N, 8.37; Cl, 10.59. Found: C, 57.50; H, 4.56; N, 8.32; Cl, 10.48.

Preparation of 2-Morpholino-3-acetamido-1,4-naphthoquinone.—Five grams of 2-chloro-3-acetamido-1,4-naphthoquinone and 3.2 ml. of morpholine in 200 ml. of benzene were heated under reflux for 20 minutes. The precipitated morpholine hydrochloride was removed and washed with 50 ml. of warm benzene. The filtrate and washings were combined and concentrated in vacuo to about one-fourth the original volume. Dark red needles separated on cooling. The product was recrystallized from toluene, dioxane and finally from 50% alcohol; yield 60%, m.p. 203.4–204.5°.

Anal. Calcd. for $C_{16}H_{16}N_2O_4$: C, 63.98; H, 5.37; N, 9.33. Found: C, 64.11; H, 5.49; N, 9.33.

PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Quinolinequinones. II. N-Substituted 6-Amino-5,8-quinolinequinones[1]

BY YOLANDA T. PRATT WITH NATHAN L. DRAKE

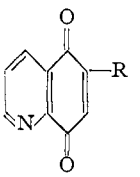
RECEIVED JUNE 25, 1954

6-Methoxy-5,8-quinolinequinone (I) has been synthesized and hydrolyzed to 6-hydroxy-5,8-quinolinequinone (II). The methoxyquinolinequinone, like the corresponding methoxynaphthoquinone is the vinylog of an ester and reacts with both primary and secondary amines to yield N-substituted 6-amino-5,8-quinolinequinones (III). The methoxyquinone readily transetherifies with ethanol to form the corresponding ethoxyquinone.

The quinolinequinones (dihydroquinolinediones) are of potential biological interest because of the physiological activities of both quinolines and quinones. In the first paper of this series[2] certain 8-amino-5,6-quinolinequinone derivatives were prepared to test the theory that such compounds are the active metabolites of the 8-aminoquinoline antimalarials. In the present work some of the isomeric N-substituted 6-amino-5,8-quinolinequinones (III) which are related to physiologically active compounds have been prepared for biological evaluation.

Taylor and Greenberg[3] have shown that certain 6-hydroxyquinolines with diethylaminoalkylamino side chains at the 8-position are effective amebicides against *E. histolytica* in guinea pigs. The hydroquinone of 8-isopropylaminoamylamino-5,6-quinolinequinone, which is rapidly converted to the quinone by air,[2] is slightly active despite the fact that the quinone is not stable and is probably rapidly destroyed *in vivo*. It was therefore of interest to synthesize the more stable isomeric types such as VI, VII and VIII (Table I) for the determination of their amebicidal activities. Certain 6-amino-5,8-quinolinequinones (*e.g.*, IX and X) are related to the 8-hydroxyquinoline amebicides[4] in that 5,8-quinolinequinone is an oxidation product of 8-hydroxyquinoline.[5] These compounds will also be tested as antibacterial agents since this type of activity is displayed by some quinolines and many quinones.[6]

Although the parent 5,8-quinolinequinone[7] was first prepared in 1884, very little research on this compound or its derivatives has been reported.[8] The starting material for the present work was 6-methoxy-5,8-quinolinequinone (I), readily obtained



I, R = $-OCH_3$
II, R = $-OH$
III, R = $-NR'R''$

by oxidizing the 5,8-diamine formed from 6-methoxy-8-aminoquinoline *via* the diazonium coupling product.[9] Despite the instability of the methoxyquinone I in aqueous acid, it could be prepared satisfactorily by oxidizing the diamine with acidic dichromate solution. Since the product is a very weak base it could be extracted into chloroform[10] as it was formed, thus minimizing acid hydrolysis. The over-all yield of pure methoxyquinone (I) from 6-methoxy-8-aminoquinoline was 57%.

Like 2-methoxy-1,4-naphthoquinone,[11] 6-methoxy-5,8-quinolinequinone (I) is the vinylog of an ester. It is hydrolyzed rapidly by dilute alkali at room temperature forming a red salt. Pure 6-hydroxy-5,8-quinolinequinone (II) is obtained in quantitative yield upon neutralization. In related work now in progress it is planned to convert this hydroxyquinone II to various types of analogs of physiologically active 2-hydroxy-1,4-naphthoquinones and hydroxyquinolines. Like the corresponding naphthoquinone, compound II appears to be a stronger acid than acetic acid since it dissolves in sodium acetate solution. It may be reconverted to the methoxy compound I by heating with methanol in the presence of acid catalysts, but the yields are only about 60% because of decomposition. Although the hydroxyquinone II, by analogy with the related naphthoquinone,[11] may exist predominately in the *p*-quinone form, as written, the facility with

(1) This investigation was supported by a research grant (PHS E-665) from the National Microbiological Institute of the National Institutes of Health, Public Health Service.

