Summary.

1. Methylenedisalicylic acid is obtained pure and in good yield by the interaction of formaldehyde and salicylic acid in molecular proportions, in the presence of 50 per cent. sulfuric acid.

2. Heated above the melting point methylenedisalicylic acid decomposes into hydroxyphenylmethylenesalicylic acid, methylenediphenol and carbon dioxide.

3. When treated with bromine or iodine, methylenedisalicylic acid as such is not halogenated.

4. The action of bromine or iodine on methylenedisalicylic acid effects a condensation in which two molecules of acid are involved, resulting in the formation of a molecule which may be designated as a halogenated anthratriquinonedihomosalicylic acid.

5. This was dehalogenated with zinc dust and potassium hydroxide.

6. When halogenated anthratriquinonedihomosalicylic acid is heated with a solution of alkaline carbonates or mineral acids, under pressure, it is decomposed yielding a monobasic acid, which may be considered as halogenated hydroxybenzylideneanthratriquinonehomosalicylic acid.

7. Halogenated hydroxybenzylideneanthratriquinonehomosalicylic acid is also formed by reacting on methylenedisalicylic acid with a large excess of halogen in the presence of a neutralizing substance like borax or an alkaline carbonate.

LABORATORIES OF PARKE, DAVIS & CO.,
DETROIT.

SYNTHESES OF PYRROLE COMPOUNDS FROM IMIDO ACIDS.
N-PHENYL-α,α'-DICARBETHOXY-β,β'-DIKETOPYRROLIDINE.

BY TREAT B. JOHNSON AND ROBERT BENGIS.

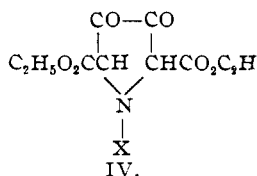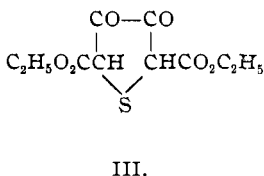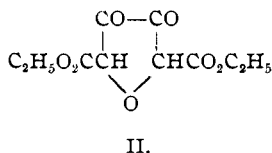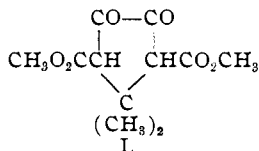In a paper entitled "Researches on Furfurans," Johnson and Johns[1] showed that diethyl diglycolate condenses with diethyl oxalate, in the presence of sodium ethylate, giving practically a quantitative yield of 2,5-dicarbethoxy-3,4-diketotetrahydrofurfurane (II). The formation of this cyclic compound, in this manner, was perfectly analogous to that of dimethyl diketocamphorate (I)[2] from diethyl oxalate and dimethyl β,β-dimethylglutarate. The authors also stated, in this same paper, their intention of continuing this work and also of examining the behavior of diethyl oxalate towards esters of thiodiglycolic and diglycolamidic acids. These esters would be expected to condense in a manner similar to the glutarates or diglycolates giving the corresponding diketotetrahy-

[1] Am. Chem. J., 31, 290 (1906).

[2] Komppa, Ber., 32, 1421; 34, 2472; 36, 4332; Dieckmann, Ibid., 32, 1933.

drothiophenes (III), and diketopyrrolidines (IV)[1] respectively. Results confirming our original assumptions have been described in a recent paper

$$
\begin{array}{cc}
\text{CO—CO} & \text{CO—CO} \\
| \quad | & | \quad | \\
CH_3O_2CCH \quad CHCO_2CH_3 & C_2H_5O_2CCH \quad CHCO_2C_2H_5 \\
\diagdown / & \diagdown / \\
C & O \\
(CH_3)_2 & \\
\text{I.} & \text{II.}
\end{array}
$$

$$
\begin{array}{cc}
\text{CO—CO} & \text{CO—CO} \\
| \quad | & | \quad | \\
C_2H_5O_2CCH \quad CHCO_2C_2H_5 & C_2H_5O_2CCH \quad CHCO_2C_2H \\
\diagdown / & \diagdown / \\
S & N \\
& | \\
& X \\
\text{III.} & \text{IV.}
\end{array}
$$

by Hinsberg,[2] in which he has shown that diethyl oxalate condenses smoothly with diethyl thiodiglycolate giving the thiophene (III). He furthermore describes several thiophene derivatives which were obtained by condensing the thiodiglycolate with certain α-ketone esters and o-diketones. In this paper we shall describe a general method of synthesizing pyrrolidines of the general formula (IV). The study of these pyrrole compounds is of especial interest because of their unique properties and also because of their possible use for further syntheses. Their investigation will be continued.

