

Material used.	Weight per cu. ft. of fine ground mixture. Lbs.	Weight of raw material consumed. Lbs.	Weight of clinker produced. Lbs.
Marl and clay mixture.	52	3.8	2.2
Limestone clay mixture.	88	5.8	3.5
Cement rock mixture.	92	6.2	3.8
Chalk and clay mixture.	70	4.8	2.8

From these results it would appear that the higher the volume weight, or the greater the weight of the ground raw cement mixture per cubic foot, the greater is the output of a kiln, and that the quantity of raw cement material measured in cubic feet, that a kiln will heat to the necessary cement-forming temperature is nearly a constant, all other conditions being the same.

A kiln therefore, using a marl and clay mixture consuming 1125 pounds of coal per hour and producing 1600 pounds cement consumes 2760 pounds cement mixture having a volume of 53 cubic feet. A kiln of the same construction working on a cement rock mixture and consuming 1125 pounds of coal per hour and producing 3200 pounds of cement per hour, burns 52 cubic feet of raw cement mixture per hour. The more dense the raw material, the less space it will occupy in a kiln, and the greater will be the resulting weight of cement which a kiln will produce.

Drying the wet marls of Michigan, Ohio, Indiana, Canada, etc., will not suffice to make them economical materials. Marl is too bulky for a rotary kiln to handle economically; chalk is also too light, and both these materials must in time cease to be a factor in the cement industry. They will gradually be displaced for reasons of economy, and their place will be filled by limestone and cement rock, and even the lighter types of limestone will give way to the heavier class. The higher the specific gravity the better, from an economical point of view.

INDIAN PORTLAND CEMENT CO.,
NEODESHA, KANSAS.

THE PREPARATION OF 6-BROM-4-KETODIHYDROQUIN- AZOLINES FROM 5-BROM-2-AMINO BENZOIC ACID AND CERTAIN OF ITS DERIVATIVES.¹

BY MARSTON TAYLOR BOGERT AND WILLIAM FLOWERS HAND.

Received November 22, 1905.

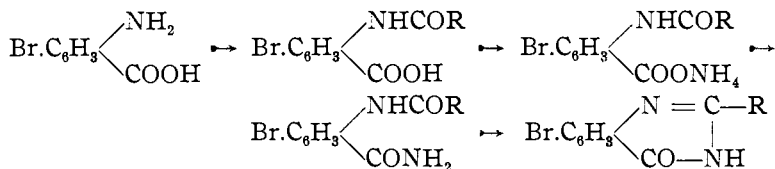
IN A recent paper² on the preparation and properties of 5-

¹ Read at the Buffalo Meeting of the American Chemical Society. June 22, 1905.

² This Journal. 27, 1476 (1905).

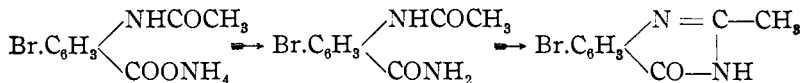
higher amides. This is in accord with Niementowski's own observations.

(3) By heating the acid with excess of glacial formic acid, or an acid anhydride, then adding excess of solid ammonium carbonate and continuing the heating.



This is essentially the same as the next method of preparation, as it probably depends upon the intermediate formation of the acylamino acid. In most cases, it is more convenient to pass thus directly to the quinazolines, without separating and purifying the intermediate acylamino acid. For the best results, the anhydride used should be freshly distilled and in considerable excess (2.5 cc. to 3 cc. of anhydride to 1 gram of the bromanthranilic acid), and, after neutralizing with ammonium carbonate, the heating should be continued for one to three hours. Too long boiling, on the other hand, may impart a yellow color to the product, which is removed only with difficulty. In practically all cases, the iso-anhydrides gave better yields than the normal. With the increase in the molecular weight of the anhydrides, we observed an increasing tendency towards the formation of tarry material insoluble in cold alkali. In the case of the butyric anhydrides, only traces appeared, with isovaleric the amount was greater, while with isocaproic it was still more prominent. If the reaction was carried out properly, the yields were generally good, and the crude products easy to purify.

II. From 5-Brom-2-acetaminobenzoic Acid by Heating Its Ammonium Salt.¹

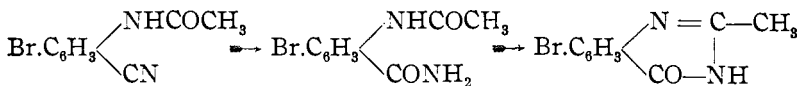


This was carried out only with the acetamino acid, the other acylamino acids not being prepared for the purpose, it being much simpler to prepare the required quinazoline by method

¹ Bischler and Burkart: Ber. 26, 1349 (1893).

