Action of Phosphorus Pentoxide on Ethyl Carbethoxyaminotartronate.—8.5 grams ethyl carbethoxyaminotartronate were mixed with 1.8 grams (1.1 mols.) of phosphorus pentoxide and placed in a tightly stoppered flask and allowed to stand at room temperature for twenty-four hours. The reaction was indicated by a darkening of color of the solution and the formation of a gummy mass. This was filtered, washed with ether, and recrystallized from alcohol. It melted at 121.5°, was colorless, and contained no phosphorus. It was analyzed.

Found: C, 46.97, 47.09; H, 6.53, 6.79; N, 8.62, 8.49.

Neither the analysis nor the lack of color corresponds to ethyl carbethoxyiminomalonate, $C_2H_5O_2C—N = C = (CO_2C_2H_5)_2$, the simple product which might be formed by loss of the elements of one molecule of water. A more complex reaction takes place, and will be further studied.

Action of Urea on Ethyl Oxomalonate.—1.72 grams finely powdered urea were added to 5 grams (1 molecule) of ethyl oxomalonate. The temperature rose quite rapidly to about 60°, and the green color of the keto ester disappeared. The mixture soon solidified. A constant melting point was not obtained, even after repeated recrystallization from ether and alcohol. The substance melted constantly at 132–133° after being three times recrystallized from hot chloroform. But even here as the following analyses show, decomposition apparently takes place during the process of crystallization from hot solutions.

Calculated for $NH_2CO.NH.C.(OH) : (COOC_2H_5)_2$: C, 41.03; H, 5.98; N, 11.96.
Found: C, 40.3, 40.2, 40.7; H, 6.0, 6.1, 5.8; N, 13.8, 13.8.

The figures correspond very closely to those of the primary addition product of urea on the keto ester, containing 5 per cent. of urea. Apparently this addition product, like most of the others we have hitherto made in the mesoxalic ester series, dissociates, when heated, into its constituent parts.[1]

URBANA, ILL.,
January 18, 1911.

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

KETO ESTER ADDITION PRODUCTS WITH ARYL AMINES AND ALCOHOLS.

BY RICHARD SYDNEY CURTISS, HARRY S. HILL AND R. H LEWIS.

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In continuing this line of investigation, which was first worked out on methyl oxomalonate,[1] we have studied the behavior of the three toluidines, aniline, and benzylamine on ethyl oxomalonate, with intent of obtaining

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[1] THIS JOURNAL, 31, 1054.

[1] Curtiss and Spencer, *Ibid.*, 31, 1053.

the intermediate unstable *addition* products. The toluidines react vigorously at low temperatures with the α-ketone group of the ester $O = C = (COOC_2H_5)_2$ and give colorless products of the form $RNH.C.(OH) : (COOC_2H_5)_2$, *i. e.*, substituted aminotartronates. These are the primary addition products in the typical reaction of an amine with a ketone group, while the second stage of the reaction gives the final *stable* product $RN : CR_2$ or $(RNH)_2 : CR_2$ by elimination of the elements of water.

Aniline, under the same careful manipulation at low temperature, yields only the secondary product of the reaction, ethyl dianilinomalonate, $(C_6H_5NH)_2 : C : (CO_2C_2H_5)_2$. The intermediate hypothetical addition product $C_6H_5NH.C.(OH) : (COOC_2H_5)_2$ appears too unstable, or too reactive to be separated out even at —15°, and instantly reacts with the aniline as it is added, in preference to the keto group of the ester, and gives the final stable dianilinomalonate. This is in marked contrast to the corresponding reaction of aniline with methyl oxomalonate,[1] where the addition product methyl anilinotartronate, $C_6H_5NH.C.(OH) : (CO_2.CH_3)_2$, was obtained as a comparatively stable compound. This, however, easily reacts further with aniline and yields methyl dianilinomalonate, $(C_6H_5NH)_2 = C = (CO_2CH_3)_2$.

Benzylamine reacts at —15° with ethyl oxomalonate with loss of color. A colorless, thick syrup results. When this primary addition product is heated it loses the elements of water.

Methyl, ethyl and benzyl alcohols in molecular quantities react with the keto ester. These products are thick, colorless syrups which, like the addition products with the methyl ester, dissociate into the original constituents when heated. They cannot be crystallized or distilled. All these experiments were carried out with thorough exclusion of moisture.

