Calculated for $C_{34}H_{20}O_6N_6$: N, 13.81.
Found: N, 14.0.

It melts at 207°. Boiled with hydrochloric acid, it turns white but does not dissolve.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY.

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

PSEUDO ACID ESTERS IN THE MESOXALIC ESTER SYNTHESIS.[1]

BY RICHARD SYDNEY CURTISS AND JOHN ANTON KOSTALEK.

Received March 25, 1911.

In a synthesis of mesoxalic esters which was discovered by one of us and reported in the *American Chemical Journal*,[2] the red oxides of nitrogen were allowed to act an malonic ester at —10°. The ethyl mesoxalate produced was removed by distillation and the residual oil was found to contain a high percentage of nitrogenous esters, having acid properties, and which produced with alcoholic potash a yellow salt. The analysis showed this salt to contain a percentage of potassium according well with that of the salt of ethyl isonitrosomalonate, $K\text{–}O\text{–}N=C=(CO_2C_2H_5)_2$, and it was at first supposed to be this compound. Isonitrosomalonic acid was made by Baeyer,[3] who found that its aqueous solution decomposes at 40° into hydrocyanic acid, carbon dioxide, and water. Conrad and Bischoff[4] confirm this result.

It was noticed at that time that no odor of prussic acid was apparent when the yellow potassium salt was boiled with alkali to saponify the ester, and subsequently heated with hydrochloric acid to liberate and decompose the isonitrosomalonic acid. The results of the test were therefore not in accordance with this characteristic of the potassium salt of isonitrosomalonic acid. The complete analysis of this salt, later, showed that it was not a derivative of ethyl isonitrosomalonate, and we wish therefore to correct the statements made in the former paper[5] concerning the identity of this salt, and in accordance with the results herein presented.

This investigation was begun by the senior author, and Mr. Ruric Creegan Roarke, to whom we owe much for the initial experiments and attempts in separating and studying the potassium salts of ethyl nitromalonate and ethyl dinitroacetate. Our primary idea was the study

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[1] Abstract of a thesis presented by Mr. Kostalek to the Graduate School of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

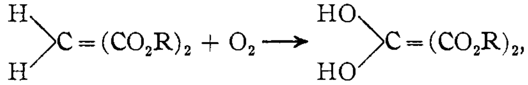
[2] Curtiss, *Am. Chem. J.*, 35, 477.

[3] *Ann.*, 131, 293.

[4] *Ibid.*, 209, 211.

[5] *Ibid.*, 35, 478, 482, 483.

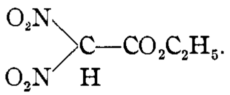
of the mechanism of the reactions which take place in the mesoxalic ester synthesis when malonic esters are treated with "nitrous anhydride." The oxidation of the methylene hydrogen atoms of ethyl malonate to hydroxyl groups,



$$\begin{matrix}H\\H\end{matrix}\!\!>C=(CO_2R)_2 + O_2 \longrightarrow \begin{matrix}HO\\HO\end{matrix}\!\!>C=(CO_2R)_2,$$

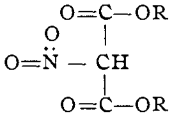
yielding ethyl dihydroxymalonate appears very simple, but the investigation has shown that a number of other products are formed which contain nitrogen attached to the methylene carbon, and some of these have acid properties. It was further found that there was a direct relation between the amount of mesoxalic ester produced and the yield of these nitrogenous esters, and that the yield of the former varied inversely with the amount of the latter present. Some of these nitrogenous derivatives are quite unstable, and undergo sudden, and at times almost explosive decomposition, during the process of distillation *in vacuo*, which is used to separate the mesoxalic ester. These facts led us to believe that they might be the intermediate compounds, in this synthesis, from which mesoxalic ester was obtained by elimination of the groups containing nitrogen. This idea was confirmed when it was found that the yield of ethyl oxomalonate, $OC=(CO_2C_2H_5)_2$, was decidedly increased when the "crude oil," obtained by the action of the red oxides of nitrogen on ethyl malonate, was directly distilled *in vacuo*, whereas the yield of the nitrogenous esters was increased, and less of the mesoxalate obtained, when they were separated by extraction with water. In this treatment of the "crude oil" with water the mesoxalic ester goes into the water and may be recovered by extraction with ether, while the nitrogenous ester derivatives remain undissolved. When the latter are distilled *in vacuo*, partial decomposition takes place yielding much nitrogen and nitric oxide, nitrogen peroxide, carbon dioxide, alcohol and other organic products.