(2) N. L. Drake and Y. T. Pratt, THIS JOURNAL, **73**, 544 (1951).

(3) D. J. Taylor and J. Greenberg, *Am. J. Hyg.*, **56**, 58 (1952).

(4) J. H. Burckhalter and W. H. Edgerton, THIS JOURNAL, **73**, 4837 (1951), and references therein.

(5) The oxidation of 8-hydroxyquinoline to 5,8-dihydroxyquinoline by means of persulfate has been described by V. J. Dalvi, R. B. Desai and S. Sethna, *J. Ind. Chem., Soc.*, **28**, 366 (1951).

(6) For example, see Buu-Hoi, *Bull. soc. chim. France*, [5] **11**, 578 (1944), for tuberculostatic 2-amino-1,4-naphthoquinones, and T. Urbanski, S. Slopek and J. Venulet, *Nature*, **168**, 29 (1951), for tuberculostatic quinoline derivatives.

(7) O. Fischer and E. Renouf, *Ber.*, **17**, 1644 (1884).

(8) R. C. Elderfield, "Heterocyclic Compounds," Vol. 4, John Wiley and Sons, Inc., New York, N. Y., 1952, pp. 192–197.

(9) K. N. Campbell, *et al.*, THIS JOURNAL, **68**, 1561 (1946).

(10) Fischer and Renouf[7] had found that the parent 5,8-quinolinequinone can be extracted from the oxidizing mixture by means of chloroform.

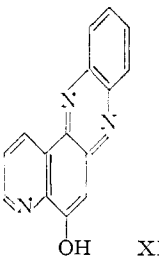
(11) L. F. Fieser, THIS JOURNAL, **48**, 2922 (1926); **50**, 439 (1928).

TABLE I
N-SUBSTITUTED 5,8-QUINOLINEQUINONES

-NR'R" in Formula III	Cmpd.	M.p.,[a] °C.	Color	Yield, %	Carbon, % Calcd.	Carbon, % Found[b]	Hydrogen, % Calcd.	Hydrogen, % Found[b]
p-$CH_3C_6H_4NH$-	IV	222–223	Dk. red	40	72.72	72.68	4.58	4.79
n-$C_6H_{13}NH$-	V	130.0–131.5	Red	73	69.74	69.55	7.02	6.90
$(C_2H_5)_2N(CH_2)_3NH$-	VI	107.5–108.5	Orange	49	66.87	66.90	7.37	7.23
$(C_2H_5)_2N(CH_2)_5NH$-	VII	102–103	Red-orange	57	69.27	69.10	8.27	8.00
$(C_2H_5)_2N(CH_2)_3CH(CH_3)NH$-	VIII	98–100[c]	Orange	55	68.54	68.55	7.99	7.89
$CH_2(CH_2)_4N$-	IX	149.5–151.0	Red	82	69.40	69.63	5.82	5.73
$(C_2H_5)_2N$-	X	.....[d]	Red	77	67.81	67.71	6.13	6.24

[a] Melting point of the analytical sample. [b] Averages of duplicates. [c] With preliminary sintering. [d] Sintered at 145°, decomposition and melting continued up to 155°.

which it reacts with *o*-phenylenediamine to yield the phenazine XI indicates that it tautomerizes readily to the *o*-quinone form.



XI

The tendency of the methoxyquinone I to undergo transetherification is consistent with the ease with which it hydrolyzes. In the absence of a catalyst it may be completely converted to the ethoxy analog by boiling for two hours with a large excess of ethanol while the by-product methanol is allowed to volatilize.

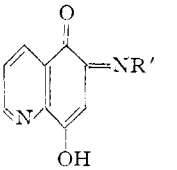
Because of the ester-like properties of 6-methoxy-5,8-quinolinequinone (I) the methoxyl group, like that of the corresponding naphthoquinone,[11,12] could be replaced by amino groups upon direct interaction with the desired amines. The N-substituted 6-amino-5,8-quinolinequinones of Table I were prepared in this manner. It was found that *p*-toluidine reacted rather slowly[13] with I even in refluxing acetic acid solution and because of side reactions the yield of product could not be increased by prolonged heating. The reaction in alcohol solution was too slow to be practicable.