I, 3, above. In the case of the acetamino acid, the yield was practically quantitative, but the product was slightly yellow.

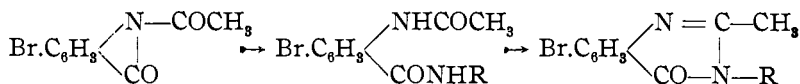
III. *From 5-Brom-2-acetaminobenzonitrile.*—(1) By warming the nitrile with an alkaline dioxide solution.¹



This is the best process of all, giving immediately a quantitative yield of pure substance.

(2) By boiling the nitrile with concentrated hydrochloric acid. The quinazoline also results when the nitrile is boiled with concentrated hydrochloric acid, the reaction involved being the same as the one just given.

IV. *From 5-Brom-2-acetantranil and Primary Amines,*²



This reaction gives good yields and can be applied to aliphatic or aromatic amines. In fact, as we have had occasion to mention in previous papers, the nitro or halogen acylantranils appear to condense to quinazoline compounds with almost any primary amino group.

The quinazolines described in this paper, with the exception of those carrying hydrocarbon radicals in position 3 (and which cannot, therefore, rearrange to enolic tautomers), are readily soluble in solutions of the caustic alkalis, but not in ammonia. Carbon dioxide precipitates them from their alkaline solutions. They can be purified conveniently by dissolving them in caustic alkali solution and precipitating by the addition of solid ammonium carbonate to the warm solution. They show but slight affinity for the mineral acids, and these salts when formed are rapidly dissociated by water.

All the melting-points recorded were taken with standardized Anschütz short-scale thermometers. Most of the quinazolines soften slightly before melting. All melting-points were taken by rapid heating, the bath being brought to within a few degrees

¹ Bogert and Hand: This Journal. 24, 1031 (1902).

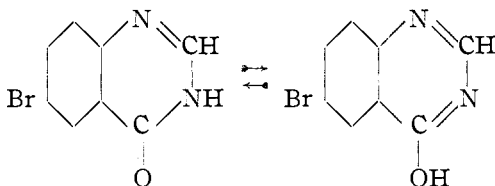
² Anschütz, Schmidt and Greiffenberg: Ber. 35, 3480 (1902); Bogert and Chambers: This Journal. 27, 649 (1905); Bogert and Seil: Ibid. 27, 1305 (1905); Bogert and Steiner: Ibid. 27, 1327 (1905).

of the correct melting-point before the introduction of the melting-point tube.

The necessary analytical work was performed by Messrs. H. J. Smith and J. E. Jacob, of the Chemical Laboratory of the Mississippi Agricultural and Mechanical College, to whom we wish to express our indebtedness for their able assistance.

EXPERIMENTAL.

6-Brom-4-ketodihydroquinazoline (6-Brom-4-oxyquinazoline).



(1) *From 5-Brom-2-aminobenzoic Acid and Formamide.*—Ten grams of the bromanthranilic acid were heated with excess of ammonia, the solution evaporated to dryness on the water-bath, and the residue boiled with 15 cc. of formamide until all ammonia was expelled. The contents of the flask were poured into a porcelain dish containing about 100 cc. of hot water, heated on the water-bath, and sufficient 20 per cent. sodium hydroxide solution added to form a clear solution. This solution was filtered hot, and carbonated by adding solid ammonium carbonate to the hot liquid. It was then cooled, filtered, the precipitate washed, treated with bone-black and crystallized from 95 per cent. alcohol. The crystals obtained appeared under the microscope as clear six-sided prisms, and melted at $272\text{--}272.5^\circ$ (corr.) when rapidly heated. The yield of crude product was 9.5 grams.

(2) *From 5-Brom-2-aminobenzoic Acid and Formic Acid.*—Five grams of the bromanthranilic acid were heated with sufficient glacial formic acid to give a clear solution on boiling (14 cc. were used). After boiling for about an hour, excess of solid ammonium carbonate was carefully added, and the temperature then raised to $210\text{--}220^\circ$, when ammonia was evolved steadily. After heating for fifteen minutes at this temperature, the condensation appeared complete, and the quinazoline was separated and purified as described above, giving rectangular prisms, melting at $272\text{--}273^\circ$ (corr.). The yield of crude product was 1.6 grams.