Experimental.

Ethyl Orthotoluidinotartronate.—3.2 grams of orthotoluidine were slowly mixed at —15°, with 5.9 grams of the keto ester (mol. quantities). The temperature rose about 60° while the color soon disappeared. The thick clear liquid soon crystallized. It was purified by recrystallization from ethyl alcohol, and melted without decomposition at 92°.

Calculated for $(CH_3)C_6H_4NH.C.(OH) : (CO_2C_2H_5)_2$: C, 59.75; H, 6.81; N, 4.97
Found: C, 59.63 H, 6.67; N, 4.79

Ethyl orthotoluidinotartronate crystallizes in balls of radiating needles. It is easily soluble in ether, chloroform, carbon tetrachloride, carbon disulfide, benzene, and hot ethyl alcohol, and slightly soluble in ligroin and cold alcohol.

Ethyl Paratoluidinotartronate.—3.9 grams of paratoluidine dissolved in 8 cc. of dry ether were slowly mixed with 6.34 grams (1 mol.) of the

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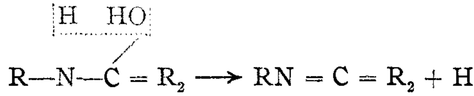
[1] To appear in THIS JOURNAL.

keto ester chilled to —13°. A vigorous reaction took place, heat was evolved, and the color rapidly faded. The mixture had completely solidified in five minutes. The product was recrystallized from absolute alcohol, and analyzed.

Calculated for $(CH_3)C_6H_4NH.C.(OH):(CO_2C_2H_5)_2$: C, 59.75; H, 6.81; N, 4.97.
Found: C, 59.74; H, 6.78; N, 4.96.

Ethyl paratoluidinotartronate is a colorless substance crystallizing in bunches of radiating needles with a melting point of 95°. It is easily soluble in ether, chloroform, carbon tetrachloride, carbon disulfide, benzene, and hot ethyl alcohol. It is slightly soluble in cold alcohol, and ligroin.

These para- and orthotoluidinotartronates, considered as the primary addition product of an amine upon a keto group, might be expected to lose water readily and give the $N=C$ double bond, which is typical of the usual final reaction product of a substituted amine upon ketone and aldehyde groups  $R—\overset{H}{N}—\overset{HO}{C} = R_2 \longrightarrow RN = C = R_2 + H_2O$ (oximes, hydrazones, etc.). This we have found to be the case with such derivatives of methyl oxomalonate.[1] In order to obtain the final product, $RN=C=(CO_2C_2H_5)_2$, from these tartronates we have used dehydrating agents to remove the elements of water.

The two toluidinotartronates described above changed but slightly during two months over sulfuric acid, only a few yellow spots appearing. Methyl anilinotartronate soon changes to the yellow iminomalonate under these conditions. These para- and orthotoluidinotartronates were mixed with phosphorus pentoxide in the proportion of one molecule of the former to four of the latter. The mixtures were heated slowly up to 150° during an hour. Although a yellow color was given to the mixture, the product when extracted with ether proved to be chiefly the unchanged tartronates.

Attempts to distil ethyl paratoluidinotartronate with phosphorus pentoxide were made. The substances were mixed, with the latter in excess. After standing three weeks the mixture was dark yellow and sticky. Distillation in a vacuum gave no satisfactory products.

The following experiments yielded better results. 0.4 gram of phosphorus pentoxide (about 3 molecules) was added to 1 gram of ethyl paratoluidinotartronate dissolved in 10 cc. of dry ether. The gummy material above the phosphoric acid residue had a greenish yellow tinge. A thick greenish oil was obtained from the ethereal solution. This could not be made to crystallize. Its properties are similar to those of methyl phenyliminomalonate,[2] $C_6H_5N = C = (CO_2CH_3)_2$. Exposed to

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[1] Curtiss and Spencer, This Journal, 31, 1057.

