Calc. for $C_{17}H_{13}O_5N$: C, 65.54; H, 4.53. Found: C, 65.3; H, 4.4.

A solution of the acid in sodium carbonate immediately reduces permanganate, and gives benzaldehyde as one of the products. The structure of the acid was definitely established by synthesis. For this purpose a mixture of 4.8 g. of meta-nitrobenzaldehyde and 6.1 g. of methyl β-benzoyl-propionate was added to a solution of 75 g. sodium in 15 cc. of absolute alcohol. After the solution had stood at the ordinary temperature for two days, the alcohol was removed by distillation, the syrupy residue dissolved in water, and acidified. The resulting oil treated with a little ether in part dissolved, and in part solidified. The solid after crystallization from aqueous methyl alcohol melted at 172°, and was found identical with the product obtained by heating the dibasic acid.

$$NO_2C_6H_4CHO + CH_2(COC_6H_5)CH_2CO_2CH_3 \longrightarrow$$

$$NO_2C_6H_4CH : C(COC_6H_5)CH_2CO_2H.$$

Methyl β-(3-Nitrobenzal)-β-benzoyl-methylmalonate, $NO_2C_6H_4CH : C(COC_6H_5)CH(CO_2CH_3)_2$.—A solution of the cyclopropane ester melting at 109.5° in absolute methyl alcohol was added to a similar solution of magnesium methylate, and the mixture boiled for nearly 8 hours. The resulting bright yellow magnesium derivative was poured into iced acid, and the colorless ester recrystallized from methyl alcohol. It separated in prismatic crystals that melted at 139.5°.

Calc. for $C_{20}H_{17}O_7N$: C, 62.54; H, 4.46. Found: C, 62.6; H, 4.8.

The substance behaves exactly like the corresponding esters obtained from other cyclopropane esters. When oxidized with permanganate in aqueous acetone, it gives meta-nitrobenzoic acid as one of the products. In anhydrous permanganate, on the other hand, it takes up only a small quantity of oxygen, and gives a sparingly soluble condensation product of unknown structure. This crystallized from glacial acetic acid in small white crystals that melted at 197°.

Analyses gave the following results:

I. 0.1300 g. substance gave 0.0527 g. H_2O and 0.3020 g. CO_2.

II. 0.1357 g. substance gave 0.0550 g. H_2O and 0.3133 g. CO_2.

Found: (I) 63.3% C and 4.5% H. (II) 63.0% C and 4.5% H.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH.]

ON AMIDES, URAMINO COMPOUNDS, AND UREIDES CONTAINING AN AROMATIC NUCLEUS.

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The material for the present paper comprises a number of substances which figured as intermediates in an investigation, the results of which we hope soon to publish. The compounds discussed are amides and ureides of certain purely aromatic acids, amides and ureides of *m*- and *p*-aminophenylacetic acids, amides and ureides of derivatives of various aminophenoxyacetic acids, ureas in which the amide function is also present in the molecule, several sulfonamide derivatives, and one or two aromatic ureas containing less easily classified side chains.

EXPERIMENTAL.

(*A*) Amides Containing the Aromatic Nucleus.

(*1*) *Amides of Substituted Benzoic Acids.*

o-**Aminobenzamide.**[1]

o-**Chloroacetylaminobenzamide.**[2]

m-**Aminobenzamide.**[3]

m-**Chloroacetylaminobenzamide.**[4]

p-**Aminobenzamide.**[5]

p-**Chloroacetylaminobenzamide.**[6]

5-Aminosalicylamide (3-amino-6-hydroxybenzamide).—This substance was first prepared by reducing *m*-nitrobenzamide according to Gattermann's electrolytic method.[7] 20 g. of the nitro amide were reduced in 150 g. sulfuric acid and then diluted with ice until the volume was doubled. The sulfate of the aminosalicylamide gradually separated on rubbing and was filtered off on alundum. The product was dissolved in water and treated with enough barium chloride solution to precipitate the sulfuric acid. After filtering the solution was concentrated to small bulk *in vacuo,* the hydrochloride crystallizing on cooling. The salt was filtered off and washed with acetone. The yield was 11.5 g. A portion of the salt was dissolved in water and the free base liberated by adding ammonia in slight excess and scratching until crystallization started. Recrystallized from water containing a little ammonia the amide forms almost colorless, silky needles which are difficult to obtain free from color, owing to the tendency of the base to oxidize in solution. When rapidly heated to 190° and then slowly it melts at 194–7° with decomposition. It is sparingly soluble in the cold in water or absolute alcohol, readily in both on heating. It dissolves in acetone but is practically insoluble in benzene. An aqueous suspension of the amide gives a deep brown color with ferric chloride.

Kjeldahl: 0.1519 g. subst.; 19.75 cc. 0.1 *N* HCl.

Calc. for $C_7H_8O_2N_2$: N, 18.43%. Found: N, 18.21%.

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[1] THIS JOURNAL, 39, 1437 (1917).

[2] *Ibid.*, 39, 1442 (1917).

[3] *Ibid.*, 39, 1438 (1917).

[4] *Ibid.*, 39, 1442 (1917).

[5] *Ibid.*, 39, 1436 (1917), paragraph 2.

[6] *Ibid.*, 39, 1443 (1917).

[7] Gattermann, *Ber.*, 27, 1927 (1894).

In later preparations of the amide it was found more satisfactory, both from the standpoint of convenience and yield, to use 5-aminosalicylic methyl ester as the starting point. 63 g. of the ester were heated in an autoclave at 110° for 6 hours with 130 cc. of concentrated aqueous ammonia. The ammonia was distilled off *in vacuo* and the residue recrystallized from water, decolorizing with bone-black. The amide was obtained in this way in a yield of 45 g. and showed all of the properties given above.

5-Chloroacetylaminosalicylamide.—The aminoamide was chloroacetylated by dissolving in a mixture of 5 parts of saturated sodium acetate solution and 5 parts of acetic acid and adding 1.5 mols. of chloroacetyl chloride, drop by drop, with stirring and cooling.[1] The resulting solution was concentrated to dryness *in vacuo*, taken up in water, filtered off, and recrystallized from 50% alcohol, using bone-black. The yield was excellent. Recrystallized again, with bone-blacking, from 85% alcohol the substance forms aggregates of minute, slightly purplish platelets which melt at 225–7° to a dark liquid which slowly evolves gas. It is soluble in hot acetone or boiling water, and is quite soluble in alcohol at room temperature. An aqueous suspension gives a violet color with ferric chloride.

Kjeldahl: 0.1670 g. subst.; 14.60 cc. 0.1 *N* HCl.
Calc. for $C_9H_9O_3N_2Cl$: N, 12.26%. Found: N, 12.25%.

(2) *Amides of Aminophenylacetic Acids.*

m-**Aminophenylacetic Methyl Ester Hydrochloride.**—56 g. *m*-aminophenylacetic acid[2] were treated with 500 cc. of dry methyl alcohol and saturated with dry hydrochloric acid gas. The resulting solution was concentrated to dryness *in vacuo*, taken up in a small quantity of dry methyl alcohol, and precipitated with dry ether. After standing in the ice box the salt was filtered off and washed with dry ether. The yield was 60 g. A portion was recrystallized by dissolving in cold absolute alcohol, bone-blacking, filtering, and adding dry ether. It separated as long, thin, glistening plates which dissolve readily in the cold in methyl or ethyl alcohol. When rapidly heated to 160° and then slowly the salt softens and melts at 167–70° with slow gas evolution. It is readily diazotized, giving a scarlet color with R-salt. An aqueous solution, treated with sodium carbonate, gave the free ester as an oil which did not solidify.

0.1955 g. subst.; 0.1385 g. AgCl.
Calc. for $C_9H_{11}O_2N.HCl$: Cl, 17.59%. Found: Cl, 17.53%.

m-**Aminophenylacetamide,** *m*-$H_2NC_6H_4CH_2CONH_2$.—55 g. of the above hydrochloride were dissolved in 200 cc. of cold, concentrated, aqueous ammonia and let stand, with occasional shaking, for 24 hours. The

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[1] Cf. THIS JOURNAL, 39, 1439 (1917).

[2] *Ibid.*, 39, 1437 (1917).

amide which had separated was filtered off, washed with a little water, and dried. The yield was 36 g. A portion was recrystallized from water, decolorizing with bone-black, and adding a drop of aqueous ammonia to the filtered solution. The amide separates slowly as transparent prisms which are anhydrous. Recrystallized again from 95% alcohol it forms leaflets which melt at 164–6° (corr.) with preliminary softening. It is readily soluble in boiling water, less easily in boiling 95% alcohol and sparingly so in acetone or ethyl acetate. The amide is readily diazotized.

Kjeldahl: 0.1402 g. subst.; 18.65 cc. 0.1 *N* HCl.
Calc. for $C_8H_{10}ON_2$: N, 18.67%. Found: N, 18.63%.

m-**Chloroacetylaminophenylacetamide.**—10 g. of the crude amide were chloroacetylated in a mixture of 50 cc. acetic acid and 50 cc. of saturated sodium acetate solution. The acyl derivative separated from the reaction mixture on scratching. After recrystallization from 50% alcohol the yield was 6 g. The substance forms prismatic needles which melt with slight preliminary softening at 187–8° to a pale brown liquid. The compound is readily soluble in boiling acetic acid, less easily in boiling water or 50% alcohol, and almost insoluble in chloroform.