The straight chain aliphatic primary amines, on the other hand, reacted very readily with I. The methoxyquinone was consumed completely in 20 minutes when the reactants were heated in alcohol at the reflux temperature, but it was found that the formation of by-products could be minimized by carrying out the preparations under milder conditions. When a suspension of the quinone in methanol containing a 10% excess of the amine was stirred at room temperature the reactions to form compounds V, VI and VII were essentially complete in four hours. The branched chain amine, 1-diethylamino-4-aminopentane, reacted much more slowly; three days were required for the complete utilization of I in the preparation of compound VIII. Of the secondary amines tried, piperidine reacted as rapidly as *n*-hexylamine but diethylamine reacted very slowly. For complete conversion at room temperature within two days a large excess of diethylamine was used since the possibility of side-reactions with this amine was slight.

Except for piperidine, which reacts more rapidly than anticipated, the relative reactivities of the amines parallel those observed in the aminolysis of esters. The slow rate with diethylamine and 1-diethylamino-4-aminopentane may be ascribed to steric effects and that with *p*-toluidine to its weak basicity.[14]

The structures of the products as indicated by analogy with those from 2-methoxy-1,4-naphthoquinone were confirmed by the analytical data, which definitely precluded the possibility that the methoxyl group was not eliminated, by the hydrolysis of 6-*n*-hexylamino-5,8-quinolinequinone (V) to the 6-hydroxyquinone (II) and by the reaction of I with *o*-phenylenediamine. This amine, like *p*-toluidine, reacted relatively slowly with I. Extensive decomposition occurred when the reactants were heated in acetic acid solution, but at room temperature a 73% yield of pure product was obtained after three weeks. This product was the expected 5-hydroxypyrido[3,2-a]phenazine (XI), identical with that prepared from 6-hydroxy-5,8-quinolinequinone (II). It is obvious that the phenazine XI could be formed from I only if one of the amino groups replaced the methoxyl group at the 6-position as indicated for the reactions of Table I.

The 6-*n*-hexylamino- and 6-*p*-toluidino-5,8-quinolinequinones (IV and V) were insoluble in water but formed salts when their alcoholic solutions were treated with dilute potassium hydroxide. Neither compound formed a salt when treated with aqueous sodium carbonate. It is therefore concluded that they probably exist predominately as the *p*-quinones, as formulated, but under the influence of strong alkali they tautomerize to salts of the 8-hydroxy-5,6-quinonimines



(12) L. F. Fieser, M. T. Leffler and co-workers, THIS JOURNAL, **70**, 3212 (1948).

(13) A 10% excess of the amine was used and the consumption of I was followed by means of Craven's test (R. Craven, *J. Chem. Soc.*, 1605 (1931)), in which the alcoholic solutions of certain quinones when treated with ammonia and ethyl cyanoacetate give an intense blue color. The test is positive for I and negative for the products III and for II which is a possible by-product.

(14) E. McC. Arnett, J. G. Miller and A. R. Day, THIS JOURNAL, **72**, 5635 (1950); **73**, 5393 (1951).

As expected, compound IX, which can exist only in form III, is less soluble in aqueous alkali than in water.

The results of biological tests of compounds VI–X will be published elsewhere.

Experimental[15]

6-Methoxy-5,8-quinolinequinone (I).—5,8-Diamino-6-methoxyquinoline was prepared by the method of Campbell.[9] The crude product was obtained in 94–98% yields and was oxidized directly since it could not be purified without considerable loss.

The oxidation was carried out with acid dichromate and as the acid was utilized rapidly at the start it was added in portions to minimize precipitation of the sulfate of the diamine and hydrolysis of the product. A solution of 20 g. of crude diamine in 10 ml. of 12 *N* sulfuric acid and 450 ml. of water was cooled to 20° and treated with stirring[16] at a maximum of 25° with a solution of potassium dichromate containing 100 g. per l. and 12 *N* sulfuric acid over a period of about two minutes in the following sequence: a mixture of 50 ml. of dichromate solution and 40 ml. of sulfuric acid, then 190 ml. of dichromate solution, 20 ml. of sulfuric acid and finally 400 ml. of chloroform. After 10 minutes, the stirrer was stopped, the organic layer was quickly drawn off into a separatory funnel and after the addition of 400 ml. of fresh chloroform, stirring was resumed. The small amount of aqueous layer or any emulsion removed in the first extraction was then separated and returned to the reaction vessel. After another 10 minutes reaction time the second chloroform layer was withdrawn and replaced in turn by two 200-ml. portions which were drawn off after 40 and 60 minutes total reaction time, respectively. The combined chloroform layers were washed twice with saturated sodium chloride solution and dried thoroughly over Drierite. The solution was then concentrated under reduced pressure to 250 ml., treated with Darco and further evaporated on the steam-bath until crystallization began. After the suspension was cooled, the remainder of the product was precipitated by the addition of a large volume of low-boiling petroleum ether. The yield of pale yellow product melting at 249.0–250.5° (dec. 245°) was 12.2 g. (60%). It could be recrystallized from methanol with little loss if the mother liquors were worked up after the first crop was removed. The light yellow needles melted at 250–251° after darkening at 245°.

