[Contribution from the Department of Chemistry, Yale University]

# THE ACTION OF ALKALI ON SUBSTITUTED URIC ACIDS. I 1,3-DIMETHYL-9-PHENYL-URIC ACID

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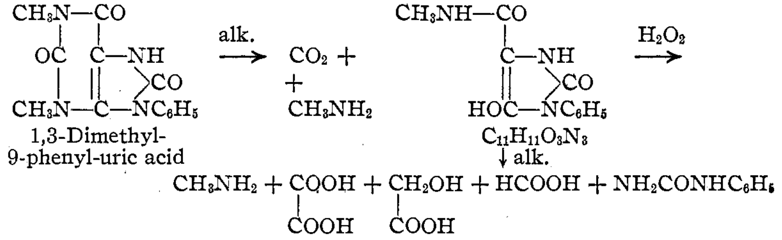
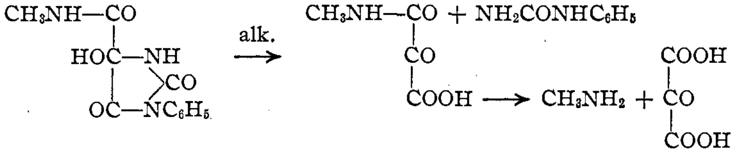
Received August 23, 1923

All of the substituted uric acids are split by alkali to some extent, the amount of decomposition depending largely on the number and position of the substituents. With one exception, that of tetramethyluric acid,[2] neither the nature of the decomposition products nor the mechanism of the reaction has been investigated up to this time. A thorough study of the action of alkali on substituted uric acids is now being made.

Of these, 1,3-dimethyl-9-phenyl-uric acid shows a smooth and interesting decomposition. The course of the decomposition and the structure of the products are considered to be as follows.

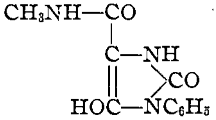


1,3-Dimethyl-9-phenyl-uric acid



Dimethyl-phenyl-uric acid is very slowly decomposed by 4 *N* alkali at room temperature; the sodium salt separates on the addition of the base, and only a small part is attacked after standing for many days. At 100° with more dilute alkali the decomposition is more rapid, and with 4 *N* alkali it is instantaneous. The gas given off is methylamine and when the solution is acidified carbon dioxide is evolved. From the acid solution on standing a crystalline product separates which melts at 250°. Analysis shows that it has the formula $C_{11}H_{11}O_3N_3$.

There are three possible structures for this substance, depending on which of the methylamino groups and which of the carbonyls are lost.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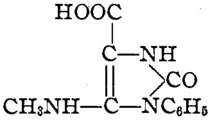
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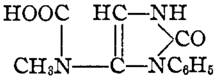
(III)

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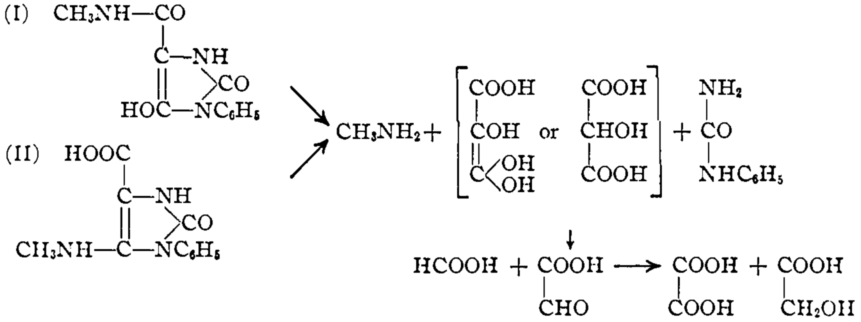
[1] National Research Fellow in Chemistry.

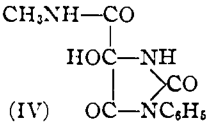
[2] Fischer, *Ber.*, 30, 3012 (1897).