A careful review of the literature, before we undertook this investigation, revealed the fact that the action of diethyl oxalate on a diglycolamidate had previously been examined. The results of this work are described in a paper entitled "The Condensation of Phenylglycinoacetic Esters in Presence of Sodium Alkyloxides," by Mouilpied,[3] in which he discusses the action of oxalic esters on esters of N-phenyldiglycolamidic acid in the presence of sodium alcoholates. The authors' conclusions, however, seemed so improbable to the writer that we deemed it necessary to repeat some of his experiments.

Mouilpied[4] observed that diethyl oxalate condenses smoothly with diethyl N-phenyldiglycolamidate, in the presence of sodium ethylate, giving a compound having the same empirical formula as N-phenyl α,α-dicarbethoxy-β,β'-diketopyrrolidine (V) and melting at 137°. He did not however assign a pyrrole structure to the condensation product because it did not undergo saponification under normal conditions and did

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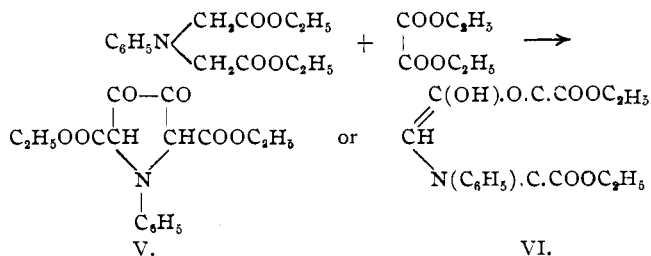[1] "These compounds are structurally represented throughout this paper as ketone compounds or pyrrolidines. They might also be represented in their tautomeric form or as hydroxyl derivatives of pyrrole and, in fact, this *enol* constitution is indicated by their acid character and by many of their reactions." (T. B. J.)

[2] *Ber.*, **43**, 901 (1910).

[3] *J. Chem. Soc.*, **87**, 435.

[4] *Loc. cit.*

not react with hydroxylamine or phenylhydrazine giving an oxime and phenylhydrazone respectively. He discusses the possibility of the

$$C_6H_5N\begin{cases}CH_2COOC_2H_5\\CH_2COOC_2H_5\end{cases} + \begin{array}{l}COOC_2H_5\\|\\COOC_2H_5\end{array} \longrightarrow$$

$$\begin{array}{cc}CO—CO\\|\quad\quad|\\C_2H_5OOCCH\quad CHCOOC_2H_5\\\diagdown\quad\diagup\\N\\|\\C_6H_5\end{array}\qquad \text{or} \qquad \begin{array}{l}C(OH).O.C.COOC_2H_5\\\diagup\!\diagup\\CH\\\diagdown\\N(C_6H_5).C.COOC_2H_5\end{array}$$

V.   VI.
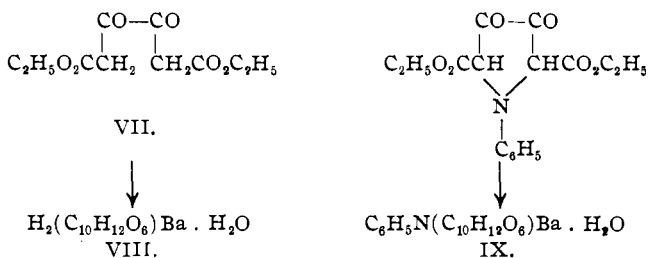
compound having a quinoid structure, VI, because it gives a yellow sodium salt, and finally concludes that a satisfactory, constitutional formula cannot be established.