Kjeldahl: 0.1451 g. subst.; 12.9 cc. 0.1 *N* HCl.
Calc. for $C_{10}H_{11}O_2N_2Cl$: N, 12.37%. Found: N, 12.45%.

p-**Aminophenylacetamide.**[1]

p-**Chloroacetylaminophenylacetamide.**[1]

(3) *Derivatives of the Aminophenoxyacetamides.*

In a first attempt to prepare *o*-chloroacetylaminophenoxyacetamide, *o*-$ClCH_2CONHC_6H_4OCH_2CONH_2$, *o*-nitrophenoxyacetamide was reduced by the ferrous sulfate and ammonia method[2] with the expectation of obtaining *o*-aminophenoxyacetamide. The only product isolated, however, was *o*-aminophenoxyacetic anhydride,[3] which was formed by the elimination of ammonia from the intermediate *o*-aminophenoxyacetamide. The desired chloroacetyl compound was finally obtained by the series of reactions outlined below, a description of *o*-nitrophenoxyacetamide being given first.

o-**Nitrophenoxyacetamide,** *o*-$O_2NC_6H_4OCH_2CONH_2$. — 47 g. *o*-nitrophenoxyacetic acid[4] were dissolved in 300 cc. of dry methyl alcohol and saturated with hydrochloric acid gas. The resulting methyl ester was dissolved in ether and the solution shaken with concentrated aqueous ammonia. The amide rapidly crystallized out and was filtered off and washed with water. The yield was 18 g. Recrystallized from water it

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[1] THIS JOURNAL, 39, 1444 (1917).
[2] *Ibid.*, 39, 1435 (1917).
[3] *Ibid.*, 39, 2190 (1917).
[4] *Ibid.*, 39, 2191 (1917).

forms long, glistening needles which melt at 194.5–5.5° (corr.). The amide is only sparingly soluble in hot water, 95% alcohol, or acetone. When boiled with dilute sodium hydroxide it is easily hydrolyzed.

Kjeldahl: 0.2180 g. subst.; 22.30 cc. 0.1 *N* HCl.
Calc. for $C_8H_8O_4N_2$: N, 14.29%. Found: N, 14.33%.

***o*-Chloroacetylaminophenoxyacetic Acid,** *o*-$ClCH_2CONHC_6H_4OCH_2CO_2H$.—6 g. potassium *o*-aminophenoxyacetate were dissolved in 120 cc. 5% aqueous sodium hydroxide solution, turbined, and treated, drop by drop, with 4.5 cc. chloroacetyl chloride. At the end the solution was acidified with acetic acid, when it remained clear, showing the absence of unchanged *o*-aminophenoxyacetic anhydride (the free *o*-aminophenoxyacetic acid does not exist under ordinary conditions). On acidifying to Congo Red with hydrochloric acid the *o*-chloroacetylaminophenoxyacetic acid separated. The yield was 5 g. It crystallizes from 50% acetic acid with 2 molecules of water of crystallization which are lost on heating *in vacuo*, finally at 110°. The air-dried substance melts partially and effervesces when rapidly heated to about 100°, while the anhydrous compound melts at 144.5–5.5° (corr.) with slight preliminary softening. The acid dissolves readily in acetone, less easily in chloroform, and very difficultly in benzene.

Air dry: 0.9989 g. subst.; 0.1350 g. loss. H_2O, 13.52%. Calc. for 2 H_2O: H_2O, 12.88%.
Anhydrous: Kjeldahl: 0.3088 g. subst.; 12.70 cc. 0.1 *N* HCl.
Calc. for $C_{10}H_{10}O_4NCl$: N, 5.75%. Found: N, 5.76%.

***o*-Chloroacetylaminophenoxyacetyl Chloride,** $ClCH_2CONHC_6H_4OCH_2COCl$.—23 g. phosphorus pentachloride were added to a suspension of 23 g. *o*-chloroacetylaminophenoxyacetic acid in 50 cc. benzene. As the reaction proceeded hydrochloric acid was evolved and the acid went into solution. At the end ligroin was added until the precipitation of the chloride was complete. The product was filtered off and washed with ligroin. The yield was 19 g. Recrystallized from ligroin the chloride forms colorless plates which melt at 52–9° with preliminary softening and dissolve readily in the usual organic solvents with the exception of ligroin.

Kjeldahl: 0.2025 g. subst.; 7.80 cc. 0.1 *N* HCl.
Calc. for $C_{10}H_9O_3NCl_2$: N, 5.35%. Found: N, 5.39%.

***o*-Chloroacetylaminophenoxyacetamide.**—18 g. of the chloride were dissolved in chloroform, chilled, and treated with concentrated aqueous ammonia. The amide, which separated at once, was more completely thrown out by the addition of petroleum ether and was filtered off and washed with water. Recrystallized from water it forms needles which melt constantly at 158–61° with preliminary softening. The substance is sparingly soluble in cold water or 95% alcohol, readily in hot, and also dissolves in acetone or hot chloroform. It gives a strong Beilstein test.

0.1485 g. subst.; 14.6 cc. N, 765 mm., 19.0°.
Calc. for $C_{10}H_{11}O_3N_2Cl$: N, 11.55%. Found: N, 11.57%.

***m*-Aminophenoxyacetamide.**—*m*-Aminophenoxyacetic ethyl ester hydrochloride[1] was dissolved in a little warm water, cooled, and shaken with concentrated aqueous ammonia. The oily ester gradually dissolved on shaking. After standing overnight the solution was evaporated to small bulk and cooled, whereupon the amide separated. This was filtered off, washed with a little water, and recrystallized, with bone-blacking, first from a little water, then from a small amount of 95% alcohol. It forms delicate, cream-colored needles which soften above 118°, melt partially at about 119°, and are completely fused at 123.5–24° (corr.). The amide is soluble in water, alcohol, methyl alcohol, or acetone, and almost insoluble in benzene. It is readily diazotized.

Kjeldahl: 0.1782 g. subst.; 21.55 cc. 0.1 *N* HCl.
Calc. for $C_8H_{10}O_2N_2$: N, 16.87%. Found: N, 16.94%.

***m*-Chloroacetylaminophenoxyacetamide.** — The amide was chloroacetylated in a mixture of 5 parts of acetic acid and 5 parts of saturated sodium acetate solution. The chloroacetyl derivative separated from the reaction mixture after a few moments. Recrystallized from acetic acid, in which it is less sparingly soluble at the boiling point than in the other usual solvents, it forms radiating masses of microscopic leaflets. Rapidly heated to 230°, then slowly, it melts 235–8° to a clear liquid which soon darkens and decomposes.

Kjeldahl: 0.1637 g. subst.; 13.25 cc. 0.1 *N* HCl.
Calc. for $C_{10}H_{11}O_3N_2Cl$: N, 11.55%. Found: N, 11.33%.

***p*-Aminophenoxyacetamide.**—40 g. *p*-aminophenoxyacetic methyl ester hydrochloride[2] were added to 80 cc. of concentrated aqueous ammonia, with cooling. The free ester separated and gradually went into solution on shaking. The amide separated on scratching, and after standing for several hours was filtered off, washed with a little concentrated aqueous ammonia, and dried. The yield was 28 g. The amide is soluble in cold water, from which it is thrown out by alkalies. It separates from hot, concentrated aqueous solutions as glistening, brownish platelets. It is sparingly soluble in cold ethyl acetate, separating from the hot solution as cream-colored prisms which soften at 125° and melt at 127.5–8.5°. It is difficultly soluble in benzene or chloroform, readily in acetone. An aqueous solution gives a slowly developing rose color with ferric chloride and is readily diazotized, yielding a scarlet dye with R-salt.

Kjeldahl: 0.1972 g. subst.; 23.60 cc. 0.1 *N* HCl.
Calc. for $C_8H_{10}O_2N_2$: N, 16.87%. Found: N, 16.77%.

***p*-Chloroacetylaminophenoxyacetamide.**—5 g. of the amide were chloro-

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[1] THIS JOURNAL, **39**, 2192 (1917).

[2] *Ibid.*, **39**, 2196 (1917).

acetylated as in previous examples. The reaction mixture set to a thick mass. The yield of chloroacetyl derivative was 6.5 g. A portion was recrystallized first from 50% alcohol, then from water, forming practically colorless needles which melt at 195–6.5° (corr.) with slight preliminary softening. The compound is sparingly soluble in absolute alcohol or chloroform, and almost insoluble in benzene or cold water.

Kjeldahl: 0.1485 g. subst.; 12.25 cc. 0.1 *N* HCl.
Calc. for $C_{10}H_{11}O_3N_2Cl$: N, 11.55%. Found: N, 11.56%.

Hexamethylenetetraminium Salt of *p*-Chloroacetylaminophenoxyacetamide.—4.5 g. of the chloroacetyl derivative and 2.3 g. hexamethylenetetramine were boiled in 250 cc. acetone for 5 hours. The suspension of chloroacetyl compound gradually changed into a heavy precipitate consisting of prisms and plates. The product was filtered off and washed with dry acetone. The yield was 4.6 g. The salt is soluble in cold water, but very sparingly so in boiling acetone, absolute alcohol, or chloroform.

0.1811 g. subst.; 0.0664 g. AgCl.
Calc. for $C_{16}H_{23}O_3N_6Cl$: Cl, 9.27%. Found: Cl, 9.07%.

***p*-Nitrophenoxyacetyl Chloride.**—Equimolecular amounts of *p*-nitrophenoxyacetic acid[1] and phosphorus pentachloride were warmed on the steam bath until evolution of hydrochloric acid had ceased and a homogeneous liquid was obtained. Ligroin was then added, precipitating the *p*-nitrophenoxyacetyl chloride in practically quantitative yield. A portion was recrystallized from benzene, forming transparent, hexagonal tablets which melt at 86–7° (corr.) with slight preliminary softening. The chloride is soluble in ether or benzene and reacts slowly in the cold with water or absolute alcohol.

0.2532 g. subst., boiled with aq. NH_3; 0.1679 g. AgCl.
Calc. for $C_8H_6O_4NCl$: Cl, 16.45%. Found: Cl, 16.40%.