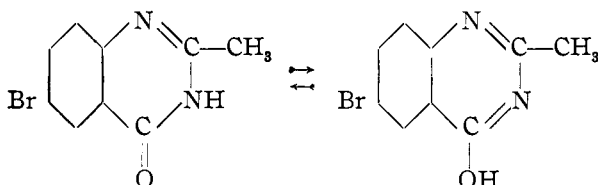
The pure quinazoline forms clear six-sided prisms, m. p. 272--

273° (corr.), when rapidly heated. It is insoluble or difficultly soluble in water, benzene, toluene, cold dilute alcohol, chloroform or carbon tetrachloride; moderately soluble in hot dilute alcohol, cold 95 per cent. alcohol, cold methyl alcohol, cold acetone or cold aniline; easily soluble in the latter solvents at their boiling-points. It crystallizes well from aniline or from dilute alcohol.

Calculated for $C_8H_5ON_2Br$: C, 42.67; H, 2.22; N, 12.44; Br, 35.53. Found: C, 43.03; H, 2.43; N, 12.53; Br, 35.59.

The *chlorplatinat*e crystallizes in short, thick prisms. Platinum found, 22.50; calculated, 22.74.

6-Brom-2-methyl-4-ketodihydroquinazoline (6-Brom-2-methyl-4-oxyquinazoline).



I. From 5-Brom-2-aminobenzoic Acid.—(1) By heating the acid in sealed tubes with acetic anhydride and acetonitrile. Three grams of the acid, 3 cc. of acetic anhydride and 3 cc. of acetonitrile were heated together in a sealed tube for five hours at 230–250°. On opening the tube, no pressure was evident. The product was washed out with water, warmed to 60° with a slight excess of sodium hydroxide solution, the solution cooled, filtered, and the quinazoline precipitated from the filtrate with carbon dioxide. The yield was small, and the color of the product golden-yellow, but, on purification, it proved to be identical with the methylquinazoline obtained by the methods described below.

Another tube, charged similarly, but heated six hours at 160–180°, gave a still smaller yield of quinazoline.

(2) By heating the ammonium salt of the acid with acetamide. The dry ammonium salt was intimately mixed with acetamide, and the mixture heated carefully over the free flame until most of the ammonia was driven off. The mass was then boiled up with water, made alkaline with caustic soda, filtered, and the quinazoline precipitated from the filtrate by the addition of solid ammonium carbonate. The precipitate was washed, then treated

with bone-black and recrystallized from alcohol, giving transparent six-sided prisms, m. p. 298–300° (corr.). The yield was only fair.

(3) By treating the acid with acetic anhydride, and then with ammonium carbonate. The acid was boiled for a few minutes with acetic anhydride, then excess of solid ammonium carbonate gradually added to the boiling liquid, and the heating continued until all the ammonia was driven off. The quinazoline was separated as described under 2. and when recrystallized from alcohol was colorless, and identical with that obtained by the other methods. Ten grams of the acid gave 4.3 grams of crude quinazoline.

II. *From 5-Brom-2-acetaminobenzoic Acid by Heating Its Ammonium Salt.*—The acetamino acid was dissolved in excess of ammonia, the solution evaporated to dryness on the water-bath, the dried residue pulverized, and heated in a round-bottomed flask in an oil bath at 220–240° for about an hour. The resultant yellow mass was dissolved in warm dilute caustic soda, the quinazoline precipitated by carbon dioxide, and recrystallized from aniline. The quinazoline obtained was identical with the products described above, except that it was rather more yellow. The crude product was golden-yellow, and it was very difficult to completely remove this color. The yield of crude product was practically quantitative.

There were indications that the reaction began even at 100°, for, after evaporating the ammonium salt to dryness on the water-bath, it continued to smell strongly of ammonia even after prolonged heating at 100°, and the residue was no longer soluble in warm water unless a little ammonia or caustic soda was added.

III. *From 5-Brom-2-acetaminobenzonitrile.*—(1) By the action of sodium dioxide solution upon the nitrile. The nitrile was added to a 5 per cent. aqueous solution of sodium dioxide, warming and stirring until solution was complete. After heating for two hours at 50–70°, the quinazoline was precipitated by a current of carbon dioxide.

Further experience with this method showed that careful heating was not essential, and equally good results were obtained by bringing the solution of the nitrile to a boil, cooling immediately, and precipitating with carbon dioxide. This

method gives a quantitative yield of pure product, and can be readily and rapidly carried out.

(2) By boiling the nitrile with concentrated hydrochloric acid. Attempts to saponify the nitrile by boiling with concentrated hydrochloric acid, instead of giving the desired acid, resulted in a good yield of fairly pure quinazoline.

