# THE SYNTHESIS AND PROPERTIES OF 3-(4'-QUINAZOLYL)-4-QUINAZOLONE

by

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## THE DIQUINAZOLYL ETHER

In the attempts to prepare 4-cyanoquinazoline by the fusion of 4-chloroquinazoline with either silver and cuprous cyanide (1) only a small amount of a fibrous material was isolated. This product appeared to be pure, and analysis suggested that it might be diquinazolyl ether. Since 4-chloroquinazoline is easily hydrolyzed by traces of water, it is possible to account for diquinazolyl ether as resulting from the condensation of chloroquinazoline with small amounts of hydroxyquinazoline impurity.

There is no record in the literature of a diquinazolyl ether. Bogert and May attempted the synthesis by refluxing sodium 4-quinazolinate with 4-chloroquinazoline in benzene medium (2). Attributing their failure to the insolubility of sodium 4-quinazolinate, this laboratory repeated the work using a dry dioxane solvent. This modified procedure gave a product which was found to be identical with that resulting from the cyanide fusions.

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1. Tomisek, A. J., and Christensen, B. E., J. Am. Chem. Soc., 67, 2114 (1945).
2. Bogert, M. T., and May, C. E., J. Am. Chem. Soc., 31, 510 (1909).

A diquinazolyl ether synthesized as above could have either of two possible structures: di-4-quinazolyl ether (Fig. 1) or 3-(4'-quinazolyl)-4-quinazolone (Fig. 2). In the alkylquinazolyl ethers, O-ethers (as Fig. 1)

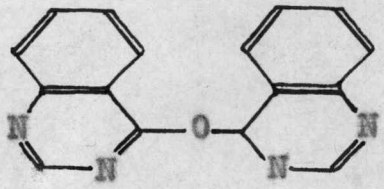


Fig. 1

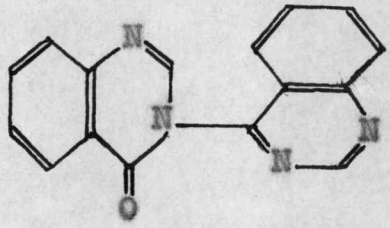


Fig. 2

and N-ethers (3) (as Fig. 2) are synthesized by two different methods (4) (Fig. 3) differing in which radical contains the halide and which the -ONa group. When both

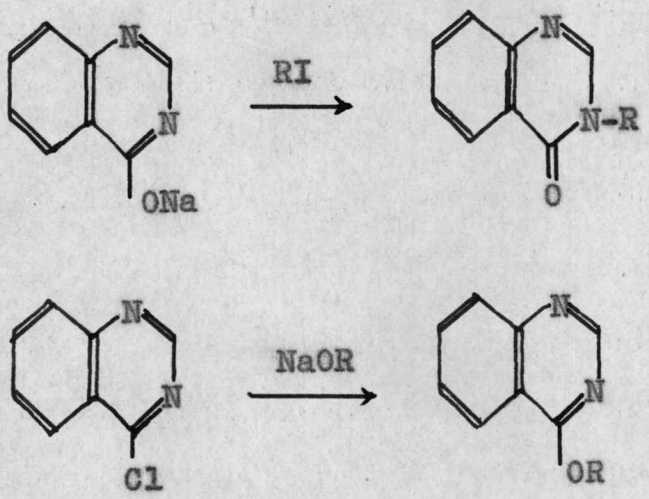


Fig. 3

radicals are quinazolyl, analogy to the alkylquinazolyl ether fails to distinguish between the two possible isomers. This interesting situation may have been the reason which prompted Bogert and May (2) to attempt the synthesis of such an ether.

O-ethers are very easily cleaved by acid in contrast to N-ethers which are stable (4). The diquinazolyl ether prepared above reacted very readily with dilute hydrochloric acid to yield a product ($C_{15}H_{13}N_3O$) which contained

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3. For other examples of this terminology, see Ref. 2, p. 508.
4. Loc. cit.

a quinazoline nucleus bound to a degraded quinazoline unit (Fig. 4). The failure to obtain 4-hydroxyquinazo-

$$C_{16}H_{10}N_4O + H_2O \xrightarrow{HCl} C_{15}H_{13}N_3O + NH_3 + ?$$

Fig. 4

line as the hydrolysis product, together with the fact that the two nuclei remain attached after hydrolysis, lends support to the N-ether type of linkage (Fig. 2). The stability of the ether toward boiling alcohol and water, its melting point behavior (melts 232° without decomposition or rearrangement) lends additional support to this point of view. The O-ethers are generally unstable under these conditions (5).