***p*-Nitrophenoxyacetmethylamide, *p*-$O_2NC_6H_4OCH_2CONHCH_3$.**—22 g. *p*-nitrophenoxyacetyl chloride in dry chloroform were poured into a well chilled solution of an equimolecular amount (8 g.) of methylamine hydrochloride in 100 cc. of 10% aqueous sodium hydroxide. On shaking, the amide crystallized out at once, and was filtered off and washed with water. The yield was 19 g. The amide dissolves in boiling water with a pale yellow color and separates from the cooled solution in brilliant needles. Recrystallized again from toluene it melts at 165.6° (corr.) with preliminary softening. It is rather difficultly soluble in hot absolute alcohol or toluene, more easily in hot water.

Kjeldahl: 0.1775 g. subst.; 16.80 cc. 0.1 *N* HCl.
Calc. for $C_9H_{10}O_4N_2$: N, 13.33%. Found: N, 13.26%.

***p*-Aminophenoxyacetmethylamide.**—5 g. of the nitroamide were added in small portions to a solution of 25 g. stannous chloride in 50 cc. of con-

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[1] Cf. THIS JOURNAL, 39, 1437 (1917).

centrated hydrochloric acid immersed in a freezing mixture. The resulting crystalline precipitate was filtered off and dissolved in an excess of well-chilled 10% sodium hydroxide solution. The aminoamide was extracted from the solution by shaking out with ethyl acetate. This was dried, concentrated to small bulk, and the amide precipitated by the addition of petroleum ether. The yield was 2.7 g. Recrystallized twice from toluene, it forms glistening, cream-colored needles which melt at 109.5–11° (corr.) with slight preliminary softening. The amide is easily soluble in water, alcohol, or acetone, difficultly in cold toluene. It is readily diazotized. An aqueous solution gives a slowly developing violet-rose color with ferric chloride.

Kjeldahl: 0.1539 g. subst.; 17.05 cc. 0.1 *N* HCl.
Calc. for $C_9H_{12}O_2N_2$: N, 15.56%. Found: N, 15.52%.

2-Methyl-4-aminophenoxyacetamide.—5 g. 2-methyl-4-aminophenoxyacetic methyl ester hydrochloride[1] were treated with an excess of concentrated aqueous ammonia. The lumpy mass was ground up in a mortar and allowed to stand for several hours, setting to a solid cake. This was disintegrated, filtered, and washed with a little water. Recrystallized first from water, then from 95% alcohol, the amide forms long, flat, glistening needles which soften at 155° and melt at 155.5–56° (corr.). It is sparingly soluble in cold water or 95% alcohol, readily on boiling, and dissolves also in acetone or methyl alcohol. When diazotized, it yields a deep red color with R-salt. An aqueous solution gives a brown coloration with ferric chloride, changing through purple to violet.

Kjeldahl: 0.1602 g. subst.; 17.90 cc. 0.1 *N* HCl.
Calc. for $C_9H_{12}O_2N_2$: N, 15.56%. Found: N, 15.65%.

3-Methyl-4-aminophenoxyacetamide.—2 g. 3-methyl-4-aminophenoxyacetic ethyl ester hydrochloride[2] were treated with an excess of concentrated aqueous ammonia and allowed to stand two days, with occasional stirring. The oily ester was gradually converted into the crystalline amide. This was filtered off and recrystallized twice from water, forming faintly pinkish, radiating masses of long, fine hairs which melt at 136–7° with slight preliminary softening and slight gas evolution. The amide is readily soluble in 85% alcohol or acetone, less easily in water or chloroform, and sparingly in benzene. It is easily diazotized, giving a red color with R-salt, and, in aqueous solution, yields a brown color with ferric chloride, rapidly changing to purple.

Kjeldahl: 0.1502 g. subst.; 16.60 cc. 0.1 *N* HCl.
Calc. for $C_9H_{12}O_2N_2$: N, 15.56%. Found: N, 15.48%.

2,5-Dimethyl-4-aminophenoxyacetamide.—3 g. 2,5-dimethyl-4-amino-

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[1] THIS JOURNAL, **39**, 2199 (1917).

[2] *Ibid.*, **39**, 2201 (1917).

phenoxyacetic methyl ester hydrochloride[1] were suspended in alcohol and an excess of concentrated aqueous ammonia added. The amide separated from the clear solution on standing overnight. The mixture was concentrated to remove the alcohol and the amide then filtered off and recrystallized first from water, then from 95% alcohol. It forms delicate, silky needles which soften above 151.5° and melt at 153–4° (corr.). It is sparingly soluble in the cold in water, chloroform, or benzene, readily on warming, and is more soluble in the cold in 95% alcohol or acetone. It is readily diazotized, giving a carmine color with R-salt, and in aqueous solution yields a slowly developing, deep violet color with ferric chloride.

Kjeldahl: 0.1551 g. subst.; 15.85 cc. 0.1 *N* HCl.
Calc. for $C_{10}H_{14}O_2N_2$: N, 14.43%. Found: N, 14.32%.

2-Methyl-4-amino-5-isopropylphenoxyacetamide.—2 g. 2-methyl-4-amino-5-isopropylphenoxyacetic methyl ester hydrochloride[2] were suspended in alcohol and treated with an excess of concentrated aqueous ammonia. After 2 days the clear solution was concentrated on the water bath and cooled after adding a few drops of ammonia. The amide which separated was filtered off, dried, and recrystallized by dissolving in hot benzene, decolorizing with bone-black, adding ligroin until the turbidity first formed just dissolved, and seeding. 1.2 g. of the amide separated slowly in the form of aggregates of minute prisms and plates. Recrystallized again from water, from which it separates as slightly pinkish rhombs, then from toluene, the amide forms aggregates of diamond-shaped plates which melt at 108–9° (corr.) and are soluble at room temperature in water and the usual organic solvents except ligroin. A diazotized solution of the amide gives a deep red color with R-salt, while an aqueous solution gives a slowly developing violet-blue with ferric chloride. A dilute acetic acid solution gives a transitory blue color with sodium nitrite.

Kjeldahl: 0.1532 g. subst.; 13.75 cc. 0.1 *N* HCl.
Calc. for $C_{12}H_{18}O_2N_2$: N, 12.62%. Found: N, 12.57%.

3-Methyl-4-amino-6-isopropylphenoxyacetamide.—3 g. 3-methyl-4-amino-6-isopropylphenoxyacetic methyl ester hydrochloride[3] were taken up in alcohol and treated with an excess of concentrated aqueous ammonia, enough alcohol being present to prevent separation of the oily ester. After standing overnight the solution was evaporated to small bulk on the water bath, treated with a few drops of ammonia, cooled, and stirred, whereupon the amide crystallized. It was filtered off and recrystallized, first from water, using bone-black, then from toluene, forming pointed

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[1] THIS JOURNAL, 39, 2205 (1917).
[2] *Ibid.*, 39, 2206 (1917).
[3] *Ibid.*, 39, 2207 (1917).

leaflets which soften at 124.5° and melt at 125–5.5° (corr.). It is sparingly soluble in cold water, more readily in hot, melting down before dissolving, and separating on cooling as pinkish needles. It is readily soluble in the cold in acetone, alcohol, or chloroform; difficultly in cold benzene or toluene and readily on warming. An aqueous suspension gives a gray color with ferric chloride, changing through purple to violet-blue. When diazotized the amide gives a carmine color with R-salt.

Kjeldahl: 0.1454 g. subst.; 12.95 cc. 0.1 *N* HCl.
Calc. for $C_{12}H_{18}O_2N_2$: N, 12.62%. Found: N, 12.48%.

2-Bromo-4-aminophenoxyacetamide.—3 g. 2-bromo-4-aminophenoxyacetic methyl ester hydrochloride[1] were taken up in alcohol and treated with an excess of concentrated aqueous ammonia. After two days the clear solution was concentrated on the water bath and treated with a few drops of ammonia. The amide separated and was filtered off and recrystallized first from water, using bone-black, then from a small volume of 95% alcohol. It forms radiating masses of long, flat, cream-colored needles which melt at 159–60° (corr.) with slight preliminary softening. It is soluble in acetone or boiling water, more readily in boiling 95% alcohol, and sparingly in the last two in the cold. The amide is readily diazotized and, in aqueous suspension, gives a slowly developing wine-red color with ferric chloride.

Kjeldahl: 0.2649 g. subst.; 21.70 cc. 0.1 *N* HCl.
Calc. for $C_8H_9O_2N_2Br$: N, 11.43%. Found: N, 11.47%.

4-Amino-6-methoxyphenoxyacetamide. — 4 g. 4-amino-6-methoxyphenoxyacetic ethyl ester hydrochloride[2] were decomposed with aqueous ammonia. On standing the oily ester gradually changed to the crystalline amide. This was filtered from the deep blue solution and recrystallized first from water, with bone-blacking, then from 95% alcohol. It forms almost colorless, glistening needles which melt at 177.5–8.5° (corr.) with preliminary softening. It is sparingly soluble in cold water or 95% alcohol, readily on heating, and also dissolves with difficulty in acetone, the crystalline form changing on heating with this solvent. When diazotized it gives a purplish red color with R-salt, while in aqueous solution it gives a brown color with ferric chloride, rapidly changing through purple to brown-lilac.

Kjeldahl: 0.1560 g. subst.; 16.00 cc. 0.1 *N* HCl.
Calc. for $C_9H_{12}O_3N_2$: N, 14.29%. Found: N, 14.37%.