[2] *Ibid.*

the air it absorbs moisture, slowly losing color and the glycerol-like product soon crystallizes in radiating needles. The properties of this substance show it to be the addition product of water on the N=C double bond in $(H_3C)C_6H_4N=C=(CO_2C_2H_5)_2$, regenerating ethyl paratoluidinotartronate. Dry aniline was added to this greenish-yellow oil, much heat was evolved, the color of the oil disappeared immediately and the mass soon crystallized. This also suggests the presence of the N=C double bond. The substance has not been further studied owing to lack of time.

Phosphorus trichloride reacts with ethyl paratoluidinotartronate, as shown by the production of heat and a *yellow* color. After heating the mixture, ether removes a yellow compound which turns white in the air and liberates a gas (HCl?). Its aqueous solution produces an emulsion of paratoluidine when potassium carbonate is added. Phosphorus trichloride has here apparently acted as a dehydrating agent. The resulting ethyl paratoluyliminomalonate $(CH_3)C_6H_4N=C=(CO_2C_2H_5)_2$ is apparently broken up by aqueous alkalies into toluidine and ethyl mesoxalate. This is in perfect analogy with the reaction of water on methyl phenyliminomalonate.[1]

Action of Acetic Anhydride upon Ethyl Paratoluidinotartronate.—1.5 grams of acetic anhydride were slowly added to 3 grams of the tartronate. Reaction takes place with the evolution of heat and the appearance of a deep *yellow* color. The mass solidifies in a short time. Its ethereal solution was shaken in a separatory funnel with a 1 per cent. sodium hydroxide solution, then washed, and dried over calcium chloride, and the ether evaporated. The product was recrystallized from benzene and melted at 150°. Thus prepared it was analyzed.

Calculated for $(CH_3)C_6H_4NH.(CH_3CO_2):C:(CO_2C_2H_5)_2$:

	C	H	N
Calculated	59.45:	6.50;	4.34.
Found:	59.66, 59.42;	6.71, 6.82;	4.37, 4.42.

Ethyl acetylparatoluidinotartronate crystallizes in beautiful needles, with satin luster. It is easily soluble in ether, chloroform, carbon disulfide, hot benzene, and hot alcohol, slightly soluble in cold benzene, ligroin, and ethyl alcohol. The acetyl group in this compound may be either upon the oxygen or upon the nitrogen. As this experimental work was done by Mr. Lewis towards the close of the semester some of these products have not been completely studied.

Action of Metatoluidine upon Ethyl Oxomalonate.—0.6 gram of metatoluidine was slowly added to 1 gram of the keto ester (molecular quantities). This caused a rise of about 25° in temperature, loss of color, and the production of a thick honey-like oil. We did not succeed in

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[1] To appear in THIS JOURNAL.

crystallizing this substance nor purifying it by fractional distillation. The analysis was therefore not made.

Benzylamine upon Ethyl Oxomalonate.—Molecular quantities of these substances were mixed at —13°. Much heat was produced by the reaction and the color quickly changed to a pale yellow. The product was of a glycerol-like consistency, and was turbid, due to the presence of water separated in the reaction. This shows that with this amine the secondary stage in the reaction occurs, in which the elements of water are eliminated. The product could not be distilled and therefore was not analyzed.

Action of Aniline upon Ethyl Oxomalonate.—5.19 grams of aniline in an equal quantity of sodium dry ether were slowly dropped into 9.7 grams of the keto ester (molecular quantities). The mixture was made at —13°. The two liquids reacted intensely with the evolution of much heat. A colorless glycerol-like liquid resulted which crystallized in balls of radiating needles. The product was recrystallized from 50 per cent. alcohol and had a melting point of 117°. The analysis follows:

Calculated for $(C_6H_5NH)_2 = C = (CO_2C_2H_5)_2$: C, 66.62; H, 6.49; N, 8.18.
Found: C, 66.94; H, 6.71; N, 8.08.