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5. Bogert, M. T., and Seil, H. A., J. Am. Chem. Soc., 29, 526 (1907).

## THE DIQUINAZOLYL ETHER CLEAVAGE PRODUCT

Further study centered about the diquinazolyl ether acid-hydrolysis mentioned above (Fig. 4). This reaction resulted in an almost quantitative conversion to a product having the empirical formula $C_{15}H_{13}N_3O$.

As a means to determining the structure of this cleavage product, numerous attempts were made to identify its by-products. The liquors from one hydrolysis reaction mixture were diluted to volume and aliquots were analyzed for ammonia content in a standard Kjeldahl apparatus. This test indicated approximately one mol of ammonia for each mol of diquinazolyl ether. The hydrolysis reaction evidently involved the splitting out of a carbon atom; but no such product could be identified. A ferric-hydroxylamine spot-test for carboxylic acids (6) came out positive; but attempts to isolate formic acid as a derivative of p-bromaphenacyl bromide were never successful. The failure to observe gaseous products during the diquinazolyl ether cleavage eliminates carbon dioxide as a possible product; and tests with Fehling's solution were also negative.

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6. Feigl, Fritz, Spot Tests, Nordemann Publishing Co., New York, 1937, p. 266.

Microquantitative analysis indicated it was possible to introduce two acetyl groups into each molecule of the cleavage product. In macro-scale acetylation of the cleavage product the second acetyl group was too unstable to permit isolation of the diacetyl derivative, and the monoacetyl derivative was the one isolated. It should be noted in this connection that 4-hydroxyl groups on quinazolines cannot be esterified.

Upon acetylation the molecule retained its solubility in base but lost its ability to reduce cold, basic permanganate.

Miscellaneous properties of the cleavage product may be tabulated as follows: moderately soluble in aqueous sodium hydroxide, but insoluble in aqueous sodium bicarbonate; unchanged by one day boiling in dilute hydrochloric acid; unchanged by six hours standing with Lucas reagent, or by a few minutes' warming with phosphorous oxychloride; Lieberman's test for the phenolic group --- negative; 2,4-dinitrophenylhydrazone test for carbonyl group --- negative.

The cleavage product did not react with acidic potassium permanganate solution. In basic solution it rapidly reduced permanganate to the green manganate; further reaction to manganese dioxide proceeded only

slowly at room temperature. Evolved ammonia was readily detectable in the oxidation mixture, but in only one instance was any other oxidation product isolated. Among numerous attempts, one run did yield a small amount of 4-hydroxyquinazoline, which was identified by mixed melting point. The cleavage product was unaffected by warm hydrogen peroxide in either basic solution or dilute sulfuric acid suspension.

To determine whether the cleavage product was a 3-substituted-4-quinazolone, several attempts were made to apply the 3-substituent replacement reaction of Bogert and Cairncross (7). Following the general procedure of Leonard and Curtin (8), and using n-butylamine under conditions of one to four days at 125°, recovery was high and the small amounts of reacted material could never be obtained sufficiently pure for the determination of significant data. One run using hydrazine hydrate in place of butylamine gave slightly better results: the reacted material was obtained sufficiently pure to prove it was not 3-amino-4-quinazolone.

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7. Bogert, M. T., and Cairncross, S. E., Collection Czechoslovakian Chem. Communic., 7, 522 (1935).
8. Leonard, N. J., and Curtin, D. Y., J. Org. Chem., 11, 346 (1946).

## DIAZOTIZED CLEAVAGE PRODUCT

Diazotized cleavage product was not obtained in analytically pure form; but the approximate empirical formula indicated that a coupling reaction had spontaneously followed the diazotization reaction. Diazotized cleavage product would not couple with β-naphthol. This would normally be taken to indicate the absence of a primary aromatic amino group. But when the cleavage product was methylated by dimethyl sulfate-sodium hydroxide after the aminoid group had been protected by acetylation, and the acetyl group was subsequently removed by boiling one day in dilute hydrochloric acid, the resulting product (not isolated) did diazotize and couple with β-naphthol. This intramolecular coupling with β-naphthol could be possible only if the methylation had effectively blocked the functional group responsible for the normal intermolecular coupling.