When warmed with alkali or even on standing about an hour with cold alkali, the product is completely decomposed to phenylurea, methylamine, oxalic acid and formic acid. The phenylurea separates after standing only 15 minutes but no oxalic acid can be detected at this point unless the solution is first warmed, showing that the formation of oxalic acid is due to a secondary reaction. Most probably, glyoxalic acid is first formed, and this is converted into oxalic acid and glycolic acid when warmed or allowed to stand for a long time with alkali.

On the basis of this decomposition, Structure III for $C_{11}H_{11}O_3N_3$ must be excluded, as there is no possibility of the formation by hydrolysis of either oxalic or formic acid. Carbon dioxide and glycolic acid would be the products formed. Either of the other two structures can give these products of hydrolysis, however.



To decide between these structures, the substance was oxidized by hydrogen peroxide in dilute alkaline solution. A product melting at 194–195° was isolated. Its empirical formula was found to be $C_{11}H_{11}O_4N_3$. The most probable structural formula for this substance is IV, and such a substance can result from the alkaline decomposition product only if it has Structure I.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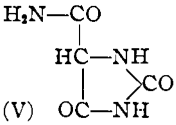
(V)

Furthermore, the oxidation product is itself instantly decomposed by cold alkali, and the products of decomposition are phenylurea and the methylamide of mesoxalic acid.[3] On boiling with alkali the decomposition goes further. Methylamine is evolved, phenylurea separates from the alkaline solution, and mesoxalic acid can be isolated in the form of its phenylhydrazone.

One of the most interesting things about this decomposition is that the

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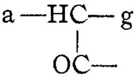
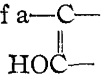
[3] Torrey, *Ber.*, **31**, 2162 (1898).

oxidation product is of the same type of compounds as those Biltz[4] has obtained in his caffolide decompositions. It bears a close relationship to alloxanic acid[5] and other similar hydantoin derivatives, for it is the methylamide of 3-phenyl-5-hydroxyhydantoin-5-carboxylic acid. This type of substance Biltz obtained from caffolide or substituted caffolides by boiling with water, and he found that they were all easily decomposed by alkali to give an amine, a urea and mesoxalic acid, just as is the oxidation product of $C_{11}H_{11}O_3N_3$. On reduction they gave hydantoin-carboxylic acid derivatives of Type V which differs from the structure assigned to the alkaline decomposition product, $C_{11}H_{11}O_3N_3$, only in having a  $\begin{matrix}-\mathrm{HC}-\\ |\\ \mathrm{OC}-\end{matrix}$ group instead of a  $\begin{matrix}-\mathrm{C}-\\ \|\\ \mathrm{HOC}-\end{matrix}$ group. $C_{11}H_{11}O_3N_3$ cannot, however, be such a hydantoin derivative; it is not decomposed by alkali to a hydantoin or a hydantoin-carboxylic acid as the amides of the hydantoin-carboxylic acids have been found to be.[6] There was the possibility that phenylhydantoin had been formed and further decomposed by alkali to phenylurea. When 3-phenylhydantoin was prepared, however, and treated with alkali, it gave only phenylhydantoic acid. The alkaline decomposition product must, therefore, be an isohydantoin derivative, namely 3-phenyl-isohydantoin-5-carboxylic acid methylamide.

The experimental part of this paper gives an account of 1,7-dimethyl-9-phenyl-uric acid which has been synthesized for the first time. Like 9-phenyl-uric acid and 7-methyl-9-phenyl-uric acid,[7] it is quite stable toward alkali when boiled for a short time.