Anal. Calcd. for $C_{10}H_7O_3N$: C, 63.49; H, 3.73; N, 7.41. Found: C, 63.51, 63.54; H, 4.01, 3.78; N, 7.41, 7.27.

6-Hydroxy-5,8-quinolinequinone (II).—When 1 g. of I was treated with a solution of 10 ml. of 1 *N* potassium hydroxide solution diluted with an equal volume of water the methoxy compound dissolved rapidly. After about 10 minutes the red solution was treated with 5 ml. of 2 *N* hydrochloric acid and cooled in an ice-bath. The hydroxy compound precipitated in quantitative yield as golden yellow needles which gradually decomposed above 200° becoming black and partly melting at 220°.

Anal. Calcd. for $C_9H_5O_3N$: C, 61.72; H, 2.88. Found: C, 61.94, 61.93; H, 3.04, 3.11.

5-Hydroxypyrido[3,2-a]phenazine (XI). A. From 6-Hydroxy-5,8-quinolinequinone (II).—One millimole of II was dissolved in about 15 ml. of boiling absolute ethanol, cooled slightly and treated with one equivalent of powdered *o*-phenylenediamine. The product began to separate immediately and the suspension was warmed on the steam-bath for 10 minutes. Upon cooling and washing with a large volume of ethanol there was obtained a 93% yield of pale yellow needles melting at 254.0–254.5°. After recrystallization from benzene the product melted at 256.0–256.5° with preliminary sintering.

Anal. Calcd. for $C_{15}H_9N_3O$: C, 72.86; H, 3.67. Found: C, 73.04, 73.00; H, 3.91, 3.84.

B. From 6-Methoxy-5,8-quinolinequinone (I).—One millimole of the methoxyquinone (I) in 5 ml. of chloroform was treated with a 10% excess of *o*-phenylenediamine and 3 ml. of absolute ethanol. The flask was tightly stoppered and allowed to stand at room temperature (26–30°) for three weeks. The product, which had crystallized, was filtered off and washed with absolute ethanol. It melted at 256.0–256.5° and did not depress the melting point of the phenazine obtained from II (above).

Etherification of 6-Hydroxy-5,8-quinolinequinone (II).—Two hundred milligrams of *p*-toluenesulfonic acid monohydrate was dissolved in benzene and dehydrated by distilling off the azeotrope. The last traces of benzene were removed under reduced pressure and one millimole of II and 4 ml. of methanol were added. The solution was heated under reflux for 1 hour and then cooled and treated with 2 ml. of water and excess sodium acetate. The cold suspension was filtered and the light brown crystalline product (0.105 g.) was washed with cold water. Extraction of the mother liquor with chloroform yielded only 0.01 g. of additional product. The crude material melted at 238–242° after decomposition began at about 220°. Upon recrystallization from methanol the melting point was raised to 247.0–249.5° and a mixture of this product and an authentic sample of 6-methoxy-5,8-quinolinequinone melted at 248–250°. Similar results were obtained by following the procedure of Fieser[17] with boron trifluoride as the catalyst but the yield was slightly lower.

Transetherification of I with Ethanol.—One gram of the methoxyquinone (I) was dissolved in 120 ml. of hot absolute ethanol and the solution was gently boiled on the steam-bath while the by-product methanol and the solvent distilled slowly through a short air condenser. More ethanol was added when necessary to prevent crystallization. At intervals 1- to 2-ml. samples were removed and evaporated to dryness in a vacuum oven. The dried residue was powdered and well mixed for a melting point determination. After 1 hour the melting point was 209–216°[18] (dec., preliminary sintering), after 2 hours, 205–206° dec.; after 2.5 hours, 205–206° dec. The solution was allowed to evaporate until crystallization began (about 25 ml.), the total heating period being 3 hours. The first crop of pale yellow needles obtained upon cooling weighed 0.84 g. and melted at 206–207° dec. After recrystallization from absolute ethanol, the melting point was 207.5–208.° (dec. 206°).