4-Amino-6-carbethoxyphenoxyacetamide.—1.8 g. 4-amino-6-carbethoxyphenoxyacetic ethyl ester hydrochloride[3] were treated with an excess of concentrated aqueous ammonia. The oily ester gradually changed

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[1] THIS JOURNAL, **39**, 2209 (1917).
[2] *Ibid.*, **39**, 2212 (1917).
[3] *Ibid.*, **39**, 2214 (1917).

to the crystalline amide. After standing overnight the amide was filtered off and recrystallized twice from 95% alcohol, forming minute leaflets which melt at 135–6° (corr.) with preliminary softening. It is difficultly soluble in cold water, readily on boiling, and is quite soluble in alcohol at room temperature, less easily at 0°. On adding sodium hydroxide to an aqueous solution the amide is salted out, but on boiling it redissolves, ammonia is evolved, and the solution gives the iodoform test, thus demonstrating both the amide and ester functions.

Kjeldahl: 0.1917 g. subst.; 15.65 cc. 0.1 *N* HCl.

Calc. for $C_{11}H_{14}O_4N_2$: N, 11.76%. Found: N, 11.43%.

4-Amino-6-acetophenoxyacetamide.—3 g. 4-amino-6-acetophenoxyacetic methyl ester hydrochloride[1] were treated with alcohol and concentrated aqueous ammonia, using sufficient alcohol to keep the ester from separating. After several days the solution was concentrated on the water bath, adding a few drops of ammonia at the end. The amide, which separated on cooling, was recrystallized, first from a small volume of water, using bone-black, then from a small amount of 95% alcohol. It forms brownish yellow leaflets, many of which are diamond-shaped. The amide melts at 138–9° with preliminary softening and slight gas evolution. It is easily soluble in boiling water or 95% alcohol, sparingly in the cold, and dissolves in dilute hydrochloric acid without color. It is soluble in acetone, difficultly in benzene. An aqueous solution gives a slowly developing, deep brown color with ferric chloride.

Kjeldahl: 0.2539 g. subst.; 24.20 cc. 0.1 *N* HCl.

Calc. for $C_{10}H_{12}O_3N_2$: N, 13.47%. Found: N, 13.36%.

(4) *Derivatives of Aminobenzenesulfonamides.*

***m*-Aminobenzenesulfonamide** is perhaps most easily accessible through the reduction of the nitro compound. As we were in the possession of a considerable quantity of metanilic acid we decided to attempt the preparation with this as starting material. The reaction was carried out in the following steps: metanilic acid ⟶ sodium *m*-acetaminobenzenesulfonate ⟶ *m*-acetaminobenzenesulfone chloride ⟶ *m*-acetaminobenzenesulfonamide ⟶ *m*-aminobenzenesulfonamide. The only new substance isolated in a state of purity was the *m*-acetaminobenzenesulfonamide.

***m*-Acetaminobenzenesulfonamide,** *m*-$CH_3CONHC_6H_4SO_2NH_2$.—129 g. metanilic acid were acetylated by dissolving in 750 cc. of normal sodium hydroxide solution (1 mol), adding 90 cc. acetic anhydride (1.2 mols), and shaking. The resulting solution was concentrated to dryness *in vacuo* and the residue of sodium *m*-acetaminobenzenesulfonate taken up in acetone, filtered off, and dried at 120°. The yield of crude salt was 155 g. 50 g. of this were ground up in a mortar with 50 g. phosphorus penta-

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[1] THIS JOURNAL, **39**, 2215 (1917).

chloride, the mass liquefying, evolving hydrochloric acid, and finally hardening to some extent. Ice-water was then added, yielding two layers, of which the upper was decanted and the lower layer of crude chloride washed twice more with ice-water by decantation. The product was then ground up with 50 cc. of aqueous ammonia (d. 0.94), causing gradual crystallization of the amide. This was filtered off and washed with a little water. The yield was 11.2 g. Recrystallized first from 50% alcohol, then from acetic acid, the amide forms minute rhombs which melt constantly at 216–9° with slight preliminary softening. When pure the amide is soluble in acetone or hot acetic acid and sparingly so in the other usual solvents, while the crude substance is considerably more soluble. When hydrolyzed with 1 : 1 hydrochloric acid it yields *m*-aminobenzenesulfonamide in about 75% of the theory and corresponding in its properties with those recorded in the literature.

Kjeldahl: 0.1495 g. subst.; 13.85 cc. 0.1 *N* HCl.
Calc. for $C_8H_{10}O_3N_2S$: N, 13.08%. Found: N, 12.98%.

m-**Chloroacetylaminobenzenesulfonamide.**—18.8 g. *m*-aminobenzenesulfonamide were brought into solution in a mixture of 95 cc. acetic acid and 95 cc. saturated sodium acetate solution by warming gently. The solution was cooled to 0° and treated, drop by drop, with shaking and cooling, with 11.3 cc. chloroacetyl chloride. The chloroacetyl derivative separated on scratching and was filtered off and combined with an additional amount obtained by concentrating the filtrate *in vacuo*. After recrystallization from water the yield was 24.5 g. Recrystallized, with bone-blacking, from 95% alcohol the compound forms aggregates of minute needles which soften slightly when heated, melt incompletely at 153–5°, and form a clear melt at about 165°. It dissolves readily in boiling water, sparingly in the cold, is almost insoluble in chloroform or benzene, and dissolves in acetone or 95% alcohol at room temperature.

Kjeldahl: 0.1540 g. subst.; 12.25 cc. 0.1 *N* HCl.
Calc. for $C_8H_9O_3N_2ClS$: N, 11.27%. Found: N, 11.14%.

p-**Chloroacetylaminobenzenesulfonamide.** — *p*-Aminobenzenesulfonamide was prepared essentially as directed by Gelmo,[1] the only new feature being the acetylation of sodium sulfanilate as given above in the case of the *meta* isomer. 10 g. of the amide were warmed with 50 cc. 50% acetic acid, 50 cc. saturated sodium acetate solution, and 50 cc. acetic acid until dissolved, cooled in ice-water, and treated in the usual way with 6 cc. chloroacetyl chloride. The chloroacetyl derivative separated almost immediately and was filtered off and washed well with 50% acetic acid and water. Recrystallized from 95% alcohol it forms needles which melt with slight preliminary softening at 215–7° to a clear liquid which soon darkens. The substance is soluble in hot water or 95% alcohol, cold ethyl

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[1] Gelmo, *J. prakt. Chem.*, [2] 77, 369 (1907).

acetate or acetone, and difficultly so in chloroform or benzene. It also dissolves in sodium hydroxide solution.

Kjeldahl: 0.1433 g. subst.; 11.55 cc. 0.1 *N* HCl.
Carius: 0.1820 g. subst.; 0.1037 g. AgCl, 0.1733 g. $BaSO_4$.
Calc. for $C_8H_9O_3N_2ClS$: N, 11.27%; Cl, 14.26%; S, 12.90%.
Found: N, 11.29%; Cl, 14.09%; S, 13.08%.

(*B*) Ureides Containing the Aromatic Nucleus.

(*1*) *Ureides of Substituted Benzoic Acids.*

o-Aminobenzoylurea.[1]

o-Chloroacetylaminobenzoylurea, o-$ClCH_2CONHC_6H_4CONHCONH_2$.—10 g. o-aminobenzoylurea were dissolved by warming with 300 cc. 50% acetic acid, 25 cc. saturated sodium acetate solution, and 25 cc. acetic acid. The solution was rapidly cooled until lukewarm and treated with 7 cc. chloroacetyl chloride. The chloroacetyl derivative slowly separated. After cooling and letting stand the product was filtered off, washed with 2.5% hydrochloric acid containing a little alcohol to remove unchanged amino compound, and finally washed with water and dried. The yield was 6.2 g. Recrystallized from 50% alcohol it forms long, glistening needles which are difficultly soluble in water, dilute or 95% alcohol, and acetone at their boiling points. When rapidly heated to 220°, then slowly, it softens slightly and melts with effervescence at 222–3°, then darkens and decomposes. On boiling in aqueous solution with sodium hydroxide, ammonia is evolved and the resulting solution contains chlorine ion.

0.1202 g. subst.; 17.2 cc. N, 760 mm., 22.5°.
Calc. for $C_{10}H_{10}O_3N_3Cl$: N, 16.44%. Found: N, 16.53%.

***m*-Aminobenzoylurea.**[2]

***m*-Chloroacetylaminobenzoylurea.**—12 g. *m*-aminobenzoylurea were dissolved in a mixture of 150 cc. 50% acetic acid and 150 cc. acetone. 20 g. sodium acetate were then added, followed by 8 cc. chloroacetyl chloride, added drop by drop, with vigorous shaking. The chloroacetyl derivative separated at once and was filtered off after diluting the mixture with water. The yield was 14 g. Recrystallized from water, it forms delicate needles which are difficultly soluble in the usual solvents. When rapidly heated to 250°, then slowly, it decomposes at 252–3°.

0.1122 g. subst.; 16.0 cc. N, 758 mm., 20.5°.
Calc. for $C_{10}H_{10}O_3N_3Cl$: N, 16.44%. Found: N, 16.55%.

***p*-Nitrobenzoylurea,** *p*-$O_2NC_6H_4CONHCONH_2$.—40 g. *p*-nitrobenzoyl chloride and 30 g. urea were boiled in 100 cc. benzene on the water bath for several hours. After cooling the mixture was treated with water, filtered, washed with water and acetone, and dried. The yield was 38 g.

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[1] THIS JOURNAL, **39**, 1438 (1917).

[2] *Ibid.*, **39**, 1439 (1917).

Recrystallized from acetic acid, it forms aggregates of microscopic prisms which are less difficultly soluble in acetic acid than in the other usual solvents. When rapidly heated to 240°, then slowly, it melts at 243–5° with gas evolution and slight preliminary softening.