This new uric acid is 1,7-dimethyl-9-phenyl-uric acid and not 3,7-dimethyl-9-phenyl-uric acid for, as Biltz[8] has proved, when there is only one substituting group in the pyrimidine ring, the ring closing of the pseudo-uric acids always takes place so that this group is in Position 1 of the uric acid. A further proof that the methyl occupies Position 1 is that methylation of 7-methyl-9-phenyl-uric acid with dimethyl sulfate gives, along with some trimethyl phenyl uric acid, the same dimethyl phenyl uric acid as obtained above, and it is well known that dimethyl sulfate always methylates first on the nitrogen whose hydrogen is least acidic.[9]

The investigation of the action of alkali on tetramethyluric acid and on

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[4] Biltz, *Ber.*, **43,** (a) 1511, (b) 1589, (c) 1600, (d) 1618, (e) 1632 (1910); **44,** (f) 1511, (g) 1524 (1911); **46,** (h) 3407 (1913). *Ann.*, **413,** (i) 2, (j) 56, (1917); **423,** (k) 119 (1921).

[5] Ref. 4j, p. 68.

[6] Ref. 4h, p. 3409. Ref. 4d, p. 1619.

[7] Moore and Gatewood, THIS JOURNAL, **45,** 140 (1923).

[8] Biltz, *Ann.*, **413,** 127 (1917); **423,** 256 (1921).

[9] Biltz, *Ber.*, **54,** 169 (1921).

1,3,7-trimethyl-9-phenyl-uric acid is already well advanced, and work on 1,3,9-trimethyl-uric acid will be begun shortly.

In conclusion, the writer wishes to express her appreciation to Professor F. J. Moore, of the Massachusetts Institute of Technology, for his valuable advice during the course of this investigation.

## Experimental Part

### 1,3-Dimethyl-9-phenyl-uric Acid

**Action of Alkali.**—1,3-Dimethyl-9-phenyl-uric acid[10] was prepared from the corresponding pseudo-uric acid, which was obtained by the action of phenyl isocyanate on 1,3-dimethyl-uramil.

One hundred cc. of 4 *N* sodium hydroxide solution was added to 2 g. of finely powdered dimethyl-phenyl-uric acid. The solution was heated gradually to boiling and boiled about half a minute, cooled slightly, and then acidified with dil. hydrochloric acid. After the solution had stood for several hours (sometimes longer), a crystalline substance started to separate. It was left overnight, and when filtered and dried gave from 1.2 to 1.4 g. of phenylisohydantoin-carboxylic acid methylamide, in a yield of about 80%. It crystallized from hot water in bunches of needles which melted at 249–250° to a clear, viscous, yellow liquid. It was recrystallized again and dried in a vacuum over sulfuric acid for analysis.

*Analyses.* Subs., 0.1541, 0.1511: $CO_2$, 0.3174, 0.3100; $H_2O$, 0.0677, 0.0653. Subs., 0.1411, 0.0965: N, 22.9 cc. (23.5°, 759.1 mm.), 15.8 cc. (23°, 759.1 mm.). Calc. for $C_{11}H_{11}O_3N_3$: C, 56.62; H, 4.76; N, 18.03. Found: C, 56.22, 56.28; H, 4.92, 4.76; N, 18.14, 18.34.

Optical Properties.—Habit, rectangular plates; extinction, parallel, $\alpha$ parallel to elongation; interference figure, biaxial, large optic angle; indices, $\alpha = 1.571$, $\gamma = 1.620$.

The other products of decomposition, methylamine and carbon dioxide, were determined—the first as methylamine chloroplatinate and the second by absorption in soda lime.

On the addition of chloroplatinic acid to the hydrochloric acid solution of the gas evolved from the alkaline solution, orange crystals were obtained melting at 230–233°; mixed with a known sample of methylamine chloroplatinate they melted at 233°. The optical properties were also the same: habit, thin hexagonal plates; optical orientation, isotropic; index of refraction, 1.74.

One molecular equivalent of carbon dioxide was given off when the alkaline solution was acidified.

*Analysis.* Subs., 2.00: $CO_2$, 0.391 g. Calc. for 1 mol.: 0.32 g.

Dimethyl-phenyl-uric acid is only very slowly attacked by cold 4 *N* alkali. The sodium salt of the uric acid separates and after 20 days at room temperature most of the acid is regained when the solution is acidified. From the filtrate, on standing, a small amount of phenylisohydantoin-carboxylic acid methylamide, melting at 240°, was obtained.