This reaction was several times repeated but ethyl dianilinomalonate was the only product separated.[1]

Ethyl dianilinomalonate is a white crystallin compound, easily soluble in chloroform, acetone, carbon tetrachloride, benzene, hot methyl alcohol, and ligroin. It is fairly soluble in cold methyl alcohol, ligroin, and water. This product is identical with that prepared by one of us by the action of aniline on ethyl dihydroxymalonate,[2] and also on ethyl dibromomalonate.[3]

Action of Alcohols upon Ethyl Oxomalonate.—0.26 gram of absolute ethyl alcohol was added at —13° to 1 gram of ethyl oxomalonate (molecular quantities). This caused an elevation of temperature of 50°, a rapid loss of color, and the production of a thick glycerol-like oil. It does not crystallize when cooled to —50°. Attempts at distillation caused a dissociation into the original constituents as indicated in the return of the color of the ketone, and the condensation of alcohol in the upper part of the tube. These reassociate on cooling and the color is again lost. This is in perfect analogy with ethyl dihydroxymalonate where the dissocia-

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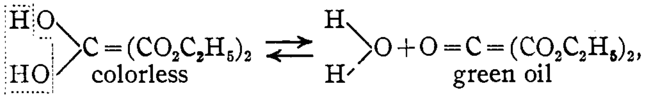
[1] Mr. Paul S. Burgess, working in this laboratory, has obtained evidence of the existence of the intermediate addition product of aniline upon ethyloxomalonate, $C_6H_5NH.C:(OH) = (CO_2C_2H_5)_2$. It appears to be unstable and a very reactive substance, so much so that after many experiments at low temperature and high dilutions of the reagents, we have been unable as yet to obtain it in a pure form.

[2] Curtiss, *Am. Chem J.*, 35, 355.

[3] *Ibid.*, 19, 695.

tion into water and the green keto ester takes place around 60°–70°



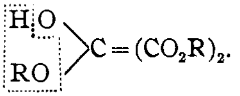
$$\left.\begin{array}{l}\mathrm{H\,O}\\ \mathrm{HO}\end{array}\right\rangle \underset{\text{colorless}}{C=(CO_2C_2H_5)_2} \rightleftarrows \left.\begin{array}{l}\mathrm{H}\\ \mathrm{H}\end{array}\right\rangle O + \underset{\text{green oil}}{O=C=(CO_2C_2H_5)_2},$$

and reassociation with loss of color occurs a few degrees lower.

Methyl alcohol was mixed in molecular proportions with the ethyl keto ester at —15° and behaved in every way like ethyl alcohol under these conditions. Attempts to purify the thick, colorless syrup by crystallization and distillation failed for the same reasons as mentioned above.

Molecular quantities of benzyl alcohol were likewise mixed at —13° with ethyl oxomalonate. Here also, there was an intense reaction indicated by the evolution of considerable heat and the gradual loss of color of the mixture. The thick oil likewise dissociated when heated into its constituent parts, nor could it be crystallized.

The very characteristic appearance of the reactions, as well as the products, in these keto ester condensations with alcohols leaves no doubt in our minds that these unstable compounds are the primary addition products of the alcohol upon the keto group. $ROH + O=C=(CO_2R)_2 \longrightarrow$



$$\left.\begin{array}{l}\mathrm{H\,O}\\ \mathrm{RO}\end{array}\right\rangle C=(CO_2R)_2.$$

They are perfectly analogous to the product formed by ethyl alcohol on methyl oxomalonate. This was obtained first as a colorless glycerol-like syrup, then in the crystallin state, and was readily dissociated, with reappearance of color, into alcohol and methyl oxomalonate when gently heated.[1]

URBANA, ILL.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE STEREOCHEMICAL CONFIGURATIONS OF THE SUGARS FUCOSE AND RHODEOSE.[2]

BY C. S. HUDSON.

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From the fact that certain varieties of kelp (*Fucus*) yield methylfurfural when distilled with acid, Bieler and Tollens[3] concluded that a methylpentosan is present in these plants. Günther and Tollens[4] hydrolyzed kelp with dilute acid and obtained from it by way of the hydrazone a crystallin sugar which they named *fucose*. Analysis proved it to be a methyl pentose, $CH_3.C_5H_9O_5$, and Laniewsky and Tollens[5] found its

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[1] Curtiss and Spencer, THIS JOURNAL, **31**, 1055.

[2] Read at the Minneapolis meeting of the American Chemical Society.

[3] *Ber.*, **22**, 3062; *Ann.*, **258**, 110 (1889); cf. Maquenne, *Compt. rend.*, **109**, 603–6 (1889).

[4] *Ber.*, **23**, 2585–6 (1890).

[5] *Ber.*, **33**, 141 (1900).