–9° (cor.), insoluble in water or in aqueous solutions of alkalies, and not readily soluble in dilute hydrochloric acid. It diazotizes readily, the diazonium salts being difficultly soluble.

2-Methyl-6-nitro-3-p-aminophenyl-4-quinazolone,

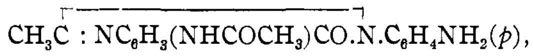


$$CH_3C : NC_6H_3(NO_2)CO.N.C_6H_4NH_2(p),$$

prepared by fusing together an equimolecular mixture of 5-nitroacetanthranil and *p*-phenylenediamine, was obtained as a dark brown powder, melting with apparent decomposition at 259–60° (cor.), and dissolving easily in dilute hydrochloric acid or in 95 per cent. alcohol.

Not enough of either of the above substances was available for an analysis, but there seems no reason for assuming that the condensation in these cases followed any other course than that already described for similar mixtures.

2-Methyl-6-acetamino-3-p-aminophenyl-4-quinazolone,



$$CH_3C : NC_6H_3(NHCOCH_3)CO.N.C_6H_4NH_2(p),$$

was prepared in the same way as the corresponding 7-acetamino body (which follows) and shows similar properties. It was purified by solution in dilute hydrochloric acid and reprecipitation with potassium hydroxide. The purplish precipitate thus thrown down softens and shrinks together somewhat at 170–5°, and melts at about 280° (uncor.).

Calculated for $C_{17}H_{16}O_2N_4$: N, 18.18.
Found: N, 18.06.

2-Methyl-7-acetamino-3-m-aminophenyl-4-quinazolone.—An equimolecular mixture of 4-acetaminoacetanthranil and *m*-phenylenediamine was heated gradually. It first softened, then hardened again, solidifying at about 110°. Dissolved in dilute hydrochloric acid and reprecipitated with potassium hydroxide, it came down in an amorphous, colorless form, gradually browning on standing, and was quite sticky. Dried thoroughly in a desiccator, it melted above 310° (cor.).

Calculated for $C_{17}H_{16}O_2N_4$: N, 18.18.
Found: N, 18.3.

2-Methyl-7-acetamino-3-p-aminophenyl-4-quinazolone.—An equimolecular mixture of 4-acetaminoacetanthranil and *p*-phenylenediamine was heated in the oil bath with constant stirring. At 80–100° the mass became sticky, at 100–10° most of the reaction was completed. The mass does not melt then even if carried up to 195°. The dark-colored product when cold was pulverized fine, washed with ten per cent. sodium hydroxide solution, then with water, redissolved in dilute hydrochloric acid filtered, the filtrate made alkaline with sodium hydroxide, the precipitate filtered out, washed thoroughly with water and dried. It is a dark purplish blue powder, melting above 360°, slightly soluble in cold water, readily soluble in 95 per cent. alcohol, soluble in dilute mineral acids, and but very slightly soluble in dilute aqueous caustic alkalies. It is strongly triboelectric. From 2 g. of the anthranil, 2.85 grams of the crude condensation product (before re-solution and reprecipitation) were secured.

Calculated for $C_{17}H_{16}O_2N_4$: C, 66.23; H, 5.20; N, 18.18.
Found: C, 65.83; H, 5.26; N, 18.40.

2-Methyl-7-amino-3-p-aminophenyl-4-quinazolone.—The above acetyl derivative was boiled with excess of dilute (20 per cent.) hydrochloric acid for three hours and the purple solution then made alkaline with sodium hydroxide. The free base separated as a dark bluish precipitate which became crystallin on standing. It was purified by re-solution in dilute hydrochloric acid and reprecipitation with alkali, the pure substance melting at 287° (cor.). Its solubilities are about the same as those of the acetyl derivative and it, too, is triboelectric.

Calculated for $C_{15}H_{14}ON_4$: N, 21.05.
Found: N, 20.97.

2-Methyl-7-acetamino-3-aminotolyl-4-quinazolone,

$\overline{\mathrm{CH_3C : NC_6H_3(NHCOCH_3)CO.N}}\mathrm{.C_6H_3(NH_2)}(m)\mathrm{(CH_3)}(o, \text{ or } p)$.—An intimate mixture of 0.3 gram 2,4-diaminotoluene and 0.5 gram 4-acetaminoacetanthranil was carefully heated. At 70° the mass became adhesive, and at 100° it fused to a thick paste. The temperature was finally raised to 115°. The crude product was purified as described above, the pure substance being light brown and melting at 290° (cor.).