The diazotized cleavage product was unstable to hot acid; boiling in dilute hydrochloric acid first formed an intensely purple solution, then a white, sparingly acid-soluble precipitate. The addition of excess alkali to the liquors caused the evolution of rather large amounts of ammonia. This diazotized-and-hydrolyzed product was insoluble in aqueous sodium bicarbonate, but

soluble in aqueous sodium hydroxide. The following qualitative tests on this compound came out negative: a sodium fusion test for halide, a 2,4-dinitrophenylhydrazone test for the carbonyl group, a diazotization and β-naphthol coupling test for the primary aromatic amino group, and a (basic) permanganate reduction test.

## 2-(AND 3-)AMINOBENZYL-4-QUINAZOLONES

The structure of the compound formed by acid hydrolysis of the diquinazolyl ether (Fig. 4) remains unknown. No hypothetical structure could be devised to fit all the observed properties. The two most likely structures, 2-(and 3-)o-aminobenzyl-4-quinazolones, were synthesized and found different from the unknown compound.

Methyl N-(o-nitrophenylacetyl)anthranilate was prepared as a possible starting material in two projected syntheses of 2-(o-nitrobenzyl)-4-quinazolone. Both of these projected syntheses failed because the ester linkage was more stable than the amide linkage. First attempted was the cyclization with ammonia (Fig. 5),

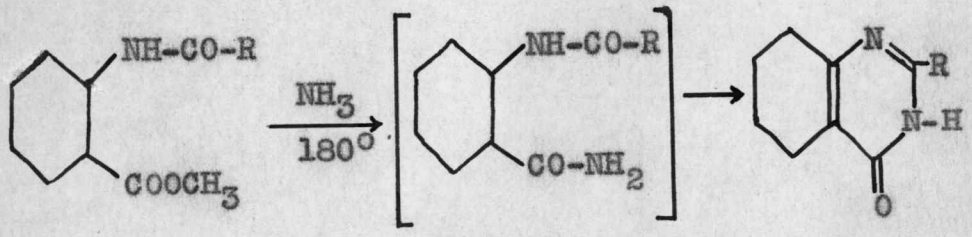


Fig. 5

which had been employed successfully by Weddige (9) and Zacharias (10) for the case R=methyl. Thieme (11) reported

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9. Weddige, A., J. prakt. Chem., [2], 36, 145 (1887).
10. Zacharias, E., J. prakt. Chem., [2], 43, 441 (1891).
11. Thieme, P., J. prakt. Chem., [2], 43, 473 (1891).

amide ammonolysis as a side reaction (R still = methyl). In the present work (R=nitrobenzyl) the amide ammonolysis product was obtained in good yield, and the desired quinazolone was not found at all. The second attempt (Fig. 6) involved direct cyclization to the anthranil (2-alkyl-1-keto-2,4,1-benzoxazine) by elimination of

