the solution boiled for 2 hours. Iodine was evolved immediately and deposited on the surface of the condensing tube. After cooling and diluting with water, the iodine was reduced by addition of sulphur dioxide solution, when we obtained a clear pale yellow solution. This was finally concentrated, decolorized with charcoal, and cooled. Beautiful, colorless prisms deposited, which did not melt below 300°. The compound was identified as 2,6-dioxypyrimidine-5-acetic acid. The yield was nearly quantitative. A mixture of this and thymine melted below 260°. The compound contained no halogen, was soluble in alkali, and was precipitated from its alkaline solution by addition of acids. When the above mother liquor (HI solution) was digested with an excess of sodium hydroxide, ammonia was evolved, showing the presence of ammonium iodide in the solution. Analysis (Kjeldahl):

Calculated for $C_6H_6O_4N_2$: N, 16.47.
Found: N, 16.44.

2,6-Dioxypyrimidine is not reduced at the double bond in the 4,5-positions by the action of hydriodic acid. One-half a gram of the acid was recovered unaltered after digestion for 3 hours. There was no coloration of the acid, due to the formation of any free iodine. This stability of the unsaturated ring, in presence of hydriodic acid, is remarkable.

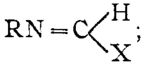
NEW HAVEN, CONN.

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

METHYL PHENYLIMINOMALONATE AND ITS REACTIONS.

BY RICHARD SYDNEY CURTISS AND F. GRACE C. SPENCER.

Received April 26, 1911.

We have for some time sought a method of making the above-named compound, $C_6H_5N=C(CO_2R)_2$, but without avail. Considered as a dicarboxyl addition product of phenyl isocyanide, $C_6H_5N=C$, or as an analog of phenyl isocyanate, $C_6H_5N=C=O$, containing the negative carbomethoxyl groups in place of oxygen, one might predict its chemical properties and behavior with some degree of accuracy. As Nef[1] and others have so well shown in the case of isocyanides and isocyanates, they possess a great reactivity on the N=C double bond—adding on at this point many compounds having easily dissociable hydrogen atoms. In such cases of addition with isocyanides, RN=C, in which the carbon is bivalent, it is the higher valences of the carbon atom which show the greatest reactivity. They first become saturated, yielding compounds of the isocyanate type, RN=C=O and  $RN=C{<}^{H}_{X}$; further addition takes place on the N=C double bond; for instance with ammonia; the phenyl

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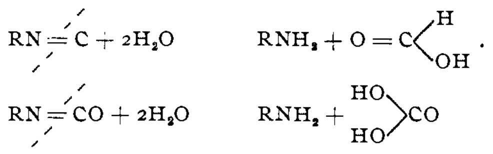
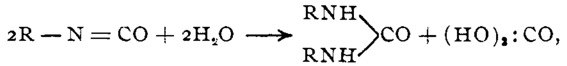
[1] *Ann.*, 270, 268–335; 280, 291–342; 287, 265–359; and other papers.

isocyanate, $R—N = CO$, yields carbonic acid derivatives, $RNH.CO.NH_2$,
$+$
$H — NH_2$
ureas. The well-known action of water upon these isocyano compounds results in their hydrolysis and the formation of an amine, and an acid,



$$RN = C + 2H_2O \qquad RNH_2 + O = C\begin{matrix}H \\ OH\end{matrix} .$$
$$RN = CO + 2H_2O \qquad RNH_2 + \begin{matrix}HO \\ HO\end{matrix}\!\!>\!CO$$

The latter reaction proceeds with the formation of one or more less stable intermediate reaction products of the isocyanate with water; for instance one of these reactions yields disubstituted ureas,

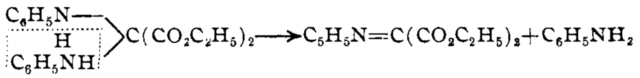


$$2R — N = CO + 2H_2O \longrightarrow \begin{matrix}RNH \\ RNH\end{matrix}\!\!>\!CO + (HO)_2{:}CO,$$

and the latter may be further hydrolyzed to the final products, an amine and carbonic acid.

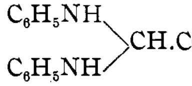
As far as we have been able to find, the exact mechanism of the reaction of water with the isocyanates, producing the above compounds, has not been discovered. In the last reaction it is apparent that the R—N radical must dissociate from the carbon of the isocyanate in order to produce the second amine group which is present in the product. Whether or not this dissociation of the nitrogen from carbon precedes, or follows, the addition of the elements of water upon the $N = C$ double bond remains to be proved. The exact mechanism of the hydrolysis of the isocyanides and isocyanates is of much importance, and is discussed here, inasmuch as the study of the phenyliminomalonates and their reactions throws an interesting light upon this point.