0.0902 g. subst.; 15.8 cc. N, 767 mm., 22.0°.
Calc. for $C_8H_7O_4N_3$: N, 20.10%. Found: N, 20.46%.

p-**Aminobenzoylurea.**—35 g. of the finely powdered nitrobenzoylurea were heated on the water bath in a mixture of 400 cc. ammonium sulfide solution and 100 cc. alcohol, with frequent shaking. The character of the precipitate suddenly changed, indicating that reduction had taken place. After one hour's heating the aminobenzoylurea was filtered off and washed well with water. The yield of crude product was 30 g. For analysis a portion was ground up with dilute sulfuric acid and treated with water until most of the material had dissolved. The solution was filtered and the free base precipitated with ammonia. The urea was filtered off and washed successively with water, alcohol, and benzene. It is very difficultly soluble in the usual solvents, including acids, and separates from boiling water as minute, colorless plates. A suspension in dilute hydrochloric acid yields a soluble diazonium salt with sodium nitrite, coupling with R-salt to give a scarlet color. The urea decomposes partly at about 240° but does not melt below 285°.

Kjeldahl: 0.1113 g. subst.; 18.50 cc. 0.1 *N* HCl.
Calc. for $C_8H_9O_2N_3$: N, 23.46%. Found: N, 23.29%.

The nitrobenzoylurea may also be reduced by the ferrous sulfate and ammonia method,[1] adding an equal volume of alcohol to the mixture after reducing and again bringing to a boil before filtering. The yield by this method, however, was only about 40% of the theory.

p-**Chloroacetylaminobenzoylurea.**—Owing to the sparing solubility of *p*-aminobenzoylurea in dilute acetic acid the chloroacetylation is best accomplished by the procedure used by us for chloroacetylating the uramino group.[2]

10 g. chloroacetic acid were melted on the water bath and 3 g. crude *p*-aminobenzoylurea added to the melt. To the suspension so obtained 2.1 cc. chloroacetyl chloride were added, causing an immediate reaction marked by the evolution of hydrochloric acid gas and solidification of the mixture. An additional 5 g. chloroacetic acid were added to increase the fluidity of the mixture, the lumpy mass was disintegrated and the heating continued for a total of one-half hour. Water was then added and the product filtered off and washed well with water. The yield of crude product was 4.6 g. A portion was recrystallized from a large volume of hot water, forming minute needles and prisms which dissolve with

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[1] *Loc. cit.*

[2] THIS JOURNAL, 39, 1446 (1917).

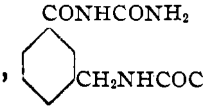
less difficulty in boiling acetic acid than in the other usual solvents. When rapidly heated to 275°, then slowly, the urea decomposes at 275–80° with slight preliminary softening.

Kjeldahl: 0.1000 g. subst.; 11.65 cc. 0.1 *N* HCl.
Calc. for $C_{10}H_{10}O_3N_3Cl$: N, 16.44%. Found: N, 16.32%.

Salicylylurea (*o*-**hydroxybenzoylurea**), *o*-$HOC_6H_4CONHCONH_2$.—47 g. of finely powdered urea were added to a solution of 75 g. acetylsalicylyl chloride in 280 cc. benzene. The mixture was boiled under a reflux condenser for 6–8 hours and the supernatant liquid poured off. The residue was ground up in a mortar with water, filtered off, and thoroughly washed with water. The crude acetylsalicylylurea so obtained was suspended in water, turbined, and carefully treated with sodium hydroxide in the cold so that the reaction of the mixture was kept just alkaline to phenolphthalein. When permanent alkalinity was reached the solution was filtered from a small amount of unchanged material and acidified with acetic acid. The pale yellow precipitate which formed was filtered off and recrystallized from 50% alcohol, giving the salicylylurea in a yield of 11.1 g. as pale yellow microcrystals which melt with effervescence at 184–6°. In 50% alcohol it gives a brown color with ferric chloride. The urea is very difficultly soluble in acetone or benzene, sparingly soluble in ethyl acetate, hot water, or methyl and ethyl alcohols in the cold, and soluble in hot methyl or ethyl alcohol. It dissolves in dilute ammonia, yielding a solution which couples readily with diazotized sulfanilic acid.

0.1113 g. subst.; 15.0 cc. N, 761 mm., 21.5°.
Calc. for $C_8H_8O_3N_2$: N, 15.56%. Found: N, 15.64%.

m(?)-**Chloroacetylaminomethylbenzoylurea** (*m*-**Carboxureidochloroacetylbenzylamine**,



.—16.4 g. benzoylurea were dissolved in 100 g. sulfuric acid and treated, with cooling, with 12.3 g. methylolchloroacetamide, the procedure being that of Einhorn[1] for introducing the $CH_2NHCOCH_2Cl$ group into aromatic compounds. After standing for 2 days the clear solution was poured onto ice and the resulting white precipitate filtered off and washed well with water. In order to remove all adherent sulfuric acid the product was ground up in a mortar with sodium acetate solution until neutral to Congo Red. The yield was 20 g. Recrystallized from acetic acid it forms a microcrystalline powder which begins to darken above 190°, softens above 200°, and melts at about 225–8° with decomposition. It is very difficultly soluble in the usual solvents with the exception of boiling acetic acid. On boiling with dilute sodium hydroxide ammonia is evolved and the solution

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[1] Einhorn, *et al.*, *Ann.*, **343**, 207 (1905); **361**, 113 (1908).

contains chlorine ion. In the absence of definite proof it is held likely that the chloroacetylaminomethyl group is in the *meta* position in accordance with the usual directive influence of the carbonyl group.

Kjeldahl: 0.1469 g. subst.; 16.50 cc. 0.1 *N* HCl.
Calc. for $C_{11}H_{12}O_3N_3Cl$: N, 15.59%. Found: N, 15.73%.

(2) *Derivatives of Phenylacetylurea.*

Phenylchloroacetylurea, $C_6H_5CHClCONHCONH_2$. — 30 g. phenylchloroacetylchloride,[1] 19 g. urea (2 mols), and 200 cc. benzene were heated on the water bath under a reflux condenser for about 5 hours, occasionally breaking up the solid mass which formed. The product was ground up in a mortar with water, filtered, washed well with water, and recrystallized from 95% alcohol. The yield was 23.8 g., 5.8 g. of this having been recovered from the alcoholic mother liquor on concentration. The urea forms delicate needles which melt with slight preliminary softening at 198° to a yellow liquid which evolves gas. It is sparingly soluble in cold methyl alcohol or acetone, readily on warming, and is very difficultly soluble at the boiling point in water, benzene, or chloroform.

Kjeldahl: 0.2303 g. subst.; 21.60 cc. 0.1 *N* HCl.
Calc. for $C_9H_9O_2N_2Cl$: N, 13.18%. Found: N, 13.13%.

***p*-Nitrophenylacetylurea,** *p*-$O_2NC_6H_4CH_2CONHCONH_2$.—Crude *p*-nitrophenylacetyl chloride was obtained by treating 63 g. *p*-nitrophenylacetic acid with 75 g. phosphorus pentachloride in benzene solution and concentrating *in vacuo*. To a solution of the chloride in 180 cc. benzene 42 g. (2 mols) urea were added and the mixture heated for about 6 hours on the water bath, the lumpy mass being occasionally broken up with a glass rod. At the end the supernatant liquid was poured off and the solid ground up with water, adding sodium acetate solution until neutral to Congo Red. The urea was then filtered off and washed well with water. The yield was 67 g. A small portion was recrystallized from water, from which it separates as delicate, hair-like needles which are difficultly soluble in boiling water or 95% alcohol. The compound softens and turns yellow above 225° and melts with effervescence to an orange-brown liquid at 250–2°.

Kjeldahl: 0.2375 g. subst.; 31.55 cc. 0.1 *N* HCl.
Calc. for $C_9H_9O_4N_3$: N, 18.83%. Found: N, 18.61%.

***p*-Aminophenylacetylurea.**—55.5 g. *p*-nitrophenylacetylurea were added to a boiling solution of 470 g. ferrous sulfate in 1600 cc. water. The mixture was made alkaline with ammonia, shaking vigorously, and the boiling continued for about 10 minutes. 1600 cc. alcohol were then added and the mixture digested for about three-quarters of a hour on the water bath. On filtering the hot solution and concentrating the filtrate to small bulk the aminourea was obtained in a yield of 35 g. Recrystallized from

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[1] Staudinger and Bereza, *Ber.*, 44, 536 (1911).

50% alcohol, adding a few drops of ammonia to the solution before cooling, the urea forms almost colorless, felted needles which are soluble in boiling water, more easily in hot methyl alcohol, and sparingly so in ethyl alcohol. It melts at 198–9° with gas evolution. The diazotized compound couples with R-salt to form a red dye which changes to purplish brown with an excess of sodium carbonate.

Kjeldahl: 0.1014 g. subst.; 15.7 cc. 0.1 *N* HCl.
Calc. for $C_9H_{11}O_2N_3$: N, 21.76%. Found: N, 21.69%.

***p*-Chloroacetylaminophenylacetylurea.**—20 g. sodium acetate were added to a solution of 12 g. *p*-aminophenylacetylurea in 120 cc. 50% acetic acid. 8 cc. chloroacetyl chloride were then added to the solution, with vigorous shaking, causing immediate precipitation of the chloroacetyl derivative. After diluting with water the substance was filtered off and washed well with water. The yield was 16 g. Recrystallized from 95% alcohol it forms delicate needles which dissolve sparingly in boiling water, more easily in boiling alcohol, and readily in boiling acetic acid. When rapidly heated to 235°, then slowly, the urea melts at 241° with gas evolution and preliminary softening and darkening.

Kjeldahl: 0.1108 g. subst.; 12.45 cc. 0.1 *N* HCl.
Calc. for $C_{11}H_{12}O_3N_3Cl$: N, 15.59%. Found: N, 15.74%.