In investigating these acid esters containing nitrogen we have separated, by means of their potassium salts, two oils having acid properties. They have been identified as ethyl nitromalonate, $O_2N-\underset{H}{C}=(CO_2C_2H_5)_2$, and ethyl dinitroacetate,

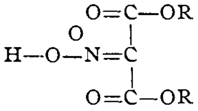


$$\begin{matrix}O_2N\\O_2N\end{matrix}\!\!>\underset{H}{C}-CO_2C_2H_5.$$

The separation of these two potassium salts has been slow and difficult, owing to their instability, the slight difference in their solubilities, and the fact that they are readily decomposed when their solutions are heated, and often explode in the combustion tube when burned. We have prepared the pure potassium salt of each of the above pseudo acids as well as some of the salts with ammonia, hydrazine, aniline, sodium and silver. All of these occur in the colored form. From the pure potassium salts we have regenerated the pseudo acids and analyzed them. A peculiar interest attaches to these acid oils inasmuch as they are colorless, but yield colored alkali salts. Some of these salts exist in two forms, the colorless, the yellow, or the red. These interesting facts of color were investigated by Hantzsch and formed a part of his celebrated work upon the "pseudo acids"[1] and "chromo-isomers." He explains the appearance of color in the potassium salt of ethyl nitromalonate, $O_2N—\underset{H}{C} = (CO_2C_2H_5)_2$, by a molecular rearrangement of the pseudo acid into the "aci" form,

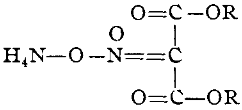


Pseudo acid, colorless.

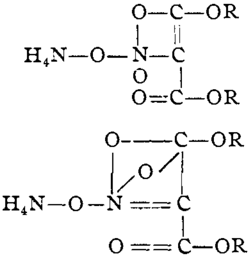


Leuco "Aci" form, colorless.

and as the nitro group is not a chromophore[2] it becomes so only when interacting with an adjacent carbonyl, or nitro group,[3] as illustrated below. The possibility of such colored or "chromo" isomers is here shown, with the ammonium salt of ethyl nitromalonate,[4] which we have made in both the leuco and colored forms:



Leuco form.



Chromo forms.

The salts of the "aci" derivatives of this, the "nitroketone," type[5] are not as highly colored as the salts of the "aci" dinitroparaffin type, and only in a very few cases are the two colored modifications, the red and the yellow, known. The "aci" derivatives of the first-named series can, in most cases, be easily obtained in the leuco form. Thus, ammonium ethyl nitromalonate, $H_4NO.ON = C(COOC_2H_5)_2$, can be obtained in the leuco form by recrystallization of the yellow chromo form from absolute alcohol. Dissolved in water, hot or cold, or in absolute alcohol, the leuco ammonium ethyl nitromalonate yields a yellow solution, indicating that in solution the leuco ion is not stable and changes into the chromo ion, but may be deposited in the leuco form as it separates out.

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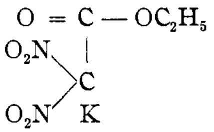
[1] *Ber.*, 32, 578, 579, 583; 35, 1001; 40, 1523.