We have now re-examined this compound of Mouilpied's melting at 137°, and have obtained evidence which we believe proves that this substance has not the quinoid formula VI and have therefore assigned to it the constitution of an oxypyrrolidine as represented by the formula V. The fact that the compound does not undergo saponification normally, does not preclude the structure of a pyrrole compound. The stability of this substance, in the presence of alkali and acids, might be predicted. Johnson and Johns[1] observed this same stability in the case of the corresponding tetrahydrofurfurane (II), and Hinsberg[1] makes the following statement regarding the stability of the tetrahydrothiophene (III). "Der Dioxy-thiophendicarbonsäureester wird beim kochen mit überschüssigem Alkali bedeutend schwieriger verseift—offenbar, weil die beiden Hydroxylgruppen einen schützenden Einfluss auf die benachbarten Carboxymethyl-Gruppen ausüben." A lactone ring as represented by the quinoid formula VI would be expected to undergo saponification very easily. That the compound does not react with hydroxylamine and phenylhydrazine is very probably due to the fact that it functionates here as a hydroxyl compound instead of an o-diketone.

If Mouilpied's condensation product, melting at 137°, has a quinoid structure (VI), it would contain only one acid hydrogen atom, and therefore give only a mono-sodium salt. We now find that this substance dissolves in alkali giving a characteristic disodium salt, which is yellow in color and very soluble in water. It reacted smoothly with para-nitrobenzyl chloride giving a dialkyl derivative, insoluble in alkali, and combined with the required amount of barium chloride giving a quantitative yield of a mono-barium salt containing one molecule of water of crystallization (IX). This latter observation is significant because the corresponding acyclic compound, diethyl ketipate (VII), gives an analogous
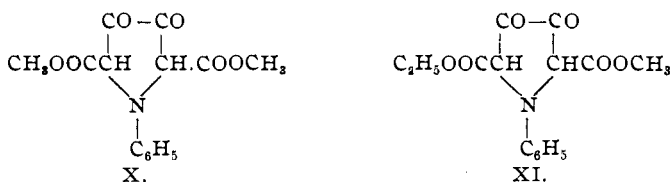
[1] *Loc. cit.*

yellow barium salt (VIII), containing also one molecule of water.[1] Their relationship is shown by the following formulas:

$$\begin{array}{cc}
\overset{\displaystyle CO\text{—}CO}{\underset{\displaystyle C_2H_5O_2CCH_2 \quad CH_2CO_2C_2H_5}{|\qquad\quad|}} &
\overset{\displaystyle CO\text{--}CO}{\underset{\displaystyle C_2H_5O_2CCH \quad CHCO_2C_2H_5}{|\qquad\quad|}} \\
& \diagdown\!\diagup \\
& N \\
\text{VII.} & | \\
& C_6H_5 \\
\downarrow & \downarrow \\
H_2(C_{10}H_{12}O_6)Ba\,.\,H_2O & C_6H_5N(C_{10}H_{10}O_6)Ba\,.\,H_2O \\
\text{VIII.} & \text{IX.}
\end{array}$$

When this yellow disodium salt was digested in alcohol with the hydrochloride of an aromatic base (aniline, phenylenediamine, etc.) only one atom of sodium was displaced by hydrogen, and a quantitative yield of the mono-sodium salt was obtained. This salt is difficultly soluble in cold water, is colorless, and dissolves in sodium hydroxide solution, giving a deep yellow solution of the disodium salt. It is our intention to study further these interesting sodium salts and also the corresponding potassium salts.

The interesting observation was also made by Mouilpied that, while diethyl oxalate and diethyl N-phenyldiglycolamidate condense in the presence of sodium ethylate giving the pyrrolidine melting at 137°, if the same esters are condensed in the presence of sodium methylate, this compound is not obtained, but the corresponding dimethyl ester (X), melting at 188°, is formed. This interesting result led him to carry out

$$\begin{array}{cc}
\overset{\displaystyle CO\text{--}CO}{\underset{\displaystyle CH_3OOCCH \quad CH.COOCH_3}{|\qquad\quad|}} &
\overset{\displaystyle CO\text{--}CO}{\underset{\displaystyle C_2H_5OOCCH \quad CHCOOCH_3}{|\qquad\quad|}} \\
\diagdown\!\diagup & \diagdown\!\diagup \\
N & N \\
| & | \\
C_6H_5 & C_6H_5 \\
\text{X.} & \text{XI.}
\end{array}$$

all the possible condensations of the dimethyl and diethyl esters of oxalic and N-phenyldiglycolamidic acids in the presence of sodium ethylate and sodium methylate. Among these eight possible condensations, he observed the formation of the compound melting at 137° in only the one case mentioned above. Identical condensation products, melting at 146–7°, were obtained by condensation of dimethyl oxalate with diethyl N-phenyldiglycolamidate and diethyl oxalate with dimethyl N-phenyldiglycolamidate in the presence of sodium ethylate. On the other hand when these esters were condensed in the same order, in the presence of sodium methylate, the product of the two reactions melted at 188°. Diethyl and dimethyl oxalates condensed with diethyl and dimethyl

[1] Fittig, Daimler and Keller, Ann., 249, 193.