In attempting to prepare the esters of phenyliminomalonic acid, $C_6H_5N = C(CO_2H)_2$, we have tried the effect of heat upon ethyl dianilinomalonate in the hope of dissociating one molecule of aniline, but without success.



$$\begin{matrix}C_6H_5N— \\ H \\ C_6H_5NH\end{matrix}\!\!>\!C(CO_2C_2H_5)_2 \longrightarrow C_6H_5N{=}C(CO_2C_2H_5)_2 + C_6H_5NH_2$$

As we have since learned, the reactivity of the product sought is so great that it could not exist in the presence of aniline, which reverses the reaction completely. This is in marked contrast to the behavior of dianilinoacetic acid, which loses aniline at ordinary temperature.

Ostromisslenskii[1] obtained phenyliminoacetic acid, $C_6H_5N = CH.CO_2H$, from dianilinoacetic acid,  $\begin{matrix}C_6H_5NH \\ C_6H_5NH\end{matrix}\!\!>\!CH.CO_2H$, by simply allowing the

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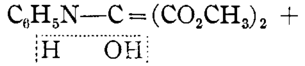
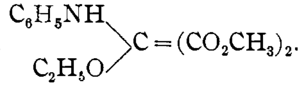
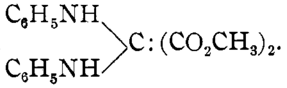
[1] *Ber.*, 41, 3029.

substance to stand in a desiccator, but with better results by heating, alone or in the presence of acetic acid. The product is yellow, reactive at the point of the $N=C$ double bond, and easily polymerizes.

We have, however, produced methyl phenyliminomalonate in nearly theoretical yield and in a pure form by the action of phosphorus pentoxide upon methyl anilinotartronate,  $C_6H_5N—C=(CO_2CH_3)_2 + \underset{\boxed{H \quad OH}}{}$ $P_2O_5 = C_6H_5N=C=(CO_2CH_3)_2$. The product is a thick greenish-yellow oil, with great reactivity on the $N=C$ double bond, which here acts also as a chromophore group. It reacts vigorously with water, alcohols, dry ammonia, dry hydrochloric acid, amines, and acids, with loss of color, and the formation of substituted anilinomalonates. It polymerizes readily to gums and resins.

Even the moisture of the air rapidly changes the yellow oil to colorless crystallin compounds, methyl dianilinomalonate and methyl dihydroxymalonate. This reaction has been studied quantitatively. Its mechanism is complex and appears to be in perfect analogy with that of water upon phenyl isocyanate producing diphenylurea, as mentioned above.

We have also studied the action of ethyl alcohol upon methyl phenyliminomalonate. It yields a crystallin addition product, methyl anilinoethoxymalonate,  $\begin{matrix} C_6H_5NH \\ C_2H_5O \end{matrix} \rangle C=(CO_2CH_3)_2$.

Methyl phenyliminomalonate adds one molecule of aniline at ordinary temperatures and yields methyl dianilinomalonate,  $\begin{matrix} C_6H_5NH \\ C_6H_5NH \end{matrix} \rangle C:(CO_2CH_3)_2$. This compound we have also made for comparison by the action of aniline upon methyl dihydroxymalonate.

It was formerly observed by one[1] of us that ethyl anilinomalonate was converted into ethyl dianilinomalonate by simply heating the substance, in dry ligroin solution, with freshly precipitated mercuric oxide. The latter is quickly reduced. We have tried the same reaction on methyl anilinomalonate. With this ester the reduction of the mercuric oxide proceeds much more slowly and incompletely, but in like manner yields the substituted diaminomalonate and dihydroxymalonic ester.

The mechanism of this reaction is complex. It is closely related to the production of the same dianilinomalonates when water acts upon phenyliminomalonates as described above on this page.