(3) *Derivatives of Aminophenoxyacetylureas.*

***o*-Nitrophenoxyacetyl Chloride,** *o*-$O_2NC_6H_4OCH_2COCl$.—45 g. *o*-nitrophenoxyacetic acid, 54 g. phosphorus pentachloride, and 50 cc. toluene were heated on the water bath until evolution of hydrochloric acid ceased. The solution was then concentrated *in vacuo* and the residue dissolved in an equal volume of toluene. On adding petroleum ether until just turbid and scratching the chloride separated in large plates. More ligroin was added to complete the deposition of the chloride, which was then filtered off, washed with ligroin, and dried. The yield was 45 g. A portion was recrystallized from hot ligroin (b. 80–90°), adding a little ligroin to the solution as it cooled, in order to prevent too early deposition of the chloride as an oil. As obtained in this way it forms long, silky, faintly yellow needles which melt at 41–2° (corr.) with slight preliminary softening. It dissolves readily in the usual organic solvents with the exception of ligroin.

0.1847 g. subst., boiled with aq. NH_3; 0.1204 g. AgCl.
Calc. for $C_8H_6O_4NCl$: Cl, 16.45%. Found: Cl, 16.13%.

***o*-Nitrophenoxyacetylurea.**—40 g. of the chloride were dissolved in 100 cc. benzene and heated on the water bath for 5 hours with 25 g. of well powdered urea. The mixture was then ground up with water, filtered off, and thoroughly washed with water. The yield of crude product was 44 g. A portion was recrystallized from 50% alcohol, forming cream-colored, irregular prisms and long needles which change into the prisms on letting the mixture stand overnight. A little ammonia was added before filtering off, in order to hold back any saponified material. When rapidly heated to 180°, then slowly, the urea softens and finally melts at 186–8° with slow gas evolution. It dissolves in the cold in acetone and in boiling water or alcohol.

0.1276 g. subst.; 19.8 cc. N, 756 mm., 25.0°.
Calc. for $C_9H_9O_5N_3$: N, 17.57%. Found: N, 17.68%.

An attempt to reduce the nitrophenoxyacetylurea resulted only in the isolation of *o*-aminophenoxyacetic anhydride. This is the more easily understood by the ease with which the nitro urea undergoes saponification, short boiling with dilute ammonia sufficing to produce a deep orange color in the originally almost colorless solution.

***p*-Nitrophenoxyacetylurea.**—This was obtained from *p*-nitrophenoxyacetyl chloride (see p. 2424) and urea as in previous examples. Recrystallized from acetic acid it forms minute crystals which are less difficultly soluble in boiling acetic acid than in the other usual solvents. When quickly heated to 245°, then slowly, it softens slightly and then melts at 250° with gas evolution to a yellow liquid which soon darkens.

Kjeldahl: 0.2145 g. subst.; 26.70 cc. 0.1 *N* HCl.
Calc. for $C_9H_9O_5N_3$: N, 17.57%. Found: N, 17.43%.

***p*-Aminophenoxyacetylurea.**—50 g. of the well powdered nitrourea were added to a boiling solution of 450 g. ferrous sulfate in 1100 cc. water. The mixture was made alkaline with ammonia, shaking vigorously, diluted with 1100 cc. alcohol, again brought to a boil, and filtered hot. The amino compound separated from the filtrate on cooling in a yield of 20 g. Recrystallized from 50% alcohol, adding a few drops of ammonia to hold back any acid present, the urea forms long needles which soften above 190°, melt with gas evolution at 198–9°, resolidify, and melt again with gas evolution above 240°. It is soluble in boiling water, difficultly in boiling acetone or absolute alcohol. An aqueous suspension gives a slowly developing reddish color with ferric chloride, while a diazotized solution couples with R-salt to give a deep red color.

0.1134 g. subst.; 19.65 cc. N, 763 mm., 23.0°.
Calc. for $C_9H_{11}O_3N_3$: N, 20.09%. Found: N, 20.06%.

***p*-Chloroacetylaminophenoxyacetylurea.**—This substance was obtained by chloroacetylating the aminourea in 50% acetic acid solution as in numerous preceding examples. The chloroacetyl derivative was filtered from the diluted reaction mixture and washed with water. Recrystallized from acetic acid it forms aggregates of minute, flat needles which melt and decompose at 238–40° with preliminary softening. The urea is practically insoluble in the usual solvents with the exception of acetic acid.

0.1328 g. subst.; 17.3 cc. N, 756 mm., 26.0°.

Calc. for $C_{11}H_{12}O_4N_3Cl$: N, 14.72%. Found: N, 14.80%.

Owing to the poor yield obtained in the reduction of *p*-nitrophenoxyacetylurea a method was sought by which to prepare *p*-chloroacetylaminophenoxyacetylurea in better yield, reckoning from the starting material. This was accomplished by the following series of steps:

_p_-Chloroacetylaminophenoxyacetic Acid, *p*-$ClCH_2CONHC_6H_4OCH_2CO_2H$.—10 g. *p*-aminophenoxyacetic acid were dissolved in an excess of 10% sodium hydroxide solution and treated with 6 cc. chloroacetyl chloride, with shaking and chilling. On acidification with hydrochloric acid the chloroacetyl compound separated as a thick mass. This was filtered off, washed with water, and dried. The yield was 12 g. Recrystallized first from water, then from acetic acid, the substance forms practically colorless rosets of delicate needles which contain one molecule of acetic acid of crystallization which is lost at 100° *in vacuo* over sulfuric acid. When the air-dry substance is boiled with water acetic acid is evolved. After freeing from acetic acid the compound melts, with preliminary softening, at 167–9° to a brown liquid which clears completely at 170°.

Air-dry: 1.0325 g. subst.; loss, 0.1965 g. HOAc, 19.03%.

Calc. for $C_{10}H_{10}O_4NCl.CH_3CO_2H$: HOAc, 19.76%.

Anhydrous: Kjeldahl: 0.3242 g. subst.; 13.40 cc. 0.1 *N* HCl.

Calc. for $C_{10}H_{10}O_4NCl$: N, 5.75%. Found: N, 5.79%.

_p_-Chloroacetylaminophenoxyacetyl Chloride.—30 g. of the acid were suspended in 60 cc. of dry benzene and treated with 30 g. phosphorus pentachloride. A vigorous reaction occurred, but the substance did not dissolve. The mixture was finally warmed on the water bath until the evolution of hydrochloric acid ceased, after which it was cooled and filtered. The resulting chloride was washed with benzene and dried *in vacuo* over sulfuric acid, the yield of crude product being 34 g. Recrystallized from toluene it forms aborescent aggregates of platelets which melt at 147–52° with gas evolution and subsequent darkening. The chloride is soluble in dry acetone but dissolves only sparingly in dry chloroform or toluene.

Kjeldahl: 0.1951 g. subst.; 7.5 cc. 0.1 *N* HCl.

Calc. for $C_{10}H_9O_3NCl_2$: N, 5.35%. Found: N, 5.38%.

16 g. of the chloride were boiled in benzene with 7.5 g. urea for about 8 hours and worked up as in previous examples. A quantitative yield of *p*-chloroacetylaminophenoxyacetylurea was obtained in this manner, the product being identical in every way with that prepared by chloroacetylating *p*-aminophenoxyacetylurea.

_p_-Chloroacetylaminophenoxyacetic Methyl Ester.—A small portion of the chloride was boiled with dry methyl alcohol until dissolved and the solution then evaporated to small bulk. On diluting with hot water and cooling cautiously the ester was obtained crystalline. It was filtered off, washed with a little very dilute sodium carbonate solution to remove any acid that had been formed, and recrystallized from 85% alcohol, forming flat needles which melt at 170–3° with preliminary softening and slight browning. It is soluble in acetone or hot alcohol and but sparingly in benzene or boiling water.

0.1585 g. subst.; 8.0 cc. N, 746 mm., 23.0°.
Calc. for $C_{11}H_{12}O_4NCl$: N, 5.44%. Found: N, 5.71%.

(*C*) Aromatic Ureas Containing an Amide Group.

***o*-Uraminobenzamide,** *o*-$H_2NCONHC_6H_4CONH_2$.—20 g. *o*-aminobenzamide[1] were dissolved in 200 cc. 50% acetic acid, chilled in ice-water, and treated with a solution of 12.5 g. potassium cyanate. On scratching, 17 g. of the urea separated as thick, cream-colored, hexagonal plates. On attempting to recrystallize the substance from boiling water, copious evolution of ammonia occurred, ring condensation taking place with formation of benzoyleneurea as long needles. (Calcd. for $C_8H_6O_2N_2$: N, 17.28%. Found: N, 17.33%.) The crude, air-dried *o*-uraminobenzamide was therefore analyzed. When rapidly heated to 180°, then slowly, it melts, effervesces, and resolidifies at 184–5° and does not remelt up to 280°.

0.1037 g. subst.; 21.0 cc. N, 770 mm., 22.0°.
Calc. for $C_8H_9O_2N_3$: N, 23.46%. Found: N, 23.74%.

***m*-Uraminobenzamide.**—This substance was first prepared by Menschutkin,[2] who does not give a melting point. 20 g. of the hydrate of *m*-aminobenzamide were treated as in the case of the *o*-isomer. The yield of urea was 20 g. Recrystallized from water it forms flat needles. When rapidly heated to 230°, then slowly, it melts with effervescence at about 235°, resolidifying and turning yellow on further heating, but not melting below 280°. If slowly heated it softens and evolves gas above 220°, but does not melt.

Kjeldahl: 0.1171 g. subst.; 19.60 cc. 0.1 *N* HCl.
Calc. for $C_8H_9O_2N_3$: N, 23.46%. Found: N, 23.45%.

***m*-Chloroacetyluraminobenzamide,** *m*-$ClCH_2CONHCONHC_6H_4CONH_2$.—10 g. *m*-uraminobenzamide were dissolved in 30 g. chloroacetic acid on the water bath, treated with 6 cc. chloroacetyl chloride, and heated one-half hour. The chloroacetyl derivative separated in a yield of 9 g. on pouring the melt into water. Recrystallized from water it forms aggregates of microscopic needles which decompose at 223–4° with preliminary darkening and softening. It is very sparingly soluble in hot water, acetone, or alcohol, and dissolves readily in hot acetic acid, difficultly in the cold.