N-phenyldiglycolamidates, respectively, in the presence of sodium methylate, giving compounds melting at 175° and 195°. On the other hand, dimethyl oxalate and dimethyl N-phenyldiglycolamidate gave, in the presence of sodium ethylate, a product melting at 159°. Therefore, six different compounds, melting at 137°, 146–7°, 159°, 175°, 188° and 195°, were formed in these eight condensations.

We have repeated all these possible condensations and used in each case two molecular proportions of the alcoholate, but are unable to confirm in every case the observations of Mouilpied. We succeeded in isolating, in a pure condition, only two definit condensation products, viz.: N-phenyl-α,α'-dicarbethoxy-β,β'-diketopyrrolidine melting at 137° and the corresponding dimethyl ester (X), melting at 188–9°. Mouilpied intimates that his compounds may possibly be structural isomers, but the results obtained by us indicate that the condensation products melting at 146–7°, 159° and 175° are only indefinit mixtures of the pyrrolidines melting at 137° and 188° and not definit compounds. In no case did we obtain a substance melting at 195°. It is possible that one of the compounds described by Mouilpied was the mixed ethyl methyl ester represented by formula XI.

Our results show conclusively that the constitution of the product of these reactions is determined by the structure of the alcoholate used in the condensation, and not by that of the esters used. If sodium ethylate is employed, a diethyl ester of the pyrrolidine is formed and a dimethyl ester is obtained if sodium methylate is used. Our results are perfectly analogous with those described by other investigators who have observed similar metathetical changes.[1]

Experimental Part.

The N-phenyldiglycolamidic acid $C_6H_5N(CH_2COOH)_2$,[2] which was used in this work, was prepared according to the following directions: One hundred and twelve grams of chloroacetic acid were dissolved in 100 cc. of water and this solution added to a mixture of 300 cc. of water and two hundred and ninety-six grams of anhydrous sodium carbonate. This mixture was then heated in an oil bath to 80° and ninety-three grams of phenylglycine added in small portions so as to avoid too violent an effervescence of carbon dioxide. After heating two hours at 110–120°, the solution was cooled to 0° and the diglycolamidic acid precipitated by careful addition of an excess of hydrochloric acid. If insufficient acid is added, a mono-sodium salt of the diglycolamidic acid separates. The yield obtained by this procedure was about 80–85 per cent. of the theoretical

[1] Purdie, Ber., 20, 1554. Israel, Ann., 231, 220. Peters, Ibid., 257, 353. Leuchs and Theodoresen, Ber., 43, 1239. Hinsberg, Ibid., 43, 904. Dieckmann, Ibid., 43, 1028. Komnenos, Monatsh., 31, 111, 687; 32, 77. Pfannl, Ibid., 31, 301.
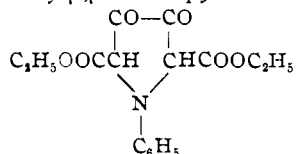
[2] Hansdörfer, Ber., 22, 1798; 23, 1990.

and the acid generally melted at 152–155° with effervescence without further purification.

Diethyl N-phenyldiglycolamidate, $C_6H_5N(CH_2COOC_2H_5)_2$,[1] and *dimethyl N-phenyldiglycolamidate*, $C_6H_5N(CH_2COOCH_3)_2$.[2] These esters can easily be prepared by esterification of the diglycolamidic acid in the usual way, in presence of hydrochloric or sulfuric acid. The simplest method however is to dissolve fifty grams of the acids in about 150 cc. of the absolute alcohol and after the addition of 15 cc. of concentrated sulfuric acid, to digest on the steam bath for seven to eight hours. The excess of alcohol is then removed by heating at 50° under diminished pressure, the ester washed with dilute sodium carbonate solution, dissolved in ether and dried over anhydrous sodium sulfate. They are then purified by distillation under diminished pressure, the ethyl ester boiled at 200–206° at 6 mm. and the methyl ester at 216–218° at 25 mm.

Condensations in the Presence of Sodium Ethylate.