The mechanism of the formation of diphenylurea, amine, and acid, by the hydrolysis of phenyl isocyanates (p. 986), is no doubt to be ex-

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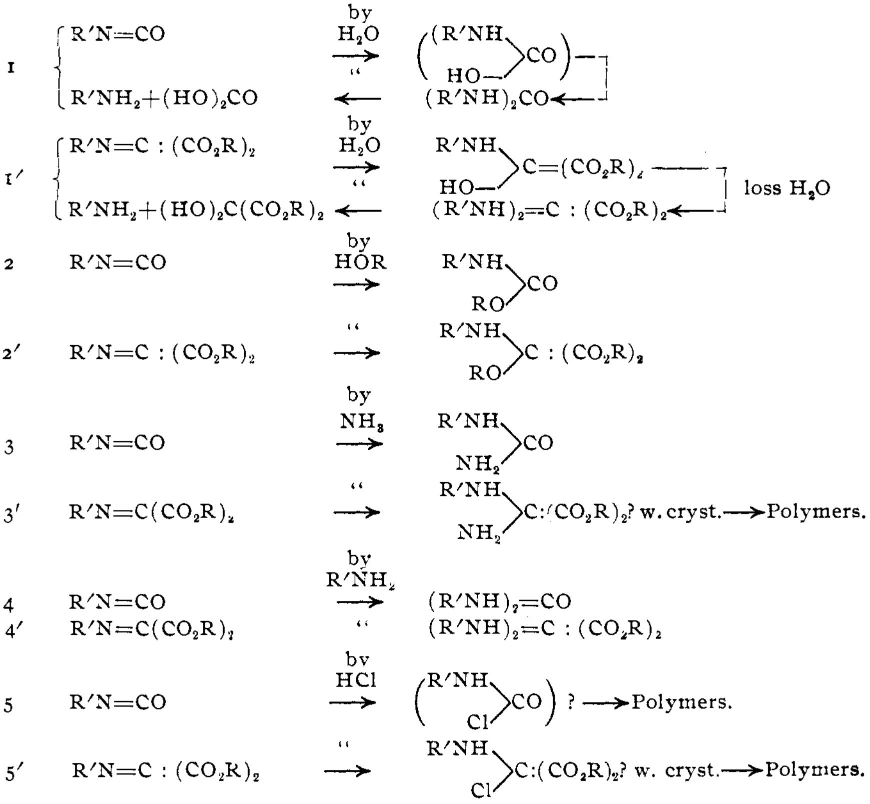
[1] Curtiss, *Am. Chem. J.*, 19, 694.

plained in a similar manner. These related reactions are the subject of further investigations in this laboratory, with the purpose of determining what unstable intermediate products may be formed, or for a time exist, between the starting point and the production of the stable end products.

The above-mentioned analogies between the addition reactions of methyl phenyliminomalonate and those of phenyl isocyanate is brought out in the following tabulation, in which R′ represents the phenyl radical, and the parentheses enclose the hypothetical addition products which have not yet been separated out.



The reactions of phenyliminomalonates with water, dry ammonia, and hydrochloric acid gas yield colorless, unstable, intermediate products which quickly pass over into more stable ones.

Experimental.

Methyl Phenyliminomalonate, $C_6H_5N=C(CO_2CH_3)_2$: *The Action of Phosphorus Pentoxide on Methyl Anilinotartronate.*—Ten grams of methyl anilinotartronate[1] were thoroughly mixed with two and five-tenths

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[1] Preparation, see Curtiss and Spencer, THIS JOURNAL, 31, 1057.

grams of phosphorus pentoxide (one mol. = 1.97 grams) and allowed to stand at the room temperature. At the end of two days it was a yellow sticky mass. (Sometimes the reaction begins almost immediately when mixed, and in one case it stood two weeks before any change was noticed.) At the end of six days it had separated into a heavy yellow and a hard yellow-red solid. The oil cannot be purified by vacuum distillation as it decomposes, nor can it be crystallized. A portion of the oil was decanted, and the remainder was dissolved in five times its volume of sodium-dry ether. The solid portion was insoluble in ether. Analysis was made on both the decanted sample and the one which had been extracted with ether, after the ether had been evaporated in a vacuum desiccator, over sulphuric acid.

Calculated for $C_6H_5N=C(COOCH_3)_2$: C, 59.69 ; H, 5.02 ; N, 6.33.
Found: C, 59.98, 60.01; H, 5.00, 4.79; N, 6.10, 6.61.

Methyl Phenyliminomalonate is a thick golden yellow oil, having a sharp biting taste. The presence of the double bond $N=C$, reacting with the two adjacent carbonyl groups, acts as a chromophore and gives it color, and also makes it an extremely reactive substance. As already mentioned, it combines readily with the moisture of the atmosphere when exposed to the air, adds on the dissociated parts of water, alcohols, acids, ammonia, amines, and other compounds containing easily dissociable hydrogen atoms, and in many ways suggests the great reactivity of the unsaturated isocyano group in the isocyanides, $RN = C$, and isocyanates, $RN = CO$.