The sodium salt of dimethyl-phenyl-uric acid was dried at 100–110° and analyzed.

*Analysis.* Subs., 0.2092: $NaSO_4$, 0.0500. Calc. for $C_{13}H_{11}O_3N_4Na$: Na, 7.823. Found: 7.905.

Phenylisohydantoin-carboxylic acid methylamide when refluxed for $1^1/_2$ hours with acetic anhydride gave, after evaporation of the mixture to dryness and addition of

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[10] Ref. 7, p. 143.

ether, a product melting at 185–187°. There was not sufficient material for analysis.

The alkaline decomposition product did not react with phenylisocyanate either when heated to 165°, or in alkaline solution at 0°, showing it to be an acid amide.

**Action of Alkali on Phenylisohydantoin-carboxylic Acid Methylamide.**—1. One g. of the alkaline decomposition product was heated with 4 cc. of 4 *N* alkali and the gas given off absorbed in a little dil. hydrochloric acid. This solution gave, on the addition of chloroplatinic acid and subsequent evaporation, the characteristic orange crystals of methylamine chloroplatinate, melting at 228–230°.

Phenylurea separated from the alkaline mother solution as it cooled. It melted at 144°; mixed with a pure sample of phenylurea, it melted at 146°. The optical properties were the same: habit, plates; extinction, parallel, $\gamma$ parallel to elongation; interference figure, biaxial, large optic angle; birefringence, weak; indices, $\alpha = 1.602$, $\gamma = 1.627$. To identify the substance further as phenylurea, it was boiled with aniline, and diphenylurea was obtained in good yield. It melted at 236–238°; a mixture with a pure sample of diphenylurea, melted at 237–238°. The optical properties were identical: habit, long needles; extinction, parallel, $\gamma$ parallel to elongation; interference figure, biaxial; birefringence, strong; indices, $\alpha = 1.620$, $\gamma$, indeterminate.

When the filtrate was acidified with acetic acid and a solution of calcium chloride added, a fine, white precipitate of calcium oxalate was obtained.

2. When 0.1 g. of the decomposition product was allowed to stand at room temperature with 1 cc. of 4 *N* sodium hydroxide, crystals of phenylurea began to separate after 15 minutes and the odor of methylamine could be detected. After half an hour the solution was filtered. The yield of phenylurea was 0.015 g.; m. p., 145°. Half of the filtrate was acidified with acetic acid and a solution of calcium chloride added. The solution remained clear, showing that no oxalic acid was present. The other half was first warmed and then tested for oxalic acid as before. A precipitate of calcium oxalate separated at once.

3. When 0.1 g. was left at room temperature with 1 cc. of 4 *N* sodium hydroxide for over 1 hour, 0.02+ g. of phenylurea was obtained, and the filtrate gave calcium oxalate but the precipitate was not as heavy as in 1.

4. When 0.1 g. was dissolved in 8.2 cc. of water and 0.4 g. of potassium hydroxide and evaporated to dryness at 30–40°, the residue gave, after the addition of water, 0.02 g. of phenylurea (52%) and 0.035 g. of calcium oxalate (63%).

5. Formic acid was identified as one of the products of decomposition by its reduction of an ammoniacal solution of silver nitrate. Phenylisohydantoin-carboxylic acid methylamide was boiled with 4 *N* sodium hydroxide, the solution acidified with sulfuric acid and distilled. The distillate was warmed with ammoniacal silver nitrate; metallic silver was precipitated. The distillate was also tested for formaldehyde but with negative results.

**Oxidation of Phenylisohydantoin-carboxylic Acid Methylamide with Hydrogen Peroxide.**—On oxidation of the alkaline decomposition product with peroxide in very dilute alkaline solution, phenylurea and oxalic acid are obtained when the oxidation solution is allowed to stand for 3 hours or longer at room temperature. The decomposition is doubtless due only to the alkali, for a solution of the same concentration but without the peroxide gave the same products.