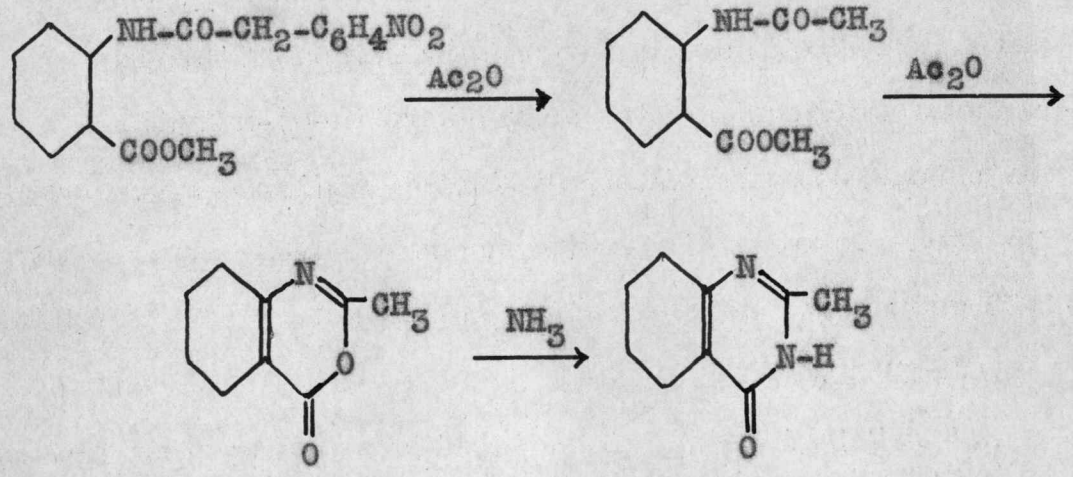


Fig. 6

methanol. The quinazolone isolated was not the one desired, since acyl exchange had preceded the cyclization.

The synthesis of 2-(o-nitrobenzyl)-4-quinazolone was carried out by two closely related methods (Fig. 7). $N^2$-(o-Nitrophenylacetyl)anthranilamide was readily converted to nitrobenzylquinazolone by the action of aqueous

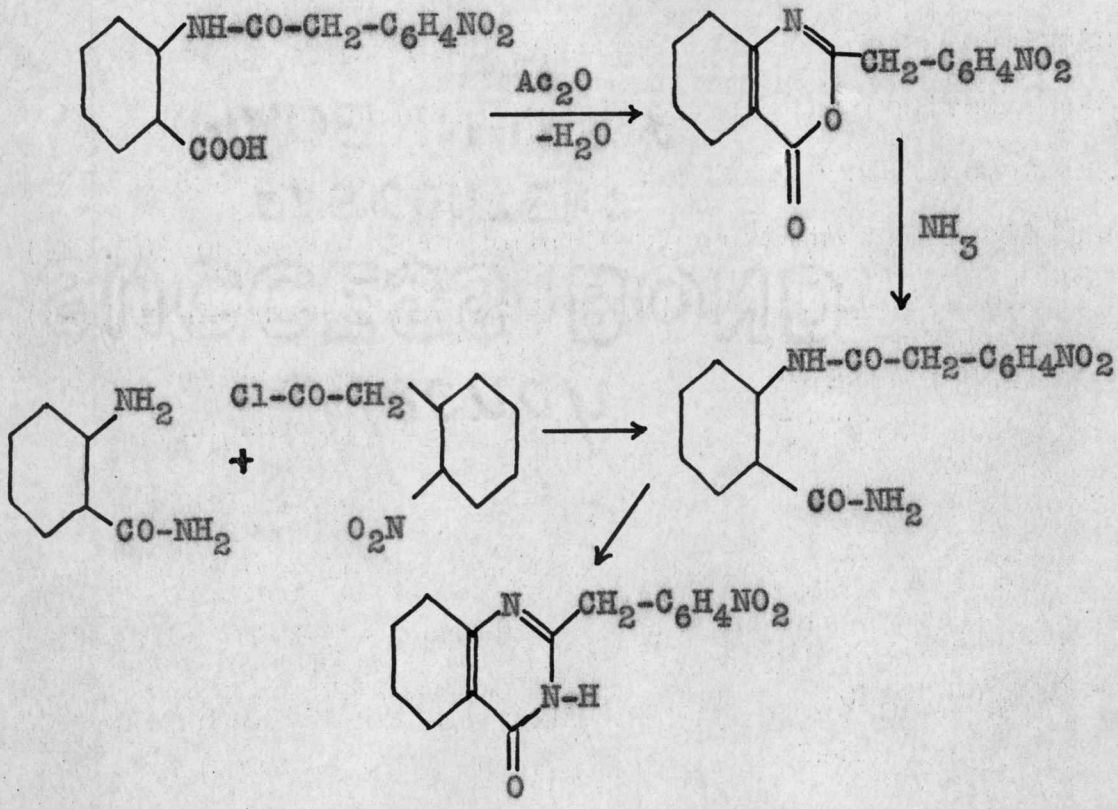


Fig. 7

sodium hydroxide. N-(o-Nitrophenylacetyl)anthranilic acid was readily dehydrated to its anthranil (3-(o-nitrobenzyl)-1-keto-2,4,1-benzoxazine); and the conversion of the anthranil to the quinazolone was accomplished in good yield. This last reaction probably proceeds via the anthranilamide, since this intermediate has been isolated in certain analagous cases (12).