N-Phenyl-α,α'-dicarbethoxy-β,β'-diketopyrrolidine.

$$\begin{array}{c} CO{-}CO \\ | \qquad | \\ C_2H_5OOCCH \quad CHCOOC_2H_5 \\ \diagdown \quad \diagup \\ N \\ | \\ C_6H_5 \end{array}$$

I. By Condensation of Diethyl Oxalate with Diethyl-N-phenyldiglycolamidate.

One and two-tenths grams of sodium were dissolved in 50 grams of boiling, absolute alcohol and the solution cooled. A mixture of 6.7 grams of diethyl *N*-phenyldiglycolamidate and 3.7 grams of diethyl oxalate were then added at once to the ethylate, when a violent reaction set in, by gentle warming, with evolution of heat and formation of a yellow disodium salt of the pyrrolidine. After heating at 100° for 3–4 hours, to complete the reaction, the salt was dissolved in cold water, the solution washed with ether to remove a trace of oil and the pyrrolidine precipitated by addition of an excess of hydrochloric acid. The pyrrolidine separated at once in yellow, prismatic crystals, which melted at 135°. It crystallized from hot alcohol or glacial acetic acid in beautiful needle-like prisms which melted at 137–8° to a clear oil without effervescence. The yield was 7.5 grams or 93.7 per cent. of theory. The yield of the pyrrolidine was diminished by condensing the esters in more dilute solutions of sodium ethylate. Analysis (Kjeldahl):

Calculated for $C_{16}H_{17}O_6N$: N, 4.39. Found: N, 4.8; 4.46.

II. By Condensation of Diethyl-N-phenyldiglycolamidate with Dimethyl Oxalate.

[1] Bischoff, *Ber.*, **30**, 2309.

[2] Mouilpied, *Loc. cit.*

Molecular proportions of the two esters were condensed under the same conditions as described in the preceding experiment. The reaction was complete after heating for 15 minutes and a homogeneous disodium salt was obtained. The diethyl ester separated at once on adding hydrochloric acid to an aqueous solution of the salt and melted at 133–5°. After two crystallizations from 95 per cent. alcohol, it melted constant at 137°. Analysis (Kjeldahl):

Calculated for $C_{16}H_{17}O_6N$: N, 4.39. Found: N, 4.2.

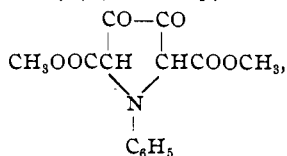*III. By Condensation of Dimethyl N-Phenyldiglycolamidate with Diethyl Oxalate.*

In this experiment, we obtained from 1.85 grams of the oxalate and 3.0 grams of the diglycolamidate, 2.2 grams of the diketopyrrolidine, melting at 135–7°. The alcoholic filtrates, after purification of the cyclic ester, were concentrated and cooled, when a crystallin product separated, which melted at about 147° to an oil. This melting point was assigned by Mouilpied[1] to the compound obtained by condensation of the above esters in presence of sodium ethylate. An examination of this material, however, showed that it was not a definit substance, but a mixture, apparently, of two compounds crystallizing in needles and stout, well-developed prisms. The needles predominated and, after being separated mechanically from the prisms, melted at 136°. A sufficient quantity of the prisms for safe identification was not obtained.

IV. By Condensation of Dimethyl N-Phenyldiglycolamidate with Dimethyl Oxalate.

By proceeding in exactly the same manner as in the three preceding experiments we obtained, in this case, a product which melted before purification at about 143–5° to a turbid oil. After two crystallizations, however, from 95 per cent. alcohol, the pure cyclic diethyl ester was obtained and melted sharply at 136–7°. A mixture of this substance and the ester from Experiment I melted at exactly the same temperature. Mouilpied states that the product of the condensation, in this case, melts at 159°. An attempt to convert the diethyl ester, melting at 137°, into the corresponding dimethyl ester (see below) by digestion with a methyl alcohol solution of sodium was unsuccessful. It was recovered unaltered after digestion for five hours.

Condensations in the Presence of Sodium Methylate.