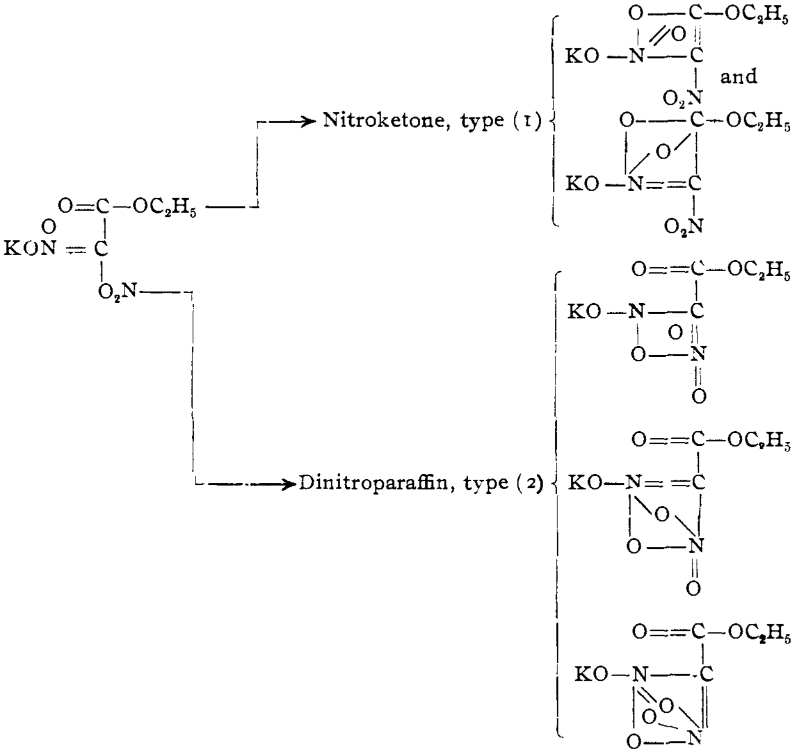
[2] *Ibid.*, 39, 1084, 1096.

[3] *Ibid.*, 32, 578, 610, 626; 39, 3156; 40, 1533.

[4] See Hantzsch, *Ber.*, 40, 1523.

[5] *Ibid.*, 40, 1535, 1536.

In potassium ethyl dinitroacetate,  , with two nitro groups and a carbonyl group linked to the same carbon atom, both the nitroketone type and "aci" dinitroparaffin type[1] of rearrangement, suggested by Hantzsch, are possible, five colored isomers in all.



Two of these forms only are known: the yellow, more stable form, probably of type (1), and the red form probably of type (2) which is known only in solution. The cold aqueous solution of the yellow form is likewise yellow, but changes to red when heated, and again reverts to the original color when cooled. The two forms exist in solution as an equilibrium mixture, the amount of each varying with the temperature. The changing color indicates change of structure. The solution in absolute alcohol remains yellow even when heated to boiling.

Experimental.

Preparation of the Pseudo Acid Oils by the Action of Nitrogen Oxides

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[1] *Ber.*, 40, 1535, 1536.

on Ethyl Malonate.—These oils were prepared according to the method used by Curtiss,[1] with some slight modifications.

A stream of nitrogen oxides, prepared by the action of nitric acid, sp. gr. 1.42, on arsenious oxide, was passed into 50 cc. of malonic ester kept at —10° to —15°. In twenty minutes the mass had increased 88 grams in weight. It was then packed in ice and allowed to warm slowly, over a period of seventeen hours, to room temperature. The color of the solution had changed from dark blue to a light emerald-green. A current of air was passed through it for twenty minutes, with but very little loss of dissolved gases. The solution was then placed in a freezing mixture and on shaking an abundant crystallization of ethyl dihydroxymalonate took place. These crystals were filtered off and found to weigh 23 grams.

The filtrate, a thick, light green oil, possessed a very pungent odor and was very irritating to the eyes. It was washed twice with 100 cc. of water at 0°. The aqueous wash removed the substance possessing the pungent odor almost completely. The oil was then dissolved in 25 cc. of ether, and dried over anhydrous sodium sulfate for two hours. After evaporating the ether over sulfuric acid in a vacuum desiccator, 23 grams of a light greenish oil of a high specific gravity remained. This oil consists of a mixture of esters containing nitrogen and having acid properties. Colored alkali salts were made from it, in general according to the method described by Curtiss[2] and Roarke.[3]

Potassium Salts of the Acid Oils.—Twenty grams of the acid oils, prepared as described above, were dissolved in 125 cc. of absolute alcohol, cooled to —10° and 46 cc. of absolute alcoholic potash (0.14 gram of potassium hydroxide per cc.) were added drop by drop by means of a separatory funnel. The first drop of alcoholic potash precipitated a yellow crystallin salt. A large amount of heat was liberated in this reaction, and if, by insufficient shaking, the temperature was allowed to rise, the potassium salt was precipitated in the form of a gummy mass very difficult of purification. The salt was filtered off and washed with absolute alcohol to remove the excess of alkali or any unchanged oils, and dried in a vacuum desiccator. Nineteen grams of a yellow salt were thus obtained. This product is a mixture composed chiefly of the salts of ethyl dinitroacetate and ethyl nitromalonate.