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12. Bogert, M. T., Amend, C. G., and Chambers, V. J., J. Am. Chem. Soc., 32, 1297 (1910).

The synthesis of 3-(o-nitrobenzyl)-4-quinazolone (first reaction, Fig. 3) was based upon the work of Bogert and Geiger (13), in which it was shown that the N-alkylation of sodium 4-quinazolinate could be carried out with benzyl chloride. The extent of O-alkylation involved in benzylation has not been determined, but the precaution was taken to destroy by acid hydrolysis any O-ether which might have been formed.

2-(o-Nitrobenzyl)-4-quinazolone was conveniently reduced by ferrous sulfate in basic solution. Since the 3-(o-nitrobenzyl)-4-quinazolone was insoluble in aqueous base, it was reduced in glacial acetic acid solution, using stannous chloride.

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13. Bogert, M. T., and Geiger, G. A., J. Am. Chem. Soc., 34, 527 (1912).

## EXPERIMENTAL (14)

3-(4'-Quinazolyl)-4-quinazolone. A solution of 5.28 g. 85% potassium hydroxide pellets (.08 mol) in 75 ml absolute alcohol was added to 12.68 g. (.08 mol) 4-hydroxyquinazoline. After removing the solvent on a steam bath, the residual sodium salt was thoroughly dried under high vacuum. The residue was pulverized and 100 ml dry dioxane and 14.38 g. (0.088 mol) 4-chloroquinazoline were added. The mixture was refluxed three days. Potassium chloride was removed by filtration while the reaction mixture was still hot. The quinazolylquinazolone separated from the liquors on cooling, and additional product was obtained by evaporating the liquors to dryness. The combined fractions were then triturated with dilute sodium hydroxide solution. The crude product (16.11 g., 73½%), purified by charcoal treatment of a hot alcoholic solution yielded 14.1 g. (64%) of pure 3-(4'-quinazolyl)-4-quinazolone. The product recrystallized from alcohol as thin, wool-like fibres, m.p. 232½°, was insoluble in water, and was soluble in dioxane or hot benzene. It was stable to long boiling in water. Anal. Calcd. for $C_{16}H_{10}N_4O$: C, 70.06; H, 3.68; N, 20.43. Found: C, 70.02; H, 3.85; N, 20.43.

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14. All melting points are corrected. All N-analyses are by the Dumas method.

Acid-hydrolysis Product of 3-(4'-Quinazolyl)-4-quinazolone. The diquinazolyl ether (10.58 g.) was added to hot dilute hydrochloric acid. The ether dissolved immediately, and within a few seconds the hydrochloride of the hydrolysis product precipitated out. The mixture was cooled and filtered. Solid material and liquors were separately treated with excess sodium bicarbonate. The free base was then filtered, washed with water and dried. The free base prepared from the precipitated hydrochloride was somewhat purer. The two fractions totaled 9.32 g. (96%) of the crude product. After pyridine-water recrystallization the fine, white needles melted 244-5°. Anal. Calcd. for $C_{15}H_{13}N_3O$: C, 71.69; H, 5.21; N, 16.72.. Found: C, 71.68; H, 5.23; N, 16.87.

The cleavage product molecular weight was determined by the Rast method (15). Calcd. for $C_{15}H_{13}N_3O$: 251. Found: 225, 246, and 257.

Microacetylations were carried out by the acetic anhydride-pyridine method as applied to hydroxyl determinations (16). The ratio of mols of acetic anhydride reacted to mols of cleavage product was 2.04 and 2.16.

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15. Niederl, Joseph and Niederl, Victor, Micromethods of Quantitative Organic Analysis, Ed. 2, John Wiley and Sons, New York, 1942, p. 217.
16. Petersen, J. W., Hedberg, K. W., and Christensen, B. E., Ind. Eng. Chem., Anal. Ed., 15, 225 (1943).

4-Hydroxyquinazolone was treated similarly and found to use up no acetic anhydride. In macro-scale acetylation of the hydrolysis product, the alcohol-recrystallized derivatives from two separate runs had 13.99 and 14.63% N, compared to the 14.33% N theoretical for the monoacetyl derivative. A sample further purified by pyridine-water recrystallization melted 276-280°.