When the oxidation is allowed to proceed for only 5 minutes at 0–10° and the solution then acidified and evaporated, an oxidation product, melting at 195–196°, can be isolated. It is the methylamide of 3-phenyl-5-hydroxyhydantoin-5-carboxylic acid.

1. To 0.5 g. of the decomposition product in 6 cc. of water, 1.5 g. of solid potassium hydroxide and 35 cc. of 3% hydrogen peroxide were added. The solution was cooled and after 3 hours acidified and evaporated. A 69% yield of phenylurea and a 50% yield of calcium oxalate resulted.

2. One g. of the alkaline decomposition product was added to 12 cc. of water and cooled to 5°; 2.9 g. of potassium hydroxide and 70 cc. of 3% hydrogen peroxide were then added, and the temperature kept below 10°. After 5 minutes the solution was acidified with dil. hydrochloric acid and evaporated in a vacuum. Large clumps of material usually separated, which weighed about 0.6 g. It was purified by recrystallization from hot water many times. A little boneblack was added the first time. The pure product consisted of glistening flakes; m. p., 194–195°. It was very soluble in hot water, alcohol, acetone, and ethyl acetate, and was insoluble in ether and chloroform. It was dried in a vacuum over sulfuric acid for analysis.

*Analyses.* Subs., 0.1397, 0.1440: $CO_2$, 0.2730, 0.2795; $H_2O$, 0.0572, 0.0531. Subs., 0.1994, 0.1478: N, 29.6 cc. (23°, 756.7 mm.), 21.9 cc. (25°, 760.0 mm.). Calc. for $C_{11}H_{11}O_4N_3$: C, 53.01; H, 4.45; N, 16.87. Found: C, 53.28, 52.93; H, 4.58, 4.13; N, 16.56, 16.44.

OPTICAL PROPERTIES.—Habit, large, thin, rect. plates; extinction, parallel, $\alpha$ parallel to elongation; interference figure, biaxial, large optic angle; indices, $\alpha = 1.545$, $\gamma = 1.583$.

On further evaporation the solution gave more of the oxidation product, mixed with another substance from which it could not be completely separated. A small amount of the latter was separated mechanically. It crystallized from water in fine needles, melting at 188–190°. It was soluble in alcohol, acetone and ethyl acetate, and insoluble in ether and chloroform. It was not decomposed by alkali.

OPTICAL PROPERTIES.—Habit, needles; extinction, parallel, $\alpha$ parallel to elongation; birefringence, strong; indices, $\alpha = 1.556$, $\gamma = 1.695$.

**Action of Alkali on the Oxidation Product.**—1. Seven cc. of 2 *N* sodium hydroxide was added to 0.2 g. of the oxidation product. It dissolved at once and in a few minutes crystals began to separate. Air was passed through the solution while it was carefully heated. The gas evolved was absorbed in dil. hydrochloric acid, chloroplatinic acid added, and the solution evaporated. Orange crystals separated which melted at 228–230°; when these were mixed with methylamine chloroplatinate the melting point was not lowered. Their optical properties were the same. Phenylurea was obtained from the alkaline solution on cooling. Its melting point, 145–146°, and optical properties agreed with those of a known sample. The filtrate gave no test for oxalic acid.

2. One cc. of 4 *N* sodium hydroxide was added to the oxidation product. The solution was warmed carefully until the crystalline precipitate that had formed dissolved. It was then cooled, 1 cc. of water added, and the phenylurea filtered off. The yield was 0.09 g. or 90%. The filtrate was carefully neutralized with dil. acetic acid and a solution of 0.06 g. of pure phenylhydrazine in 1 cc. of water and 4 drops of glacial acetic acid added. A yellow precipitate gradually formed. The solution was warmed until clear and when cool was acidified with dil. hydrochloric acid. A heavy, yellow precipitate separated which crystallized from dil. alcohol in small, hexagonal crystals; m. p., 167°. It was very similar to the phenylhydrazone of mesoxalic acid and was at first thought to be this substance. However, on preparing mesoxalic acid by the convenient method of Chattaway and Harris,[11] and from it the phenylhydrazone, it was found that they were not the same. Mesoxalic acid phenylhydrazone was more soluble in water and crystallized in fine needles melting at 165°; when mixed with the above product the mixture melted at 150°. The optical properties also were different.