In the preparation of these potassium salts of the "crude acid oil," the first few drops of alcoholic potash, in some cases, produced a deep red coloration, which would suddenly disappear and the precipitation of the yellow potassium salts immediately follow. This coloration is perhaps due to the temporary formation of the red modifications of ethyl dinitroacetate

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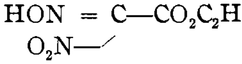
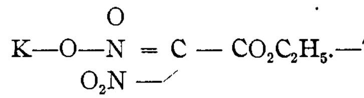
[1] *Am. Chem. J.*, 35, 478.

[2] *Ibid.*

[3] Thesis for the degree of M. A. in Chemistry, University of Illinois, 1908, p. 5.

and potassium ethyl nitromalonate, or it may indicate the presence of ethyl nitrolic acetate[1]  $\begin{array}{l}\text{HON} = \text{C—CO}_2\text{C}_2\text{H}_5\\ \qquad\ \ \text{O}_2\text{N—}\diagup\end{array}$. This compound gives a red color in alkaline solutions as do all nitrolic acids. Being unstable, and easily decomposed by water, the red color is soon lost.

Separation of the Potassium Salts of the Acid Oils; Potassium Ethyl Dinitroacetate,  $\begin{array}{l}\text{K—O—}\overset{\text{O}}{\text{N}} = \text{C — CO}_2\text{C}_2\text{H}_5\\ \qquad\quad\ \ \text{O}_2\text{N —}\diagup\end{array}$.—Thirty-three grams of the crude, yellow potassium salts, prepared as just described, were dissolved in 60 cc. of hot water. The solution was deep red when hot, becoming greenish yellow when cold. When cooled the potassium salts crystallized out in the form of greenish yellow needles. These were filtered off, washed with 15 cc. of absolute alcohol and 5 cc. of ether. Yield, 17 grams. Decomposing point, 190°. This was mostly potassium ethyl dinitroacetate. On recrystallizing it three times from hot 95 per cent. alcohol, it was obtained in the form of greenish yellow, almost colorless needles, with a constant decomposing point of 194–195°, when immersed in the bath at 180°. It was finely powdered, dried over sulfuric acid in a vacuum desiccator and analyzed.

	K	H	N	C
Calculated for $C_4H_5N_2O_6K$:	K, 18.05	H, 2.31	N, 12.96	C, 22.22.
Found:	K, 18.06, 18.01;	H, 2.70, 2.65;	N, 13.24, 12.96;	C, 22.62, 22.52.

Curtiss and Roarke[2] determined the molecular weight of this salt by the boiling-point method, using acetone as a solvent, and by the freezing-point method, using water as a solvent. These determinations show that it is unimolecular and is ionized in water solutions.

(*a*) By the freezing-point method, using water as a solvent, the results were as follows:

	s. Gram.	S. Gram.	*d.*	Mol wt.
I	0.2009	44.89	0.0800	103.5
II	0.5017	44.89	0.1830	112.9
III	0.7097	44.89	0.2500	116.9

(*b*) By the boiling-point method, using acetone as a solvent, the results were as follows:

	s. Gram.	S. Gram.	*r.*	Mol. wt.
I	0.1856	15.72	0.0800	246.4
II	0.4427	15.72	0.2100	224.0
III	0.6000	15.72	0.2600	245.1

Calculated molecular weight of $C_4H_5O_6N_2K$, 266.2. The crystals of the pure potassium salt are a very pale greenish yellow and are in the form of fine monoclinic prisms. It sometimes separates out

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[1] *Ber.*, 28, 1215.

[2] R. C. Roarke, Master's Thesis, University of Illinois, 1908, p. 10.

from an aqueous solution in glistening yellow plates, but when recrystallized again changes to needles. It is apparently dimorphous. Sunlight changes the salt to a darker shade of yellow. The salt suddenly explodes with purple flame when heated on a platinum spatula, or in a test tube. A hot aqueous solution of this salt is red but becomes yellow on cooling, suggesting an internal rearrangement. The above results identify this salt as that of ethyl aci-dinitroacetate, made by Bouveault and Wahl.[1]

Reduction of Potassium Ethyl Dinitroacetate.—Potassium ethyl dinitroacetate was submitted to the reducing action of dilute hydrochloric acid and granulated tin. The reaction mixture was extracted with ether and a heavy yellow viscous oil was obtained. This oil reduced Fehling's solution. With concentrated sulfuric acid and an aqueous solution of egg albumen,[2] it yielded a pink-purple solution, indicating the presence of glyoxylic acid. The aqueous extract was treated with hydrogen sulfide to remove the dissolved tin. The residue, obtained by evaporation of the aqueous filtrate, when heated with potassium hydroxide, showed the presence of ammonium salts. No hydroxylamine or hydrazine was found in the residue. The two nitro groups in the ester are here eliminated as ammonia and are replaced by oxygen, yielding glyoxylic ester.