N-Phenyl-α,α'-dicarbmethoxy-β,β'-diketopyrrolidine,

$$\begin{array}{c} CO\!-\!CO \\ |\qquad| \\ CH_3OOCCH\quad CHCOOCH_3, \\ \diagdown\diagup \\ N \\ | \\ C_6H_5 \end{array}$$

[1] *Loc. cit.*

I. By Condensation of Dimethyl N-Phenyldiglycolamidate with Dimethyl Oxalate.

The formation of this cyclic dimethyl ester, in this experiment and the three following, was not as smooth as that of the corresponding diethyl ester. Two-tenths of a gram of sodium was dissolved in 7 cc. of dry methyl alcohol, the solution cooled and a mixture of 2 grams of the dimethyl diglycolamidate and 1 gram of dimethyl oxalate added at once. The reaction was not vigorous and only a faint turbidity was produced. After heating on the steam bath for 6–7 hours, a heavy, yellow salt was obtained, insoluble in the alcohol. This was dissolved in water, washed with ether, and the solution acidified with hydrochloric acid. The dimethyl ester separated at once and was purified for analysis by cystallization from hot alcohol. It separated on cooling in well-defined prismatic crystals, which melted at 188–189° to a clear red oil. Analysis (Kjeldahl):

Calculated for $C_{14}H_{13}O_6N$: N, 4.81. Found: N, 4.49; 4.63.

II. By Condensation of Dimethyl N-Phenyldiglycolamidate with Diethyl Oxalate.

We used in this experiment 3.0 grams of the diglycolamidate, 1.85 grams of the oxalate and 0.6 gram of sodium dissolved in 9 cc. of methyl alcohol. The product of the condensation was crystallized once from 95 per cent. alcohol, when we obtained 1.7 grams cf the pure cyclic dimethyl ester melting at 188–9°. When the alcoholic filtrate was concentrated and cooled, a substance separated, which melted at 177° to a turbid oil. An examination of this material under the microscope, however, showed that it was a mixture. By recrystallizations from alcohol the melting point was finally raised to 181°, indicating the cyclic dimethyl ester. The impurity removed by this treatment was, without doubt, a trace of the cyclic diethyl ester melting at 137°. Analysis (Kjeldahl):

Calculated for $C_{14}H_{13}O_6N$: N, 4.81. Found: N, 4.63.

III. By Condensation of Diethyl N-Phenyldiglycolamidate with Dimethyl Oxalate.

The only product identified in this experiment was the cyclic dimethyl ester melting at 188–9°.

IV. By Condensation of Diethyl N-Phenyldiglycolamidate with Diethyl Oxalate.

In this experiment 0.4 gram of sodium was dissolved in 5 cc. of methyl alcohol and 2.0 grams of the diglycolamidate and 1.1 grams of the oxalate added in the usual manner. There was no vigorous reaction and only a slight turbidity was produced. On heating on the steam bath, the solution became perfectly clear and within 15–20 minutes, a yellow sodium salt began to deposit. The heating was continued for one hour and the salt then dissolved in cold water, the solution filtered and acidi-

fied with hydrochloric acid. A colorless crystallin compound separated at once. It crystallized from alcohol in prismatic crystals and was identified as the cyclic dimethyl ester melting at 188–9° to a clear oil. The yield was excellent. Analysis (Kjeldahl):

Calculated for $C_{14}H_{13}O_6N$: N, 4.81. Found: N, 4.68.

When the alcoholic filtrates were concentrated, a substance separated, on cooling, which melted at 157–166°. The appearance of this material under the microscope, however, was similar to that observed in the previous experiments, a mixture of needles and stout prisms. A definit compound could not be obtained by repeated crystallizations from alcohol and the crystallin appearance of the product obtained indicated a mixture of the cyclic diethyl ester melting at 137° and the methyl ester melting at 188–9°. Mouilpied states that the product of the condensation in this case is a compound melting at 175°.

The melting points of the various condensation products obtained by Mouilpied[1] and us, in the eight experiments described above, are given for comparison in the following table. The temperatures 137° and 188–9° are the melting points of *N-phenyl α,α'-dicarbethoxy-β,β'-diketopyrrolidine* and *N-phenyl-α,α'-dicarbmethoxy-β,β'-diketopyrrolidine*, respectively.

TABLE I.