OPTICAL PROPERTIES OF THE PHENYLHYDRAZONE OF MESOXALIC ACID.—Habit, fine needles; extinction, parallel, $\alpha$ parallel to elongation; indices, $\alpha = 1.450$, $\gamma > 1.800$.

OPTICAL PROPERTIES OF THE PHENYLHYDRAZONE MELTING AT 167°.—Habit, hexagonal plates; extinction, symmetrical, $\alpha$ parallel to elongation; interference figure, biaxial, large optic angle; birefringence, strong; indices, $\alpha = 1.600$, $\gamma = 1.715$.

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[11] Chattaway and Harris, *J. Chem. Soc.*, 121, 2704 (1922).

It was found to be the phenylhydrazone of the methylamide of mesoxalic acid, the same substance Torrey[8] obtained by the mild action of barium hydroxide on allocaffuric acid. He gives the melting point as 158°. The difference may be accounted for, however, by the well-known variation of the melting points of phenylhydrazones with rate of heating. Its solution in concd. sulfuric acid developed a red-violet color on the addition of ferric chloride; it was almost insoluble in water and, when boiled for a short time with sodium hydroxide, gave a substance melting at 205–210° (Torrey gives 205–209°). According to Biltz[12] this is the phenylhydrazone of glyoxalic acid methylamide.

3. When the oxidation product was boiled for several minutes with alkali, a strong odor of methylamine developed, and from the solution, after separation of the phenylurea and neutralization, mesoxalic acid itself was isolated as its phenylhydrazone. It crystallized from water in fine, yellow needles, melting at 160°, and mixed with a known sample gave the same melting point. The optical properties also were identical.

At one time it was thought that the oxidation product of phenylisohydantoincarboxylic acid methylamide had the composition $C_{10}H_{11}O_3N_3$ and that it might be the methylamide of phenyloxaluric acid, $CH_3NHCO—CONHCONHC_6H_5$. This substance was not known, but it can be easily synthesized. Oxamethane,[13] $C_2H_5OOC\text{-}CONH_2$, when heated with phenyl isocyanate, gives the ethyl ester of phenyloxaluric acid, $C_2H_5\text{-}COOC\text{-}CONHCONHC_6H_5$, and this with methylamine gives the desired compound.

**Preparation of the Ethyl Ester of Phenyloxaluric Acid.**—Five g. of oxamethane, finely powdered, was added to 10 g. of phenyl isocyanate, and heated in an open tube at 110–112° for one hour. A clear solution resulted, which solidified as it cooled to a mass still having a strong odor of phenyl isocyanate. The solid was dissolved with hot absolute alcohol and the solution filtered. A well-crystallized product separated, which weighed 4.7 g. It was recrystallized from alcohol and melted at 125–126°, with evolution of gas.

*Analyses.* Subs., 0.1579, 0.1958: N, 17 cc. (24°, 772.1 mm.); 20.8 cc. (20°, 771.4 mm.). Calc. for $C_{11}H_{12}O_4N_2$: N, 11.87. Found: 12.19, 12.28.

OPTICAL PROPERTIES.—There were two crystalline species. A. Extinction, parallel, $\alpha$ parallel to elongation; interference figure, biaxial; indices, $\alpha = 1.590$, $\gamma = 1.680$. B. Extinction angle, 17–19°; birefringence, weak; indices, $\alpha = 1.675$, $\gamma = 1.755$.

OPTICAL PROPERTIES OF OXAMETHANE.—Habit, large, thin, rectangular plates; extinction, parallel, $\alpha$ parallel to elongation; interference figure, biaxial; indices, $\alpha = 1.545+$, $\gamma = 1.620$.