Calculated for $C_{18}H_{18}O_2N_4$: N, 17.39.
Found: N, 17.59.

In order to determin in what position the quinazolone was united to the toluidine molecule, some of the above compound was boiled with excess of acetic anhydride. The substance dissolved easily in the hot anhydride and minute, colorless needles separated on cooling the solution. Recrystallized thrice from alcohol, it melted at 268.5° (cor.), and was decidedly triboelectric. On analysis, it was found to contain 14.1 per cent. nitrogen. This does not correspond to any simple acetylation product. The diacetyl derivative contains 15.4 per cent. nitrogen, the triacetyl 13.8, and the tetraacetyl 12.5. Dried for three hours at 130–60° and again analyzed, 14.53 per cent. nitrogen was found. Recrystallized from acetic anhydride and analyzed once more, 14.3 per cent. nitrogen was obtained. As the purpose of the acetylation was the protection of the amino group during oxidation, it was decided to proceed with the oxidation without further attempts to purify the acetylation product. 3.5 grams of it, 7 grams magnesium sulfate, and 500 cc. of water, were mixed in a flask with return condenser and the mixture heated to boiling. 7 grams potassium permanganate were added gradually to the boiling solution (during one and a half hours), and after two hours' boiling the solution was allowed to cool and the precipitated manganese oxide filtered out. A portion of the filtrate acidified with hydrochloric acid gave a turbidity which cleared on further addition of the acid with evolution of carbon dioxide. Acetic acid gave similar results. The filtrate was therefore carefully treated with dilute acetic acid until it became turbid, and the turbid solution then let stand. In a day or two a small amount of sticky precipitate separated from this turbid solution, leaving the supernatant liquid clear. The amount of the precipitate was too small to carry the investigation further.

2-Methyl-7-amino-3-aminotolyl-4-quinazolone.—The acetyl group was split off the above 7-acetamino compound by boiling it for an hour with ten per cent. hydrochloric acid. The free base was precipitated by alkali as a sticky paste. Purified, washed and dried, it melts at 262° (cor.).

Calculated for $C_{16}H_{16}ON_4$: N, 20.0.
Found: N, 19.95.

2-Methyl-7-acetamino-3-[4'-aminodiphenyl]-4-quinazolone, $CH_3C : NC_6H_3(NHCOCH_3)CO.N.C_6H_4.C_6H_4NH_2(4')$.—An equimolecular mixture of 4-acetaminoacetanthranil and benzidine was gradually heated. The mixture became pasty and adhesive at 100°, then hardened. On treating the crude product with dilute hydrochloric acid, a considerable amount remained insoluble. The soluble constituent was reprecipitated by alkali and dried in an air bath (causing it to darken). It decomposes at 296–7° (cor.).

Calculated for $C_{23}H_{20}O_2N_4$: N, 14.58.
Found: N, 14.70.

The product insoluble in hydrochloric acid melts with decomposition at 256° (cor.). Found: N, 12.31. This figure corresponds to the diquinazolonyl compound (*i. e.*, one molecule of the diamine condensed with two of the anthranil), $CH_3C : NC_6H_3(NHCOCH_3)CO.N.C_6H_4.C_6H_4.N.CO(CH_3CONH)C_6H_3N : CCH_3$, with six molecules of water, but not enough of the material was separated to study it further.

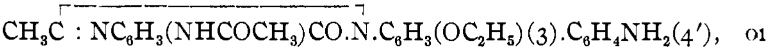
2-Methyl-7-acetamino-3-[4'-aminoditolyl]-4-quinazolone, $CH_3C : NC_6H_3(NHCOCH_3)CO.N.C_6H_3(3)(CH_3).C_6H_3(3')(CH_3)(4')(NH_2)$.—An equimolecular mixture of 4-acetaminoacetanthranil and *o*-tolidine was heated gradually to 150°. At 110° the mixture became adhesive, and pasty at 120–5°. The resultant brown paste was purified as usual and a product obtained melting at about 105°.