	N-Phenyldiglycolamidate.	Oxalic ester.	Alcoholate.	Mouilpied's melting point.	Our melting point.
1.....	$C_6H_5N(CH_2COOC_2H_5)_2$	$(COOC_2H_5)_2$	C_2H_5ONa	137°	137°
2.....	$C_6H_5N(CH_2COOC_2H_5)_2$	$(COOC_2H_5)_2$	C_2H_5ONa	146–7°	137°
3.....	$C_6H_5N(CH_2COOCH_3)_2$	$(COOC_2H_5)_2$	C_2H_5ONa	147°	137°
4.....	$C_6H_5N(CH_2COOCH_3)_2$	$(COOCH_3)_2$	C_2H_5ONa	159°	137°
5.....	$C_6H_5N(CH_2COOC_2H_5)_2$	$(COOC_2H_5)_2$	CH_3ONa	175°	188–189°
6.....	$C_6H_5N(CH_2COOC_2H_5)_2$	$(COOCH_3)_2$	CH_3ONa	188°	188–189°
7.....	$C_6H_5N(CH_2COOCH_3)_2$	$(COOC_2H_5)_2$	CH_3ONa	188°	188–189°
8.....	$C_6H_5N(CH_2COOCH_3)_2$	$(COOCH_3)_2$	CH_3ONa	195°	188–189°

The Sodium Salts of N-Phenyl α,α'-dicarbethoxy-β,β'-diketopyrrolidine.

This pyrrolidine gives two characteristic sodium salts: a disodium salt which is yellow and a monosodium salt which is colorless. The yellow salt is always formed by dissolving the ketone in aqueous alkali or by adding the pyrrolidine to alcohol containing the required proportion of sodium ethylate. It then separates as a bright yellow powder insoluble in boiling alcohol. Especially interesting is the behavior of this yellow salt when digested in alcohol with an excess of a halide of an aromatic base, *viz.:* aniline, toluidine, or phenylenediamine hydrochlorides. By this treatment, only one of the sodium atoms of the salt is displaced and a quantitative yield of the colorless monosodium salt is obtained. This salt is practically insoluble in alcohol and difficultly soluble in water, giving a neutral solution. It decomposes when heated above 260° and dissolves

[1] *Loc. cit.*

at once in warm, dilute sodium hydroxide solution giving the characteristic yellow solution of the disodium salt. When the salt was triturated with dilute hydrochloric acid, the N-phenyl α,α' dicarbethoxy-β,β'-diketopyrrolidine separated and after one crystallization from alcohol melted at 137° to a clear oil. Nitrogen determination, (Kjeldahl):

Calculated for $C_{16}H_{16}O_6NNa$: N, 4.10. Found: N, 4.5.

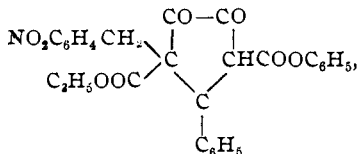*Barium Salt of N-phenyl α,α'-dicarbethoxy β,β'-diketopyrrolidine,*

$$C_6H_5N(C(COOC_2H_5)CO)_2.Ba.H_2O.$$

The diethyl ester was dissolved in water with two molecular proportions of potassium or sodium hydroxide and a slight excess of barium chloride added to the solution. The barium salt separated at once as a fine, yellow powder. After heating a few minutes to complete the reaction, the salt was filtered off, washed with hot water to remove any barium chloride and finally with alcohol. The salt is practically insoluble in these two solvents. It contained one molecule of water of crystallization, which it did not lose by standing in a desiccator over concentrated sulfuric acid.

Calculated for $C_{16}H_{15}O_6NBa.H_2O$: H_2O, 3.81; Ba, 29.02.
Found: H_2O (at 100-110°),   3.89; Ba, 28.50, 29.1.

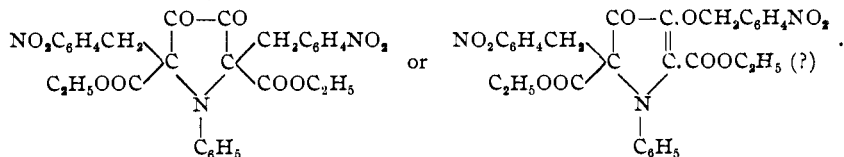*N-Phenyl α,α'-dicarbethoxy-α-paranitrobenzyl-β,β'-diketopyrrolidine,*

$$
NO_2C_6H_4CH_2
\begin{array}{c}
CO-CO \\
\diagdown C \qquad CHCOOC_6H_5, \\
C_2H_5OOC \diagup \quad \diagdown C \diagup \\
\mid \\
C_6H_5
\end{array}
$$