IV. *From 5-Brom-2-acetantranil and Ammonia.*—The anthranil was treated with strong ammonia, warmed on the water-bath, the product dissolved in caustic soda, the quinazoline precipitated by solid ammonium carbonate, and purified in the usual way. The yield was excellent.

The products obtained by the various methods outlined above were identical in all respects, and, on analysis, the following figures were secured: C, 45.48; H, 3.35; N, 11.57; Br, 33.49. Calculated for $C_9H_7ON_2Br$: C, 45.19; H, 2.92; N, 11.72; Br, 33.41.

The pure quinazoline separates from dilute alcohol or from aniline in colorless needles, which appear under the microscope as beautiful, clear six-sided prisms. When slowly heated, the compound decomposes, but melts completely at 298–300° (corr.), if plunged in a bath at 295° and rapidly heated.

It is insoluble or difficultly soluble in water, cold dilute ethyl alcohol, cold methyl alcohol, cold acetone, benzene, toluene, cold aniline, chloroform or carbon tetrachloride; moderately soluble in hot dilute ethyl alcohol or hot methyl alcohol; easily soluble in hot acetone or hot aniline. Good crystals may be obtained from either aniline or dilute alcohol. It is readily soluble in dilute solutions of caustic alkalies, and is reprecipitated from such solutions by carbon dioxide or by heating with ammonium carbonate. The compound appears to have but slight affinity for the mineral acids, the hydrochloride, for example, being immediately dissociated by water.

6-Brom-2-ethyl-4-ketodihydroquinazoline (6-Brom-2-ethyl-4-oxyquinazoline).—Five grams of the bromanthranilic acid and 5 cc. of propionic anhydride were boiled together under a return condenser, an excess of solid ammonium carbonate gradually added to the boiling mass, and the heating continued until the odor of ammonia was no longer noticeable. The quinazoline was separated and purified in the usual way, the yield of crude product being 2.71 grams. On recrystallization, fine needle-like prisms were obtained, melting at 267–268.5° (corr.) when

rapidly heated, with previous softening at 263° , and showing about the same solubilities as the methyl homologue.

Nitrogen found, 11.08; calculated for $C_{10}H_9ON_2Br$, 11.07.

6-Brom-2-normalpropyl-4-ketodihydroquinazoline (6-Brom-2-normalpropyl-4-oxyquinazoline).—This was prepared in a similar manner, from the bromanthranilic acid and normal butyric anhydride. By using 2.5–3 cc. of freshly distilled anhydride to 1 gram of the bromanthranilic acid, an excellent yield of very pure product was secured. The compound separates from dilute alcohol in needle-like prisms, melting at $255\text{--}256^{\circ}$ (corr.) when rapidly heated.

Nitrogen found, 10.47; calculated for $C_{11}H_{11}ON_2Br$, 10.49.

6-Brom-2-isopropyl-4-ketodihydroquinazoline (6-Brom-2-isopropyl-4-oxyquinazoline).—Five grams of the bromanthranilic acid and 9 cc. of isobutyric anhydride were mixed in a round-bottomed flask with return condenser, and boiled gently over the free flame until a clear solution resulted. After boiling for about an hour, an excess of powdered solid ammonium carbonate was gradually added. This caused considerable foaming; in fact, the foaming increases with the rise in the molecular weight of the anhydride used. The temperature of the flask was then raised until a clear melt was again obtained and most of the ammonia driven off. The quinazoline was separated from the melt as already described, and recrystallized from dilute alcohol or from aniline. Any excess of the latter solvent can be removed by washing the crystals with cold carbon tetrachloride, in which the quinazoline is very difficultly soluble. The yield of crude product was 4.2 grams. The pure substance forms colorless needle-like prisms, melting at $259\text{--}260.5^{\circ}$ (corr.) when rapidly heated. Too long heating, or too high a temperature, in the initial fusion gives a yellowish product.

Nitrogen found, 10.91; calculated for $C_{12}H_{13}ON_2Br$, 10.49.

6-Brom-2-isobutyl-4-ketodihydroquinazoline (6-Brom-2-isobutyl-4-oxyquinazoline).—Five grams of the bromanthranilic acid and 8 cc. of isovaleric anhydride were heated together for two hours, treated with excess of solid ammonium carbonate, boiled an hour and a half longer, cooled somewhat, boiled up with dilute caustic soda solution, cooled again, filtered, and the quinazoline precipitated in the filtrate with carbon dioxide, as before, giving a yield of 4.7 grams of crude product.