**Preparation of the Methylamide of Phenyloxaluric Acid.**—One g. of a 33% solution of methylamine was added dropwise to 1 g. of the ethyl ester suspended in 10 cc. of water. After the resulting product had stood for half an hour, it was filtered off and dried on a tile; m. p., 210–215°; yield, 0.74 g. Phenyloxaluric acid methylamide is difficultly soluble in hot water, alcohol, acetone and chloroform. No good solvent for it was found. Microscopical examination showed that the substance was mixed with phenylurea. They could be partially separated by boiling with alcohol. The residue melted over a range of more than 5°, showing it was still not pure and the analysis indicated the same.

*Analyses.* Subs., 0.1383, 0.1338: N, 20.4 cc. (21°, 756.8 mm.), 24.1 cc. (25°, 759.5 mm.). Calc. for $C_{10}H_{11}O_3N_3$: N, 18.99. Found: 19.56, 19.96.

OPTICAL PROPERTIES.—Extinction, parallel, $\alpha$ parallel to elongation; indices, $\alpha = 1.595$, $\gamma = 1.700$.

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[12] Ref. 4c, p. 1603.

[13] Weddige, *J. prakt. Chem.*, **10**, 196 (1874).

Phenyloxaluric acid methylamide was instantly decomposed by cold 4 *N* alkali. A crystalline product separated, part of which melted at 140–145° and the rest about 210°. Under the microscope it was seen to be a mixture of phenylurea and diphenylurea (impurity in the original material). Oxalic acid was found in the filtrate. The gas given off by the alkaline solution was methylamine, as it gave a chloroplatinate melting at 228–230°.

## 1,7-Dimethyl-9-phenyl-uric Acid

The starting point in the synthesis of 1,7-dimethyl-9-phenyl-uric acid is 1,7-dimethyl-uramil.[14] It was prepared by oxidizing theobromine with potassium chlorate, reducing the product to 7-methyl-dialuric acid, and treating this with methylamine.

**Preparation of 1,7-Dimethyl-9-phenyl-9-phenyl-pseudo-uric Acid.**—Sixty cc. of *N* potassium hydroxide solution was cooled to 0°, 5 g. of finely powdered dimethyl-uramil was added, and the mixture shaken until all the solid had dissolved. A violet solution resulted. To this, 3.8 g. of phenyl isocyanate was added in small portions, and the solution shaken vigorously after each addition until it became odorless. The temperature was kept at 0–2°. The color deepened and the solution became slightly cloudy. The addition required about half an hour. The mixture was filtered, and the filtrate when acidified with dil. hydrochloric acid gave a heavy, white precipitate (8 g.); m. p., 220°. It was difficultly soluble in water, about 350 cc. of solvent being necessary to dissolve 1 g. A fine, white product was obtained, which turned pink at 160°, light yellow at 210°, and melted at 220° to an orange-red liquid. It was dried in a vacuum over sulfuric acid for analysis.

*Analyses.* Subs., 0.1551, 0.1533: N, 27.2 cc. (23°, 756.8 mm.), 26.9 cc. (26°, 767.5 mm.). Calc. for $C_{13}H_{14}O_4N_4$: N, 19.32. Found: 19.57, 19.44.

OPTICAL PROPERTIES.—Habit, small, hexagonal plates; symmetrical extinction, $\alpha$ parallel to elongation; birefringence, strong; indices, $\alpha = 1.555$, $\gamma = 1.695$.

**Preparation of 1,7-Dimethyl-9-phenyl-uric Acid.**—Five g. of the pseudo acid was dissolved in 1 liter of 20% hydrochloric acid and the solution boiled over a free flame until crystallization began. It was then evaporated on the steam-bath to $^1/_3$ its volume, cooled and filtered. About 3 g. of material was obtained. It did not melt below 280°. The filtrate, on further evaporation, gave 0.8 g. more. The total yield was 3.8 g., or 80%. On recrystallization from water it was obtained as a fine, glistening, white powder. It was dried at 100–110° for analysis.