Action of Aniline on Methyl Phenyliminomalonate.—Three and two tenths grams of methyl phenyliminomalonate were mixed with one and seventy one-hundredths grams of aniline (1 mol.). The temperature rose thirty-five degrees, and the mixture turned to a thick glycerol-like syrup, which quickly changed to a colorless crystallin mass. It was recrystallized several times by dissolving in sodium-dry ether and evaporating the solvent in a vacuum desiccator over sulfuric acid, then filtered and washed with cold ether. Attempts to concentrate the solution on a water bath produced a yellow gummy mass, which it was almost impossible to purify:

Calculated for $(C_6H_5NH)_2C=(COOCH_3)_2$: C, 64.91 ; H, 5.78 ; N, 8.93.
Found: C, 64.94, 65.04; H, 5.99, 5.74; N, 8.73, 9.25.

Methyl dianilinomalonate is a white crystallin substance having a melting point between 124 and 125°. Its crystals appear as hexagonal plates. It is easily soluble in benzene, acetone, and chloroform, fairly soluble in acetic ester, absolute ethyl and methyl alcohols, and slightly soluble in ligroin, and insoluble in water. It becomes electrified when rubbed with a glass rod. These properties identify it with the product made by Conrad and Reinbach.[1] We have also prepared this substance by the following method:

The Reaction of Aniline with Methyl Dihydroxymalonate.—Forty-nine grams of methyl dihydroxymalonate were mixed with 5.58 grams of aniline and heated on a water bath for 30 minutes. At 65° the action began, water was formed and deposited on the sides of the flask, and the substance changed to a thick yellow oil When removed from the water bath it was dark in color It was extracted with ether and the dark red solution was washed thoroughly with 10 per cent. hydrochloric acid solution, and then with water to remove the excess of aniline. It was then dried with potassium carbonate and evaporated on a water bath. The crystal product was again recrystallized from dry ether and then melted at 124–125°. Analysis:

Calculated for $(C_6H_5NH)_2=C=(COOCH_3)_2$: C, 64.95; H, 5.78; N, 8.94.
Found: C, 65.13; H, 5.69; N, 9.29.

The properties of this product are identical with those of methyl dianilinomalonate prepared as was described above.

Action of Water on Methyl Phenyliminomalonate.—Two grams of methyl phenyliminomalonate were mixed with one gram of water The water immediately becomes "milky" and the oil turns to a lemon-yellow color and becomes thick and viscid. The substance changes to a hard, dry, nearly colorless crystallin mass when allowed to stand for one day. It was then washed several times with a total of seven cc. of water to remove the methyl mesoxalate which appeared as one of the products of the reaction. The remaining crystals were then dissolved in ether and washed with water. A yield of 1.28 g. of crude crystals was obtained, m. p. 112°. The substance, when purified by recrystallization from ether, weighed 0.9 gram and melted at 124°. It was submitted to analysis with the following results. Analysis:

Calculated for $(C_6H_5NH)_2=C=(COOCH_3)_2$: C, 64.91; H, 5.78; N, 8.93.
Found: C, 65.05; H, 5.61; N, 8.71.

The properties of this substance are identical with those of methyl dianilinomalonate, as given above.

All the water which was used to wash the crystallin product mentioned above was evaporated in a desiccator. 0.9 gram of a colorless crystallin compound was obtained which dissolved readily in alcohol, water, and most organic solvents. It melted at 78°. The analysis follows:

Calculated for $(HO)_2=C=(CO_2CH_3)_2$: C, 36.57; H, 4.92.
Found: C, 36.70; H, 5.49.

The solubilities and chemical properties of this substance were found to be identical with those of methyl dihydroxymalonate.[2]

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[1] *Ber.*, 35, 521.

[2] Curtiss and Tarnowski, THIS JOURNAL, 30, 1267.

So great is the reactivity of the N=C double union in methyl phenyliminomalonate with water, that it absorbs it vigorously from the air, and it is impossible to keep the yellow oil in a state of purity, except in a desiccator over a strong dehydrating agent, or in sealed tubes. Two grams of the oil were exposed to the air for a few days, the yellow color disappeared quite rapidly as water was absorbed, and a solid crystallin mass resulted. Methyl dianilinomalonate and methyl dihydroxymalonate were separated from the product in the manner above described. The compounds were identified as such, both by their analyses and by a study of their chemical and physical properties.