Diazotization of the Quinazolylquinazolone Cleavage Product. The Cleavage product was diazotized at room temperature, allowed to stand twenty minutes, then made basic with excess sodium hydroxide. The precipitate was recrystallized from alcohol and benzene to give a yellow solid which melted (decomposition with gas evolution) 214-5°. Anal. Found: C, 68.00; H, 3.81; N, 23.11.

The diazotized-and-hydrolyzed cleavage product was recrystallized from alcohol and pyridine-water to yield white needles which melted at 169°, then resolidified to melt again at 180°. Its molecular weight (15) was 265 (by a single determination); and an attempted micro-acetylation (16) showed no acetyl group had been introduced. Anal. Found: C, 65.02; H, 3.69; N, 11.31.

o-Nitrophenylacetyl chloride. o-Nitrophenylacetic acid was prepared according to the method of Mayer and

Balle (17). Five grams of the acid was converted to its acid chloride by refluxing one half hour with 10 ml thionyl chloride. Excess thionyl chloride was removed (to constant weight) under reduced pressure (15 mm) without heating. Heating on an 80° water bath was found to cause explosive decomposition.

Methyl N-(o-Nitrophenylacetyl)anthranilate. o-Nitrophenylacetyl chloride was prepared as above from 5.0 g. of the acid. It was taken up in dry benzene, and mixed with a dry benzene solution of 4.0 ml methyl anthranilate. Forty ml of 25% potassium hydroxide solution were added portionwise with shaking, and the benzene layer was further extracted with acid. During these extractions the product was held in solution by warming. The residue after benzene removal was dissolved in hot acetone, treated with charcoal and crystallized. The yield was 6.0 g. (69%), m.p. 131-3°. Recrystallization from alcohol or acetone gave white crystals of m.p. 133½-134°. Anal. Calcd. for $C_{16}H_{14}N_2O_5$: C, 61.14; H, 4.49; N, 8.92. Found: C, 61.34; H, 4.64; N, 8.92.

Methyl N-(o-nitrophenylacetyl)anthranilate was heated in a bomb with absolute alcoholic ammonia (180°, 8 hours).

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17. Mayer, F., and Balle, G., Ann., 403, 188 (1914).

A good yield of o-nitrophenylacetamide was obtained, m.p. 158-160°.

One gram of methyl nitrophenylacetylanthranilate was refluxed 15 hours in 4 ml acetic anhydride. The acetanthranil thus formed was not isolated. Instead, the reaction mixture was added cautiously to an excess of hot 14% ammonia. A few drops of 10% potassium hydroxide were added, and the mixture was heated on a steam bath for one hour. To destroy acetamide the mixture was then refluxed for an hour with an excess of potassium hydroxide, cooled, filtered, and adjusted to neutrality with hydrochloric acid. After standing two days, 0.14 g. of crude 2-methyl-4-quinazolone crystallized out. This material was identified by recrystallization from alcohol and mixed melting point with known 2-methyl-4-quinazolone. A rum similar to the above, except that the reaction time was only six hours, resulted only in recovery (0.62 g.).

N-(o-Nitrophenylacetyl)anthranilic Acid. o-Nitrophenylacetyl chloride was prepared as above from 5.0 g. of its acid, and then taken up in a little dioxane. Twenty grams of anthranilic were dissolved in 50 ml dioxane. The two solutions were mixed and allowed to stand several hours before filtering. The precipitate

was triturated with water to remove amine salts; and the residual N-(o-nitrophenylacetyl)anthranilic acid was recrystallized from glacial acetic acid. A second fraction of product was obtained by working up the dioxane liquors of the original reaction mixture. The dioxane was boiled off, and the residue was purified as follows: taking up in dilute sodium hydroxide, reprecipitating with hydrochloric acid, and recrystallizing from glacial acetic acid and dioxane-water. Both fractions were of good purity and represented a total yield of 82% (4.88 and 1.88 g. respectively). An additional recrystallization for purposes of analysis gave a white granular product which melted with slow evolution of gas, m.p. 224-5°. Anal. Calcd. for $C_{15}H_{12}N_2O_5$: C, 60.00; H, 4.03; N, 9.33. Found: C, 60.13; H, 4.03; N, 9.03.