Calculated for $C_{25}H_{24}O_2N_4$: N, 13.59.
Found: N, 13.35.

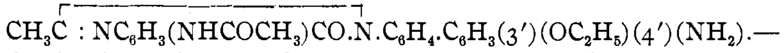
The substance does not crystallize well from 95 per cent. alcohol. It was dissolved in hot alcohol, water added to turbidity and the solution allowed to cool. The substance separated in an amorphous sticky condition. Dried and pulverized, it formed a light brown powder, melting at about 95°, darkening and decomposing at 120–5°.

Calculated (as above):	N, 13.59.
Found:	N, 13.34.

2-Methyl-7-acetamino-3-[ethoxy-4'-diphenyl]-4-quinazolone,



$CH_3C : NC_6H_3(NHCOCH_3)CO.N.C_6H_3(OC_2H_5)(3).C_6H_4NH_2(4')$, or

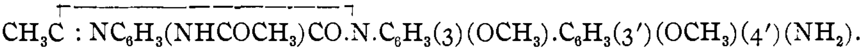


$CH_3C : NC_6H_3(NHCOCH_3)CO.N.C_6H_4.C_6H_3(3')(OC_2H_5)(4')(NH_2)$.—An equimolecular mixture of 4-acetaminoacetanthranil and ethoxybenzidine was heated gradually to 150°. At 100° the mixture softened and became pasty at 130°. The crude product, after purification in the usual way, melted at about 105–10°, and decomposed at about 120–5°.

Calculated for $C_{25}H_{24}O_3N_4$:	N, 13.08.
Found:	N, 12.56, 12.43.

As the wide melting points and low analytical results indicate, we probably failed in this case to get a pure product.

2-Methyl-7-acetamino-3-[4'-aminodianisyl]-4-quinazolone,



$CH_3C : NC_6H_3(NHCOCH_3)CO.N.C_6H_3(3)(OCH_3).C_6H_3(3')(OCH_3)(4')(NH_2)$.—An intimate mixture of 1.2 grams each 4-acetaminoacetanthranil and di-*o*-anisidine was heated carefully. At 85° it became slightly sticky, at 120° pasty. It was finally heated to 140° and then allowed to cool. The crude product dissolved in hydrochloric acid and reprecipitated with alkali separated as a white, flocculent precipitate, which gradually turned purplish. It was further purified by re-solution and reprecipitation, and then showed a melting point of about 144°.

Calculated for $C_{25}H_{24}O_4N_4$:	N, 12.61.
Found:	N, 12.23.

This unsatisfactory analytical result was due to the difficulty in thoroughly purifying the substance.

We therefore acetylated the compound with acetic anhydride, and crystallized the product twice from alcohol, getting a substance melting at 239° (cor.), which is apparently the tetraacetyl compound:

Calculated for tetraacetyl compound ($C_{31}H_{33}O_7N_7$):	N, 9.83.
Found:	N, 9.92.

IV. Condensations with Benzoylanthranils.

Benzoylanthranil and Ammonia.—Anschütz, Schmidt and Greiffenberg[1] passed ammonia into a boiling absolute alcohol solution of benzoylanthranil and obtained the *o*-benzoylaminobenzamide, melting at 214-5° with decomposition.

---

[1] Anschütz, Schmidt and Greiffenberg, *Ber.*, 35, 3484 (1902).

We boiled benzoylanthranil with excess of strong aqueous ammonia and recrystallized from alcohol the white solid which separated. Minute, colorless crystals were thus obtained, which softened at 108° (cor.) and melted to a turbid liquid at 118° (cor.), the melt becoming clear at a slightly higher temperature. From what follows, it seems probable that this is the secondary amide combination:

Calculated for $(C_6H_5CONHC_6H_4CO)_2NH$: N, 9.09.
Found: N, 9.09.

Boiled with potassium hydroxide solution, it dissolved and, on acidifying the solution, long silky needles of 2-phenyl-4-quinazolone (m. p. 237.5° (cor.)) separated, a compound already in the literature.[1]

Benzoylanthranil and p-Phenetidine.—The two were mixed dry in molecular proportion and the mixture boiled for several minutes. On cooling, the mass solidified. It was washed with alcohol, and then appeared in minute colorless crystals, melting at 213° (cor.), very difficultly soluble in alcohol. It has not been further investigated.