Kjeldahl: 0.1000 g. subst.; 11.7 cc. 0.1 *N* HCl.
Calc. for $C_{10}H_{10}O_3N_3Cl$: N, 16.44%. Found: N, 16.40%.

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[1] *Loc. cit.*

[2] Menschutkin, *Ann.*, 158, 96 (1871).

***p*-Uraminobenzamide.**—20 g. *p*-aminobenzamide were dissolved in 100 cc. of warn 50% acetic acid, quickly chilled, and treated with a concentrated aqueous solution of 13 g. potassium cyanate. The urea separated rapidly in a yield of 18 g. Recrystallized from water, adding a few drops of ammonia to the warm solution, it forms aggregates of prisms which dissolve readily in boiling water, difficultly in boiling absolute alcohol or amyl alcohol, and are almost insoluble in acetone or benzene. When rapidly heated to 240° it melts with gas evolution at 240–2°, resolidifies, and gradually melts again with continued gas evolution as the temperature is raised, forming a clear, yellow liquid at 275°.

Kjeldahl: 0.1311 g. subst.; 21.75 cc. 0.1 *N* HCl.
Calc. for $C_8H_9O_2N_3$: N, 23.46%. Found: N, 23.24%.

***p*-Chloroacetyluraminobenzamide.**—On adding 8.5 cc. chloroacetyl chloride to a partial solution of 15 g. *p*-uraminobenzamide in 45 g. chloroacetic acid on the water bath a clear solution was obtained. In a few moments the mixture set to a solid mass of the chloroacetyl derivative. After heating 15 minutes longer it was diluted with water and the precipitate filtered off. The yield was 12 g. Recrystallized from 50% alcohol, it forms hexagonal plates and prisms which darken and soften above 210° and decompose at 236–7°. It is sparingly soluble in the usual neutral solvents, but dissolves in dilute aqueous sodium hydroxide.

Kjeldahl: 0.1455 g. subst.; 16.95 cc. 0.1 *N* HCl.
Calc. for $C_{10}H_{10}O_3N_3Cl$: N, 16.44%. Found: N, 16.33%.

***m*-Uraminophenylacetamide,** *m*-$H_2NCONHC_6H_4CH_2CONH_2$. — 15 g. *m*-aminophenylacetamide (p. 2421) were dissolved in 100 cc. of normal hydrochloric acid and a few cc. of acetic acid added. The solution was then treated, with chilling, with 8.5 g. potassium cyanate dissolved in a little water. The urea separated on scratching, after which the solution was made acid to Congo Red and the urea filtered off and washed with water. The yield was 15 g. Recrystallized, with bone-blacking, from water, it forms minute, practically colorless plates which are soluble in hot water, sparingly so in hot 95% alcohol, and almost insoluble in acetone. The substance melts at 201–2° to a liquid filled with bubbles.

Kjeldahl: 0.1163 g. subst.; 18.15 cc. 0.1 *N* HCl.
Calc. for $C_9H_{11}O_2N_3$: N, 21.76%. Found: N, 21.86%.

***m*-Chloroacetyluraminophenylacetamide,** *m*-$ClCH_2CONHCONHC_6H_4$-CH_2CONH_2.—The urea was chloroacetylated in molten choroacetic acid by means of chloroacetyl chloride as in previous examples. After heating for one-half hour on the water bath the melt was poured into water, precipitating the chloroacetyl derivative as a gum which soon crystallized. This was filtered off, ground up in a mortar with sodium acetate solution until neutral to Congo Red, and recrystallized twice from 50% alcohol, forming slightly pinkish aggregates of minute plates and flat needles.

When rapidly heated to 175°, then slowly, it melts at 179–81° with gas evolution and preliminary softening. The amide is soluble in the cold in acetic acid, sparingly in acetone or 95% alcohol, and is soluble in hot water or 50% alcohol. It gives the Beilstein test.

Kjeldahl: 0.1514 g. subst.; 16.75 cc. 0.1 *N* HCl.
Calc. for $C_{11}H_{12}O_3N_3Cl$: N, 15.59%. Found: N, 15.50%.

***p*-Uraminophenylacetamide.**—20 g. *p*-aminophenylacetamide[1] were suspended in 400 cc. water and 67 cc. double normal hydrochloric acid added. To the resulting solution was slowly added a solution of 11.5 g. potassium cyanate, keeping the temperature below 5°. The urea separated in a yield of 22 g. Recrystallized from water, it forms transparent, rectangular plates which dissolve in boiling water and are scarcely soluble in boiling alcohol or acetone. When rapidly heated to 230°, then slowly, it softens, melts with effervescence at 233–6° and then resolidifies.

Kjeldahl: 0.1297 g. subst.; 20.0 cc. 0.1 *N* HCl.
Calc. for $C_9H_{11}O_2N_3$: N, 21.76%. Found: N, 21.60%.

***p*-Chloroacetyluraminophenylacetamide.**—The urea was chloroacetylated as in previous examples. After one-half hour the melt was poured into water, precipitating the chloroacetyl compound in crystalline form. Recrystallized from 95% alcohol it forms aggregates of delicate needles which are very difficultly soluble in the cold in the usual solvents and less sparingly soluble in hot alcohol or acetic acid than in the others. When rapidly heated to 195°, then slowly, it melts and decomposes at 200–1°, with preliminary softening.

Kjeldahl: 0.1539 g. subst.; 17.0 cc. 0.1 *N* HCl.
Calc. for $C_{11}H_{12}O_3N_3Cl$: N, 15.59%. Found: N, 15.47%.

***p*-Uraminophenoxyacetamide.**—30 g. *p*-aminophenoxyacetamide (p. 2423) were dissolved in 400 cc. water and 50 cc. acetic acid and treated, with cooling, with a solution of 14.6 g. potassium cyanate. The urea separated in quantitative yield on shaking. Recrystallized from water containing a little ammonia it forms radiating masses of long, flat, slightly brownish needles which are less difficultly soluble in boiling water than in the other usual neutral solvents. When rapidly heated it softens above 210°, melts with gas evolution at about 230°, resolidifies partly, and melts again completely at 260°.

0.1111 g. subst.; 19.8 cc. N, 759 mm., 27.5°.
Calc. for $C_9H_{11}O_3N_3$: N, 20.09%. Found: N, 20.22%.

***p*-Chloroacetyluraminophenoxyacetamide,** $ClCH_2CONHCONHC_6H_4$-OCH_2CONH_2.—20 g. of the urea were dissolved in 60 g. molten chloroacetic acid and treated with 10 cc. chloroacetyl chloride. After warming for 15 minutes on the water bath the melt was poured into water. The yield of chloroacetyl derivative was 14 g. Recrystallized from acetic

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[1] *Loc. cit.*

acid it forms masses of minute needles which are practically insoluble in boiling 95% alcohol or acetone but dissolve readily in hot acetic acid. When rapidly heated to 225°, then slowly, the substance softens and darkens, decomposing at 230°.

0.1372 g. subst.; 17.9 cc. N, 759 mm., 28.0°.
Calc. for $C_{11}H_{12}O_4N_3Cl$: N, 14.72%. Found: N, 14.78%.

The following two substances were prepared in an attempt to obtain *p*-chloroacetyluraminophenoxyacetamide by an indirect method. The final step was not carried out, however, owing to the satisfactory outcome of the direct chloroacetylation of *p*-uraminophenoxyacetamide.

***p*-Uraminophenoxyacetic Methyl Ester,** *p*-$H_2NCONHC_6H_4OCH_2CO_2CH_3$.—9 g. *p*-aminophenoxyacetic methyl ester hydrochloride[1] were dissolved in 100 cc. water and treated, with cooling, with a solution of 3.4 g. potassium cyanate. The urea separated in a yield of 6.3 g. Recrystallized, with bone-blacking, from 50% alcohol it forms almost colorless crystals which dissolve more readily in boiling 50% alcohol than in boiling water or 95% alcohol and are also difficultly soluble in methyl alcohol or acetone. When rapidly heated to 190°, then slowly, it melts at 192–3° with slow gas evolution.

Kjeldahl: 0.1092 g. subst.; 9.70 cc. 0.1 *N* HCl.
Calc. for $C_{10}H_{12}O_4N_2$: N, 12.50%. Found: N, 12.45%.

***p*-Chloroacetyluraminophenoxyacetic Methyl Ester.**—9 g. of the uramino ester were boiled under a reflux condenser for about 6 hours in 90 cc. of dry benzene with 4 cc. chloroacetyl chloride. The mixture was cooled, treated with water, filtered, washed with benzene and water, and dried. The yield of chloroacetyl derivative was 11 g. Recrystallized from amyl alcohol it forms flat, slightly brownish prisms which soften above 170° and melt at 181–3° with gas evolution. The substance dissolves readily in hot acetic acid, less easily in hot amyl alcohol, and only sparingly in boiling acetone or chloroform.

Kjeldahl: 0.1993 g. subst.; 13.30 cc. 0.1 *N* HCl.
Calc. for $C_{12}H_{13}O_5N_2Cl$: N, 9.32%. Found: N, 9.35%.

(*D*) Ureas with Other Substituents and Side Chains.