3-(o-Nitrobenzyl)-1-keto-2,4,1-benzoxazine. Five grams of N-(o-nitrophenylacetyl)anthranilic acid was refluxed one half hour with 20 ml pure acetic anhydride (18). The solution was seeded and cooled in an icebox. The (o-nitrophenylacet)anthranil, m.p. 162-4°, was in 4.36 g. (93%) yield. This anthranil (3-(o-nitrobenzyl)-1-keto-2,4,1-benzoxazine) on recrystallization from

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18. Compare the procedure of Bogert, M. T., Gortner, R. A., and Amend, C. G., J. Am. Chem. Soc., 33, 951 (1911).

pyridine-water, alcohol, then pyridine-alcohol gave white plates of m.p. 165-6°. Anal. Calcd. for $C_{15}H_{10}N_2O_4$: C, 63.82; H, 3.57; N, 9.93. Found: C, 63.57; H, 3.85; N, 10.10.

$N^2$-(o-Nitrophenylacetyl)anthranilamide. o-Nitrophenylacetyl chloride, prepared as above from 5.0 g. of the acid, was taken up in a little dioxane then added to a solution of 7.60 g. anthranilamide (19) in 50 ml dioxane. After several hours standing the precipitate was separated, triturated with water, refiltered and thoroughly dried. Additional product was obtained from the reaction mixture filtrate by boiling off the dioxane. The combined fractions were decolorized and recrystallized from hot pyridine-benzene solutions. The fibrous mass of crystals represented a yield of 6.06 g. (73%) of $N^2$-(o-nitrophenylacetyl)anthranilamide, m.p. 167-170°. Recrystallization from pyridine-benzene and pyridine-water raised the m.p. to 172-3°. Anal. Calcd. for $C_{15}H_{13}N_3O_4$: C, 60.20; H, 4.38; N, 14.04. Found: C, 59.90; H, 4.64; N, 14.24.

2-(o-Nitrobenzyl)-4-quinazolone from Nitrophenylacetylanthranilamide. The mixture -- 3.46 g. $N^2$-(o-nitrophenylacetyl)anthranilamide, 12 ml pyridine, 12 ml

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19. Kolbe, H., J. prakt. Chem., [2], 30, 475 (1884); Erdmann, E., Ber., 32, 2164 (1899).

water, and 1 ml 10% sodium hydroxide -- was allowed to stand 24 hours at room temperature with occasional agitation. Seventy five ml of 10% sodium hydroxide were added, and a trace of base-insoluble by-product was removed by filtration. The precipitate obtained by neutralization of the liquors was separated into two fractions on the basis of solubility in boiling glacial acetic acid. The crystals which separated from the acetic acid liquors together with the (purer) acetic acid-insoluble fraction represented a 2.85 g. (88%) yield of 2-(o-nitrobenzyl)-4-quinazolone. Purification for analysis by recrystallization from glacial acetic acid and pyridine-water gave white, granular crystals, m.p. (decomp.) 264-5°. Anal. Calcd. for $C_{15}H_{11}N_3O_3$: C, 64.05; H, 3.94; N, 14.94. Found: C, 64.15; H, 3.73; N, 14.76.

The use of alcohol-water instead of pyridine-water in the above reaction mixture resulted in a very appreciable yield of the base-insoluble by-product.

2-(o-Nitrobenzyl)-4-quinazolone from Nitrobenzylketobenzoxazine. Five grams of 3-nitrobenzyl-1-keto-2,4,1-benzoxazine were added to 25 ml of 50% pyridine which had been saturated with ammonia. This suspension was allowed to stand six hours with occasional stirring. One ml of 10% sodium hydroxide was added to the resulting

suspension of the anthranilamide, and the mixture was allowed to stand for 24 hours. Isolation procedure was as above for the synthesis starting from the anthranilamide. The combined fractions weighed 3.61 g (72%). The unidentified base-insoluble product accounted for 0.90 additional grams of material.