Benzoylanthranils and Aromatic Diamines.—Benzoylanthranil, *m*- and *p*-nitrobenzoylanthranils, were fused with *m*- and *p*-phenylenediamines. The products were insoluble in acids or alkalies, slightly soluble in alcohol, and could not be diazotized. It seems unlikely, therefore, that they were the desired quinazoline condensations. Judging by the nitrogen determinations in the case of the *m*- and *p*-nitro derivatives, the products are the diquinazolonyls. No aminoaryl quinazolones were isolated.

3,3'-m-Phenylene-bis[2-m-nitrophenyl-4-quinazolone],

$$O_2NC_6H_4.\overline{C : NC_6H_4CO.N}(1)C_6H_4(3)\overline{N.COC_6H_4N : C}.C_6H_4NO_2.$$—

An equimolecular mixture of *m*-nitrobenzoylanthranil and *m*-phenylenediamine was fused and then allowed to cool. The mass was powdered, and warmed first with dilute and then with concentrated hydrochloric acid. Little, if anything, was dissolved by this treatment. It was then washed thoroughly with water, then with strong sodium hydroxide solution (to remove any acetanthranilic acid), and again with water, and dried.

As thus purified, it is a yellowish powder, practically insoluble in water, alcohol, ethyl acetate or benzene. On heating, it darkens and shrinks at 180°, finally melting at 226°.

Calculated for $C_{34}H_{20}O_6N_6$: N, 13.81.
Found: N, 14.02.

3,3'-m-Phenylene-bis-[2-p-nitrophenyl-4-quinazolone], prepared in similar manner, using the *p*-nitrobenzoylanthranil instead of the meta isomer, was likewise obtained as a yellow insoluble powder.

---

[1] Körner, *J. prakt. Chem.*, [2] 36, 155 (1887); Bischler and Lang, *Ber.*, 28, 289 (1895); Anschütz, Schmidt and Greiffenberg, *Loc. cit.*

Calculated for $C_{34}H_{20}O_6N_6$: N, 13.81.
Found: N, 14.0.

It melts at 207°. Boiled with hydrochloric acid, it turns white but does not dissolve.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

PSEUDO ACID ESTERS IN THE MESOXALIC ESTER SYNTHESIS.[1]

BY RICHARD SYDNEY CURTISS AND JOHN ANTON KOSTALEK.

Received March 25, 1911.

In a synthesis of mesoxalic esters which was discovered by one of us and reported in the *American Chemical Journal*,[2] the red oxides of nitrogen were allowed to act an malonic ester at —10°. The ethyl mesoxalate produced was removed by distillation and the residual oil was found to contain a high percentage of nitrogenous esters, having acid properties, and which produced with alcoholic potash a yellow salt. The analysis showed this salt to contain a percentage of potassium according well with that of the salt of ethyl isonitrosomalonate, $K{-}O{-}N=C=(CO_2C_2H_5)_2$, and it was at first supposed to be this compound. Isonitrosomalonic acid was made by Baeyer,[3] who found that its aqueous solution decomposes at 40° into hydrocyanic acid, carbon dioxide, and water. Conrad and Bischoff[4] confirm this result.

It was noticed at that time that no odor of prussic acid was apparent when the yellow potassium salt was boiled with alkali to saponify the ester, and subsequently heated with hydrochloric acid to liberate and decompose the isonitrosomalonic acid. The results of the test were therefore not in accordance with this characteristic of the potassium salt of isonitrosomalonic acid. The complete analysis of this salt, later, showed that it was not a derivative of ethyl isonitrosomalonate, and we wish therefore to correct the statements made in the former paper[5] concerning the identity of this salt, and in accordance with the results herein presented.

This investigation was begun by the senior author, and Mr. Ruric Creegan Roarke, to whom we owe much for the initial experiments and attempts in separating and studying the potassium salts of ethyl nitromalonate and ethyl dinitroacetate. Our primary idea was the study

---

[1] Abstract of a thesis presented by Mr. Kostalek to the Graduate School of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Curtiss, *Am. Chem. J.*, **35**, 477.

[3] *Ann.*, **131**, 293.

[4] *Ibid.*, **209**, 211.

[5] *Ibid.*, **35**, 478, 482, 483.