Anal. Calcd. for $C_{11}H_9O_3N$: C, 65.02; H, 4.46. Found: C, 64.90, 64.78; H, 4.22, 4.24.

6-*p*-Toluidino-5,8-quinolinequinone (IV).—One gram of the methoxyquinone (I) was heated under reflux in 10 ml. of acetic acid with 0.62 g. of *p*-toluidine for 1 hour. Most of the solvent was then removed in an air-stream under reduced pressure and the residue was triturated with water. The dark red crystals thus obtained weighed 0.825 g. and melted partially at 198°. After one recrystallization from dilute ethanol (using Darco) the dark red needles weighed 0.55 g. (40%) and melted at 214–217° with preliminary sintering. The pure product was obtained by further recrystallization from dilute ethanol in about 30% yield.

6-*n*-Hexylamino-5,8-quinolinequinone (V).—A suspension of 1 g. of the methoxy compound (I) in 15 ml. of absolute alcohol containing 0.59 g. (10% excess) of *n*-hexylamine was stirred magnetically at room temperature in a closed flask. After about 40 minutes the product began to crystallize. After 3.5 hours the red reaction mixture was treated with an equal volume of anhydrous ether, cooled and filtered. A trace of starting material which remained in the bottom of the flask was discarded. After it was washed well with ether and dried, the product weighed 0.80 g. and melted at 129.5–131.0° with preliminary sintering. The mother liquor was evaporated to dryness under reduced pressure and upon trituration with anhydrous ether the residue yielded a second crop of crystals. These were recrystallized from alcohol and water to give a total yield of 1 g. (73%). The analytical sample was prepared by recrystallization from alcohol and water.

(15) All melting points are corrected. The authors wish to thank Dr. Mary Aldridge and Miss Katherine Gerdeman for the microanalyses.

(16) A large C-shaped glass stirrer seemed most satisfactory for good agitation with the minimum of emulsification. The reaction may be advantageously carried out in a globe-shaped separatory funnel.

(17) L. F. Fieser, THIS JOURNAL, **70**, 3165 (1948).

(18) A mixture of roughly equal amounts of the pure methoxy- and ethoxyquinones was later found to sinter and darken slightly at 206° and finally melt gradually at about 214–220° as it became black. The melting points of both compounds are actually decomposition points.

Anal. Calcd. for $C_{15}H_{18}O_2N_2$: N, 10.85. Found: N, 11.02.

In contrast to the results observed with piperidine (below) only a slight difference in reaction time was noted when methanol was used as the solvent.

Compounds VI and VII.—A suspension of 5 g. of the methoxyquinone (I) in 75 ml. of methanol containing a 10% excess of the amine was stirred at room temperature for 4 hours. Slight warming occurred at the start. A trace of starting material was removed by filtration and the dark orange solution was evaporated to dryness at room temperature under reduced pressure. The residue was triturated with anhydrous ether and the brownish crystals thus obtained were recrystallized from Skellysolve (90–100°). The ethereal mother liquors yielded more of the product when treated with Darco, evaporated to a small volume and cooled. The additional crystals thus obtained were recrystallized from Skellysolve (90–100°) and combined with the main product to give the indicated yields of materials melting within 0.5–1.0° of the melting points of the analytical samples.

Compound VIII.—This product was prepared as compound VI except that the reaction time was 3 days. After the solvent was removed the residue was taken up in anhydrous ether and the ether solution decanted from a black tar. When the ether solution was evaporated to a low volume, cooled and treated gradually with small portions of high boiling Skellysolve (90–100°) the crystalline product separated. Material obtained by adding a large volume of Skellysolve to the ethereal mother liquor was recrystallized from Skellysolve (90–100°) and combined with the above giving a 55% yield of product which melted at 93–96° with preliminary sintering.

Compound IX.—In the reaction of I with piperidine, carried out as above, it was found that the reaction time was more than twice as long with ethanol as the solvent than it was with methanol. (Compound I dissolves more readily in methanol than in ethanol.) The reaction was essentially complete in 4 hours in methanol solution. After removal of a trace of starting material, the red solution was evaporated to dryness and the residue was recrystallized from a small volume of dilute methanol. The product thus obtained (82%) melted at 148.5–150.0°.