The yellow disodium salt of the diketopyrrolidine was first prepared, in the usual manner, by dissolving 3.0 grams of the diethyl ester in alcohol containing the required amount of sodium (0.43 gram). The theoretical quantity of nitrobenzyl chloride was then added and the mixture digested on the steam-bath until the solution gave no alkaline reaction when tested with turmeric. After evaporation of the excess of alcohol at ordinary temperature, the crude reaction product remained as a red semi-solid, which was pasty after standing exposed to the air for several hours. This was first triturated with warm water to remove sodium chloride and the oily residue, insoluble in water, then finally triturated with cold alcohol and the material undissolved by this treatment saved (see below). When the water and alcohol solutions were allowed to concentrate by slow evaporation, the mono-paranitrobenzyl derivative separated as an orange-colored powder, resembling, in appearance, pulverized potassium dichromate. It was soluble in dilute alkali and melted at 180-182° to a bright red oil with slight effervescence. The yield was small. Analysis (Kjeldahl):

Calculated for $C_{23}H_{22}O_8N_2$: N, 6.16. Found: N, 5.87; 6.24.

Di-(paranitrobenzyl)-N-phenyl α,α'-dicarbethoxy-β,β'-diketopyrrolidine,

$$
\begin{array}{ccc}
& \text{CO—CO} & \\
\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2 & \underset{\diagdown}{|} \quad \underset{\diagup}{|} & \text{CH}_2\text{C}_6\text{H}_4\text{NO}_2 \\
& \text{C} \quad \text{C} & \\
\text{C}_2\text{H}_5\text{OOC} & \diagup \quad \diagdown & \text{COOC}_2\text{H}_5 \\
& \text{N} & \\
& | & \\
& \text{C}_6\text{H}_5 &
\end{array}
\quad \text{or} \quad
\begin{array}{c}
\text{CO—C.OCH}_2\text{C}_6\text{H}_4\text{NO}_2 \\
\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2 \;|\quad || \\
\text{C} \quad \text{C.COOC}_2\text{H}_5 \, (?) \\
\text{C}_2\text{H}_5\text{OOC} \diagdown \diagup \\
\text{N} \\
| \\
\text{C}_6\text{H}_5
\end{array} .
$$

The residue (above) insoluble in water and alcohol, which was apparently the chief product of the reaction, dissolved immediately in glacial acetic acid. When allowed to stand for about two days, the diparanitrobenzyl derivative finally separated in yellow prisms, which melted quite sharp at 132° to a clear oil. This compound was very soluble in boiling alcohol and separated, on cooling, in needle-like prisms which melted at 131–2° to a clear oil. It was insoluble in alkali and a mixture of the compound and the unaltered diethyl ester (m. p. 137°) melted at 109°. Nitrogen determination (Kjeldahl):

Calculated for $C_{30}H_{27}O_{10}N_3$: N, 7.13. Found: N, 6.98.

Behavior of N-phenyl α,α'-dicarbethoxy-β,β'-diketopyrrolidine towards Hydriodic Acid and Aluminium Amalgam.

Two attempts to reduce this compound with these reagents were unsuccessful. There was no evidence of saponification or reduction after boiling 3.0 grams of the pyrrolidine with 5 cc. of the acid for several minutes. It apparently underwent only slight decomposition by careful treatment and after being separated from the acid and decolorizing with a little sulfur dioxide water, it melted at 135–7° to an oil. By prolonged digestion, the ester was charred and was completely decomposed.

In a second experiment, the pyrrolidine was dissolved in 95 per cent. alcohol and the solution poured upon a large excess of aluminium-amalgam. After allowing to stand for 8–9 hours, when the evolution of hydrogen had ceased, the alcohol solution was filtered, concentrated and cooled. The unaltered diketopyrrolidine separated in needles and melted at 136–7°.

NEW HAVEN, CONN.

A SESQUITERPENE AND AN OLEFINIC CAMPHOR OCCURRING IN SOUTHERN CYPRESS.[1]

BY ALLAN F. ODELL.

While conducting a series of experiments on the oxidation products of sawdust, it was observed that the ethereal extract from the aqueous oxidation mixture of cypress sawdust left upon evaporation a very fragrant residue. The constant recurrence of this odor in connection with cypress wood led to an investigation of its nature.

The cypress in this section is entirely of the species *Taxodium distichum,*

[1] Paper read before the New Orleans Section, March 17, 1911.