2-(o-aminobenzyl)-4-quinazolone. To a suspension of 5.0 g. 2-(o-nitrobenzyl)-4-quinazolone in 300 ml dilute sodium hydroxide was added a solution of 33.0 g. (10% excess) ferrous sulfate hydrate in 100 ml hot water. The reaction mixture was maintained at 80° for seven hours. Iron hydroxide was separated by centrifuging and washed repeatedly with dilute sodium hydroxide till the wash liquors gave no further precipitate upon neutralization. Combined precipitates obtained by the neutralization of the washings and the reaction-mixture liquors were recrystallized with charcoal treatment from pyridine-water. The yield of 2-(o-aminobenzyl)-4-quinazolone was 3.68 g. (80%). It was purified for analysis by recrystallization from dioxane and dioxane-water; the resulting white, voluminous powder still melted (decomp.) over a wide range, starting at about 250°. Anal. Calcd. for $C_{15}H_{13}N_3O$: C, 71.69; H, 5.21; N, 16.72. Found: C, 71.40; H, 5.32; N, 16.58.

2-(o-Acetaminobenzyl)-4-quinazolone. The corresponding amino compound (1.0 g.) was refluxed one hour in 8 ml dry pyridine and 4 ml acetic anhydride. The reaction mixture was poured into water and the product collected by filtration. The precipitate was recrystallized from pyridine-water, then from acetic acid-water, to yield white needles of m.p. 258°. Anal. Calcd. for $C_{17}H_{15}N_3O_2$: N, 14.33. Found: N, 14.53.

3-(o-Nitrobenzyl)-4-quinazolone. o-Nitrobenzyl chloride was prepared from o-nitrotoluene according to the directions of Haeussermann and Beck (20). The nitrobenzyl chloride fractions were used directly, without complete separation of nitrotoluene and water. The amount of nitrobenzyl chloride present was estimated (about 10 g.) and an excess of potassium 4-quinazolinate was added (13.0 g. 4-hydroxyquinazoline (21) plus 5.88 g. of 85% potassium hydroxide pellets). After adding 200 ml alcohol the mixture was refluxed six hours. Alcoholic solvent was boiled off and replaced by a mixture of dilute hydrochloric acid and benzene. After boiling for fifteen

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20. Haeussermann, C., and Beck, C., Ber. 25, 2445 (1892).
21. A sample of 4-quinazolone was purified for purposes of m.p. calibration. On a standard thermometer the m.p. was 217.3-217.5°.

minutes to destroy any benzylquinazolyl ether which might be present, the benzene layer was separated and thoroughly extracted with 3 N hydrochloric acid. This latter step was found necessary because the 3-(o-nitrobenzyl)-4-quinazolone (part of which separated from the 3 N acid as pale yellow needles of hydrochloride) was too weak a base to form a salt in weaker acids and would otherwise remain in the benzene layer. The combined aqueous extracts were made basic with excess sodium hydroxide, and the crude product (about 3.0 g.) was separated by filtration.

Recrystallizations (with charcoal treatment) from benzene, pyridine-water and acetic acid-water were found effective in purification. The pure, white product melted 169-170°. Anal. Calcd. for $C_{15}H_{11}N_3O_3$: C, 64.05; H, 3.94; N, 14.94. Found: C, 64.34; H, 4.12; N, 14.96.

3-(o-Aminobenzyl)-4-quinazolone. A uniform suspension of 2.83 g. 3-(o-nitrobenzyl)-4-quinazolone and 7.27 g. stannous chloride dihydrate in 30 ml glacial acetic acid was prepared. The mixture was saturated with dry hydrogen chloride and allowed to stand for ten hours. The gummy precipitate was dispersed by two or three minutes of gentle warming, and the mixture was poured into water. The aqueous suspension was made strongly

basic with sodium hydroxide and filtered. The precipitate was extracted with boiling pyridine, and water was added to complete a pyridine-water recrystallization. The 1.62 g. (64%) of crude, white plates were further purified by recrystallization (with charcoal treatment) from alcohol, dioxane-water, and pyridine. The pure 3-(o-aminobenzyl)-4-quinazolone melted 178°. Anal. Calcd. for $C_{15}H_{13}N_3O$: C, 71.69; H, 5.21; N, 16.72. Found: C, 71.49; H, 5.39; N, 16.69.

# CONCLUSION

3-(4'-Quinazolyl)-4-quinazolone was synthesized by the condensation of 4-chloroquinazoline with sodium 4-quinazolinate. This quinazolylquinazolone yields an anomalous hydrolysis product upon mild treatment with acid. Some properties of this cleavage product ($C_{15}H_{13}N_3O$) are described, but its structure remains enigmatic. 2-(and 3-)o-aminobenzyl-4-quinazolones were synthesized and found different from the unknown hydrolysis product.