Compound X.—Five grams of I was suspended in 50 ml. of chloroform and stirred at room temperature to dissolve as much of the quinone as possible. Upon the addition of 50 ml. of diethylamine considerable spontaneous warming occurred. After the mixture had been stirred for 2 days the resulting dark orange solution was stirred with Darco, filtered and evaporated to dryness under reduced pressure. Upon recrystallization from benzene there was obtained 4.3 g. of red crystals which melted at 143–147° with preliminary sintering. An additional 1.5 g. of dark sticky crystals was obtained by concentrating the mother liquors, but this material was difficult to purify and only 0.4 g. of acceptable product (m.p. about 149–152° with sintering at about 140°) was readily obtained by recrystallization from benzene. The total yield was 4.7 g. (77%). After repeated recrystallization from carbon tetrachloride and from benzene the product had no definite melting point.

Hydrolysis of *n*-Hexylamino-5,8-quinolinequinone (V).—One millimole of V was dissolved in 2 to 3 ml. of absolute ethanol by heating and the warm solution was treated with 2 ml. of 1 *N* potassium hydroxide solution. The odor of hexylamine was apparent almost at once. After 1 hour at room temperature much of the starting material remained so the mixture was gently warmed. Since considerable decomposition occurred after 15 minutes, the solution was cooled and extracted with benzene. About 0.06 g. of starting material was recovered from the first benzene extract. After the aqueous layer had been freed of benzene under reduced pressure, it was neutralized with 1 ml. of 2 *N* hydrochloric acid. The brownish gold crystals of II weighed 0.06 g. (34% conversion, 44% yield). This crude product was converted to the phenazine (procedure A) which was obtained as light yellow needles (0.075 g., 39%). The melting point was 254.0–255.5° and that of a mixture with an authentic sample of the phenazine XI was the same.

COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM THE ORGANIC CHEMISTRY LABORATORIES OF THE UNIVERSITY OF FLORIDA]

Derivatives of Piperazine. XXVII. A Modified Strecker Synthesis Utilizing 1-Arylpiperazines[1]

BY C. B. POLLARD AND L. J. HUGHES

RECEIVED JUNE 12, 1954

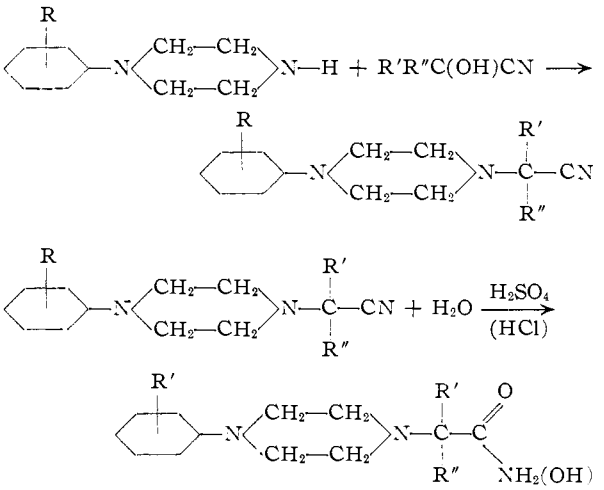
Thirty-seven new nitriles, amides and acids have been prepared from 1-arylpiperazines with chloroacetonitrile, lactonitrile or acetone cyanohydrin.

In the course of work in these laboratories on the preparation of physiologically active compounds it seemed advisable to prepare certain 2-amino acids using piperazines as the amines.

The 2-aminoalkylnitriles are best obtained by mixing the secondary amine and the cyanohydrin in the absence of a solvent.[2] A noticeable heat is evolved when the amine and cyanohydrin are mixed.

All the nitriles were obtained in quantitative yields of crude products. All compounds are solids.

The amides were made by dissolving the nitriles in concentrated sulfuric acid, allowing to stand 24 hours, and pouring the solution onto cracked ice. Isolation was effected by neutralization with ammonium hydroxide and filtration of the precipitated amide.



R = H, 2-CH_3, 3-CH_3, 4-CH_3, 2-Cl, 3-Cl, 4-Cl
R′ = H, CH_3
R″ = H, CH_3

(1) This paper is abstracted from a portion of a dissertation submitted by L. J. Hughes to the Graduate Council of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1953.

(2) R. A. Jacobson, THIS JOURNAL, **67**, 1996 (1945).