The foaming from the ammonium carbonate was rather troublesome. With the increase in the molecular weight of the anhydride used, there appeared an increasing tendency toward the formation of a tarry body, not soluble in cold alkali, but somewhat soluble in boiling alkali. Traces appeared in the case of the isopropyl derivative, a larger amount in the case of this isobutyl derivative, and still more in the preparation of the following amyl compound. Before filtering the alkaline solution of the quinazoline, therefore, it should be well cooled, as otherwise some of this tar separates from the hot filtrate on cooling.

The pure isobutyl derivative is colorless, and crystallizes in small needle-like prisms, which soften slightly at 250° , and melt with slight decomposition at $253\text{--}254^{\circ}$ (corr.) when rapidly heated. Like most of these quinazolines, when precipitated by carbon dioxide or by ammonium carbonate, it is very voluminous and difficult to dry thoroughly.

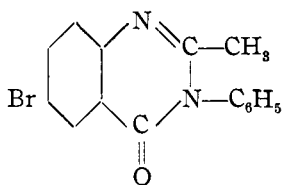
Nitrogen found, 10.32; calculated for $C_{13}H_{15}ON_2Br$, 10.0.

6-Brom-2-isoamyl-4-ketodihydroquinazoline (*6-Brom-2-isoamyl-4-oxyquinazoline*).—This was prepared in the same way as the last compound, using 5 grams of the bromanthranilic acid to 11 cc. of isocaproic anhydride. The foaming from the ammonium carbonate was excessive. In the separation of the quinazoline, an appreciable amount of tar remained undissolved by the alkali. This tar was solid at the laboratory temperature, but liquefied on the boiling water-bath. The yield of crude quinazoline was 2.5 grams.

The purified substance crystallizes in needle-like prisms, which melt at $235\text{--}236^{\circ}$ (corr.) when rapidly heated, and is insoluble or difficultly soluble in water, benzene, toluene, cold aniline, chloroform, carbon tetrachloride, dilute alcohol, cold 95 per cent. alcohol, cold methyl alcohol, or acetone; moderately soluble in hot 95 per cent. alcohol or hot methyl alcohol; easily soluble in hot aniline.

Nitrogen found, 9.80; calculated for $C_{14}H_{17}ON_2Br$, 9.46.

6-Brom-2-methyl-3-phenyl-4-ketodihydroquinazoline.



5-Brom-2-acetantranil was warmed with freshly distilled aniline. The condensation took place smoothly and rapidly. The crude product was treated with bone-black and crystallized from 95 per cent. alcohol, giving colorless six-sided prisms, melting at $185-186^{\circ}$ (corr.) when rapidly heated.

Bromine found, 25.9; calculated for $C_{15}H_{11}ON_2Br$, 25.4.

6-Brom-2-methyl-3-orthotolyl-4-ketodihydroquinazoline.—This was prepared in similar fashion, from 5-brom-2-acetantranil and *o*-toluidine. The crude product was dissolved in alcohol, precipitated by the addition of water, the precipitate washed with acetic acid to remove any excess of *o*-toluidine, and recrystallized from dilute alcohol. Colorless crystals were thus obtained, melting at $137-138^{\circ}$ (corr.) when rapidly heated.

Bromine found, 24.32; calculated for $C_{16}H_{13}ON_2Br$, 24.30.

In both this case and in the foregoing, the anthranil was carefully washed with carbon tetrachloride before use, to remove any excess of acetic anhydride which might contaminate the product with anilide or toluide.

It will be observed that, with the exception of the methyl derivative, the melting-points of these quinazolines steadily sink with rising molecular weight, and that the iso compounds melt higher than the normal. We have elsewhere called attention to the same condition of affairs in other series of quinazolines.

COLUMBIA UNIVERSITY AND
MISSISSIPPI AGRICULTURAL AND MECHANICAL COLLEGE,
November, 1905.

CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]
THE ACTION OF PYRIMIDINE ON SALICYL CHLORIDES.

BY RICHARD B. EARLE AND H. LOUIS JACKSON.

Received November 25, 1905.

(PRELIMINARY PAPER.)

THE explanation generally given of the reaction involved in the preparation of salicylic acid from sodium phenolate and carbon dioxide is that the sodium phenol carbonate, first formed, rearranges to sodium salicylate. An obvious way of explaining this rearrangement is to assume the formation of an intermediate product, an inner anhydride or lactone of salicylic acid;