The following substances were prepared in an attempt to synthesize *p*-hydroxyphenylchloroacetylurea, *p*-$HOC_6H_4NHCONHCOCH_2Cl$. In an experiment on the direct chloroacetylation of *p*-hydroxyphenylurea both the urea and hydroxyl groups were chloroacetylated and attempts were then made to cover the hydroxyl group by acetylation. Treatment of *p*-hydroxyphenylurea with acetic anhydride and sulfuric acid resulted in the acetylation of both the urea and hydroxyl groups, but acetylation of the hydroxyl group alone was finally accomplished by the pyridine method. The resulting *p*-acetoxyphenylurea could be smoothly chloroacetylated

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[1] *Loc. cit.*

and the product so obtained was as satisfactory for the synthesis in which it was required as the free hydroxy compound originally sought.

p-Chloroacetyluraminophenyl Chloroacetate, p-$ClCH_2CONHCONHC_6H_4OCOCH_2Cl$.—5. g. p-hydroxyphenylurea were heated under a reflux condenser with 25 cc. benzene and 8 g. chloroacetyl chloride as in previous examples. The mixture was finally boiled up with about 200 cc. benzene, filtered from tar, and the product obtained on cooling (2.2 g.) recrystallized twice from alcohol, forming delicate needles and long, thin plates which melt at 185.5–7.5° with preliminary softening and resolidify on cooling. The substance dissolves in the cold in acetone, on boiling in water, alcohol, or chloroform, and is sparingly soluble in benzene. It gives a strong test for halogen.

Kjeldahl: 0.1541 g. subst.; 10.2 cc. 0.1 *N* HCl.
Calc. for $C_{11}H_{10}O_4N_2Cl_2$: N, 9.18%. Found: N, 9.27%.

Diacetyl-p-hydroxyphenylurea, p-$CH_3COOC_6H_4NHCONHCOCH_3$.—4.5 g. p-hydroxyphenylurea were treated with 10 cc. acetic anhydride and a few drops of concentrated sulfuric acid.· After finally heating on the water bath for a few minutes the solution was cooled and shaken with water. The resulting solid was recrystallized from 50% alcohol, yielding 6. g. of the diacetyl derivative. Recrystallized again from ethyl acetate it forms delicate, pinkish needles which melt at 213.5–14° (corr.). It is more readily soluble in the cold in chloroform than in the other usual neutral organic solvents, but also dissolves in the others on warming.

Kjeldahl: 0.2089 g. subst.; 17.7 cc. 0.1 *N* HCl.
Calc. for $C_{11}H_{12}O_4N_2$: N, 11.87%. Found: N, 11.87%.

p-Acetoxyphenylurea.—45 g. p-hydroxyphenylurea were dissolved in 350 cc. pyridine, cooled to —5°, and treated, with shaking and cooling, with 25 cc. acetyl chloride, added drop by drop. The mixture was then allowed to warm up to room temperature and was poured into a mixture of ice and 25% sulfuric acid. The resulting precipitate was filtered off, washed thoroughly with water, and dried. The yield was 45.2 g. Recrystallized from 95% alcohol the acetate forms felted needles which melt to a brown liquid at 201–2.5° with slight gas evolution and preliminary softening. It is soluble in boiling water or alcohol and almost insoluble in boiling benzene.

Kjeldahl: 0.1607 g. subst.; 16.50 cc. 0.1 *N* HCl.
Calc. for $C_9H_{10}O_3N_2$: N, 14.43%. Found: N, 14.38%.

p-Acetoxyphenylchloroacetylurea, p-$CH_3COOC_6H_4NHCONHCOCH_2Cl$.—21 g. of the acetoxyurea were boiled under a reflux condenser for several hours with 210 cc. benzene and 13.4 g. chloroacetyl chloride In order to complete the crystallization of the chloroacetyl derivative ligroin was added on cooling. After recrystallization from 50% alcohol the yield was 19.5 g Recrystallized again from 95% alcohol it forms almost colorless spindles and plates which melt at 181–2.5° (corr.) with preliminary softening. The substance is easily soluble in hot 95% alcohol, sparingly in the cold, and is quite soluble at room temperature in acetic acid.

Kjeldahl: 0.2007 g. subst.; 15.0 cc. 0.1 *N* HCl.
Calc. for $C_{11}H_{11}O_4N_2Cl$: N, 10.36%. Found: N, 10.47%.

***p*(?)-Uraminochloroacetylbenzylamine,** *p*-$H_2NCONHC_6H_4CH_2NHCOCH_2Cl$.—13.6 g. phenylurea were dissolved in 100 g. sulfuric acid and treated with 12.3 g. methylolchloroacetamide, according to Einhorn's method for introducing the $CH_2NHCOCH_2Cl$ group into aromatic compounds.[1] After 2 days the solution was poured on to ice, yielding a gummy precipitate which gradually crystallized. After recrystallizing from alcohol the yield was 10 g. The substance forms microscopic spears, which are almost insoluble in hot toluene or acetone, sparingly soluble in hot ethyl acetate, and readily so in boiling alcohol. When slowly heated above 170° it melts with preliminary softening at 173–4° to a yellow liquid, a higher figure being obtained if the heating is more rapid.

Kjeldahl: 0.1487 g. subst.; 18.40 cc. 0.1 *N* HCl.
Hydrolysis: 0.2548 g. subst.; 0.1475 g. AgCl.
Calc. for $C_{10}H_{12}O_2N_3Cl$: N, 17.40%; Cl, 14.67%. Found: N, 17.33%; Cl, 14.33%.

***p*(?)-Uramino-ω-chloroacetophenone,** *p*-$H_2NCONHC_6H_4COCH_2Cl$.—35 g. of anhydrous aluminium chloride were added, with shaking, to a suspension of 10 g. phenylurea in 75 g. of dry carbon bisulfide. To the mixture were added, drop by drop, 9.5 g. chloroacetyl chloride, finally warming on the water bath until the reaction was over. Ice was added and the whole vigorously shaken until decomposition was complete. Recrystallized from 95% alcohol the ketone forms cream-colored, nacreous plates which melt constantly at 197–8° with decomposition. The yield was 7 g. The compound is soluble in acetone or hot alcohol and only sparingly in hot benzene.

Kjeldahl: 0.1674 g. subst.; 15.75 cc. 0.1 *N* HCl.
Hydrolysis: 0.1661 g. subst. 0.1105 g. AgCl.
Calc. for $C_9H_9O_2N_2Cl$: N, 13.18%; Cl, 16.68%. Found: N, 13.18%; Cl, 16.45%.

***p*-Aminophenoxyethyl Bromide (*p*-Aminophenyl Bromoethyl Ether) Hydrobromide.**—*p*-Acetaminophenoxyethyl bromide was smoothly hydrolyzed by boiling for one hour under a reflux condenser with 5 parts of hydrobromic acid (d. 1.49). The *p*-aminophenoxyethyl bromide hydrobromide separated on cooling and was filtered off and washed with a little acetone. A portion was recrystallized, with bone-blacking, from a little water containing a few drops of hydrobromic acid, forming thin, glistening plates which melt at 227–8° with gas evolution and preliminary softening. It is difficultly soluble in absolute alcohol at room temperature, but dissolves in water. An aqueous solution gives a slowly-developing, purple color with ferric chloride. The salt is readily diazotized.

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[1] *Loc. cit.*

0.2106 g. subst.; 8.70 cc. N, 757 mm., 26.5°.
Calc. for $C_8H_{10}ONBr.HBr$: N, 4.72%. Found: N, 4.69%.

p-Aminophenoxyethyl Bromide, p-$H_2NC_6H_4OCH_2CH_2Br$.—A portion of the crude hydrobromide was dissolved in water and made alkaline with sodium carbonate solution. The bromide separated as an oil which crystallized almost immediately. The product was quickly filtered off, washed with water, and recrystallized, with bone-blacking, from a little 95% alcohol, forming minute, glistening platelets which are readily soluble in acetone or chloroform, less easily in benzene or alcohol. The bromide melts with preliminary softening at 83-4.5° to a liquid which immediately becomes turbid and decomposes without clearing at about 260°.

Kjeldahl: 0.1958 g. subst.; 9.25 cc. 0.1 N HCl.
Calc. for $C_8H_{10}ONBr$: N, 6.48%. Found: N, 6.62%.

p-Uraminophenoxyethyl Bromide (p-Uraminophenyl Bromoethyl Ether), p-$H_2NCONHC_6H_4OCH_2CH_2Br$.—This substance was obtained by reacting crude p-aminophenoxyethyl bromide hydrobromide with potassium cyanate in aqueous solution. Recrystallized, with bone-blacking, from 95% alcohol it forms aggregates of flat needles which melt slowly at 160-2° with preliminary softening. It is quite soluble in alcohol or acetone at room temperature, sparingly in ether or chloroform.

Kjeldahl: 0.1501 g. subst.; 11.70 cc. 0.1 N HCl.
Hydrolysis: 0.1152 g. subst.; 0.0828 g. AgBr.
Calc. for $C_9H_{11}O_2N_2Br$: N, 10.82%; Br, 30.84%. Found: N, 10.92%; Br, 30.58%.

NEW YORK CITY.

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

THE CONVERSION OF METHYLENEAMINOACETONITRILE TO IMINOACETONITRILE.

BY J. R. BAILEY AND H. L. LOCHTE.

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In THIS JOURNAL,[1] Bailey and Snyder state that, contrary to the observation of M. Delépine,[2] methyleneaminoacetonitrile, $CH_2 = NCH_2CN$ readily adds on prussic acid, "when the compound is subjected to the action of either absolute or an aqueous prussic acid" giving in quantitative yield iminoacetonitrile, $NH(CH_2CN)_2$. In the work referred to above Delépine found that ethylidene-α-propionitrile, $CH_3CH = NCH(CH_3)CN$, and numerous alkylidene amines show an addition reaction with prussic acid but, after trying under modified conditions to effect the reaction that Bailey and Snyder later found proceeds so smoothly between methyleneaminoacetonitrile and prussic acid, Delépine reported as follows: "J'ai constaté que ce corps ($CH_2 = NCH_2CN$) restait absolu-

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[1] 37, 935 (1915).

[2] *Bull. soc. chim.*, 29, 1202 (1903).