Methyl dianilinomalonate has also been produced in the following interesting manner:

Oxidation of Methyl Anilinomalonate.—The methyl anilinomalonate used was prepared by the action of aniline upon ethyl bromomalonate, in a manner similar to that already described for the corresponding ethyl compound. One gram of methyl anilinomalonate, $C_6H_5NH.HC : (CO_2CH_3)_2$, dissolved in dry ligroin was mixed with 1.08 grams of freshly precipitated mercuric oxide, and the mixture heated on a water bath with a reverse condenser for fifteen hours, moisture of the air being excluded. The reduction of the oxide takes place slowly and incompletely. The grass-green solution was filtered from the mercury and mercuric oxide, and evaporated on the water bath. Crystals formed in hexagonal plates and melted in the impure form at 78°. This is the melting point of methyl dihydroxymalonate. The product was recrystallized five times and then showed a melting point of 124°, and this purified product corresponds in melting point and other properties to ethyl dianilinomalonate. The oxidation goes much more rapidly when the substance is dissolved in xylene and kept at a temperature of 130 to 150°, especially if a little hydrochloric acid is present to act as a catalyzer. The product in this test is apparently a mixture of methyl dihydroxymalonate, and methyl dianilinomalonate, by the same complex reaction which one of us has described for the corresponding ethyl ester.[1]

Action of Ammonia and of Hydrochloric Acid Gas on Methyl Phenyliminomalonate.—When dry ammonia gas is passed into an ethereal solution of methyl phenyliminomalonate, an intense reaction takes place and a white crystallin substance is formed, along with a red gummy product. The former substance is but slightly soluble in ether, and when exposed to the air it becomes gummy and rapidly loses ammonia. The product has not yet been purified. It is very unstable and seems to pass easily into polymerization products.

When dry hydrochloric acid gas is passed into methyl phenylimino-

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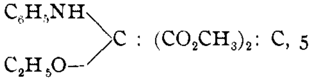
[1] *Am. Chem. J.*, 19, 694.

malonate, either in the pure form, or in solution in dry ether, a white crystallin reaction product is formed. This is also very unstable and rapidly liquefies in the air, losing hydrochloric acid, and appears to produce gummy polymerization products. This polymerization of the phenyliminomalonate appears analogous to that of phenyl isocyanate.

The Action of Alcohol on Methyl Phenyliminomalonate.—We have tested the action of methyl and ethyl alcohols, as well as benzyl alcohol, upon this substance. They all react vigorously with the evolution of heat, and loss of color of the iminomalonate, and produce well-defined, crystallin addition products. Mr. J. H. Bornmann has carried out the study of the product produced from ethyl alcohol, and in the following manner:

2.35 grams of methyl phenyliminomalonate were mixed with 0.49 gram (1 mol.) of absolute ethyl alcohol. There was an evolution of heat, a loss of color, and after a few hours the thick oil crystallized in colorless crystals. The substance was washed and recrystallized from alcohol and melted at 88° (uncor.). It is easily soluble in ether, benzene, chloroform and carbon tetrachloride; fairly soluble in alcohol; and slightly soluble in ligroin. While colorless in the pure form it slowly turns yellow when kept in a desiccator over sulphuric acid. This color change is probably due to a loss of alcohol and reproduction of the $N=C$ double bond, which here acts as a chromophore in the phenyliminomalonate:

Calculated for 

$\begin{matrix}C_6H_5NH\diagdown\\ C_2H_5O-\diagup\end{matrix}C : (CO_2CH_3)_2$: C, 58.42; H, 6.36; N, 5.24.

Found: C, 58.65; H, 6.39; N, 5.17.

URBANA, ILL.

NOTES.

Hippuric Acid as the Cause of the Failure of the Spectroscopic Test for Hemoglobin in Urine.—During the winter of 1910–1911, Passed Assistant Surgeon C. H. Lavinder, of the Division of Pathology and Bacteriology of the Hygienic Laboratory, called my attention to the difficulty he was having in the identification of blood coloring matter in the urine from a case of suspected paroxysmal hemoglobinuria. The urine in question presented an appearance which would lead a clinician to suppose blood coloring matter to be present, and yet, when examined with the spectroscope, no absorption bands such as are produced by hemoglobin and its various derivatives in solution, were to be seen. Later, Dr. Lavinder succeeded in obtaining Teichman's crystals in the usual manner, and thus demonstrated the presence of blood coloring matter in the specimen of urine under examination.