*Analyses.* Subs., 0.2796: $CO_2$, 0.5866; $H_2O$, 0.1035. Subs., 0.1460, 0.1280: N, 27.1 cc. (22°, 756.8 mm.), 23.0 cc. (21°, 765.2 mm.). Calc. for $C_{13}H_{12}O_3N_4$: C, 57.32; H, 4.44; N, 20.60. Found: C, 57.22; H, 4.23; N, 20.83, 20.50.

OPTICAL PROPERTIES.—Habit, long, rectangular and hexagonal plates; extinction, symmetrical, $\gamma$ parallel to elongation; indices, $\alpha = 1.540$, $\gamma > 1.755$.

**Action of Alkali.**—A solution of 0.2 g. of dimethyl-phenyl-uric acid in 12 cc. of 4 *N* sodium hydroxide was boiled for 10 minutes. When the solution was partly cooled and acidified, an immediate heavy precipitate of the unchanged acid, weighing 0.18 g., was obtained. It did not melt below 280°.

**Methylation of 7-Methyl-9-phenyl-uric Acid.**—One g. of 7-methyl-9-phenyl-uric acid was dissolved in 20 cc. of 2 *N* sodium hydroxide solution. Two g. of dimethyl sulfate was added, and the flask closed with a cork and shaken for 15 minutes while it was cooled with running water. A precipitate gradually separated and after 1 hour was filtered off. It weighed 0.1 g.; m. p., 258–259°. It was 1,3,7-trimethyl-9-phenyl-uric acid[15] as a comparison of melting points and optical properties showed. When the

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[14] Biltz, *Ber.*, **46**, 3671 (1913).

[15] Fischer, *Ber.*, **33**, 1708 (1900).

filtrate was acidified, an immediate heavy, white precipitate formed, which weighed 0.5 g. It did not melt below 280° and its optical properties were identical with those of 1,7-dimethyl-9-phenyl-uric acid.

## Summary

1. The action of alkali on 1,3-dimethyl-9-phenyl-uric acid has been studied, and the course of the reaction and the nature of the decomposition products have been determined.
2. The primary decomposition product is 3-phenyl-isohydantoin-5-carboxylic acid methylamide. This is further decomposed by alkali to methylamine, oxalic acid, glycolic acid, formic acid and phenylurea.
3. Phenylisohydantoin-carboxylic acid methylamide is oxidized by hydrogen peroxide to 3-phenyl-5-hydroxyhydantoin-5-carboxylic acid methylamide, which is readily decomposed by alkali to mesoxalic acid, methylamine and phenylurea.
4. 1,7-Dimethyl-9-phenyl-uric acid, and the ethyl ester and methylamide of phenyl-oxaluric acid have been prepared for the first time and characterized.
5. The action of alkali on other substituted uric acids is now being investigated.

New Haven, Connecticut

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[Contribution from the Chemical Laboratory of the University of Illinois]

# DERIVATIVES OF CAMPHORONIC ACID

By Walther F. Goebel with William A. Noyes[1]

Received August 25, 1923

## Introduction

Despite the fact that camphoronic acid and many of its derivatives have been known since the latter part of the nineteenth century, no direct proof for the special structures of these derivatives has ever been brought forward. Kachler[2] first discovered camphoronic acid in the mother liquors of a camphor-nitric acid oxidation mixture; the true structure of the acid was first suggested by Bredt[3] and later confirmed by the classical synthesis of inactive camphoronic acid by Perkin and Thorpe.[4]

Of the derivatives studied in this research there are already known one anhydro acid,[5] $C_6H_{11}(CO)_2OCOOH$, two isomeric anhydro acid chlorides,[6]

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[1] An abstract of a thesis presented to the Graduate Faculty of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Kachler, *Ann.*, **159**, 288 (1871).

[3] Bredt, *Ann.*, **292**, 67 (1896).

[4] Perkin and Thorpe, *J. Chem. Soc.*, **71**, 1169 (1897).

[5] Kachler and Spitzer, *Monatsh.*, **6**, 186 (1885).

[6] Ref. 5, p. 193.