The salt was reduced with 2 per cent. sodium amalgam in the proportion to furnish four atoms of hydrogen for one molecule of the salt. The reaction was carried out at 0°, in an aqueous solution. One-half of the hydrogen was absorbed rapidly with no smell of ammonia apparent. After this, further addition of amalgam changed the yellowish green solution momentarily red (ethyl nitrolic acetate?). An ether extract of the solution yielded a small amount of a spicy oil, which exploded violently when heated. The green aqueous solution freed of ether-soluble products suddenly became colorless, when the reduction was carried further and nitrogen was then eliminated as shown by an ammonia-like odor. The attempts to establish the presence of intermediate reduction products was not carried further.

Action of Alkyl Halides on Potassium Ethyl Dinitroacetate.—Potassium ethyl dinitroacetate does not react with ethyl or methyl iodide in the presence of 95 per cent. alcohol, or absolute alcohol, to any appreciable extent, even if heated in a sealed tube to 145° to 150°. In the presence of 50 per cent. alcohol a reaction did take place. Equimolecular quantities of potassium ethyl dinitroacetate and methyl as well as ethyl iodide were heated with 50 per cent. alcohol in a sealed tube for one hour at 100° to 110°. A yellow viscous oil was obtained by extraction of the reaction mixture with ether, which did not crystallize. This oil was formed to the extent of 20 per cent. of the potassium salt used. It was not further

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[1] *Compt. rend.*, 136, 159.

[2] Hopkins and Cole reaction.

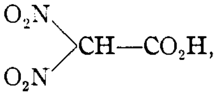
studied, because of the ease with which it decomposed when any attempt was made to purify it.

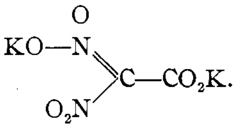
Potassium ethyl dinitroacetate reacted more readily with ethyl sulfate than with alkyl halides.

Molecular quantities of these substances were heated for thirty minutes in a sealed tube to 100°–110 with 50 per cent. alcohol. Potassium sulfate and potassium nitrite were formed in the reaction. On extraction with ether a 50 per cent. yield of heavy oil was obtained. It did not crystallize and on distillation under diminished pressure it was found to be a mixture of oils, which were not further studied because of lack of time.

The stability of this salt toward alkylation was further shown by Mr. Roarke who found that it could be boiled for several hours with benzyl chloride in a solution of 50 per cent. alcohol with no apparent change.

Saponification of Potassium Ethyl Dinitroacetate.—Three grams of this (1 mol.) were boiled for half an hour with a solution of potassium hydroxide (2 mols.) in 98 per cent. alcohol. The product was washed with hot alcohol and dried over sulfuric acid. 2.3 grams of a brilliant chrome yellow salt were obtained and recrystallized from 75 per cent. alcohol. It exploded very violently at 210°, often blowing the melting-point tube through the bottom of the flask.

The free acid was obtained from 2 grams of this salt by suspending it in 6 cc. of water and 15 cc. of ether and slowly dropping into it 14 cc. of 2 *N* sulfuric acid. It was kept at —13° and thoroughly agitated during the operation. A continuous evolution of carbon dioxide occurred until one-third of the acid had been run in. The washed ethereal solution was evaporated over sulfuric acid in a vacuum desiccator for twelve hours. An extremely unstable, limpid, yellow oil remained (0.6 g.). When taken from the vacuum which had been maintained over night it immediately began to give off a gas and to heat rapidly. It was at once replaced in the desiccator and evacuated. The reaction ceased. When air was again admitted to it a half hour later it instantly exploded with great violence, with a flash of flame followed by a dense cloud of vapors of the red oxides of nitrogen. We did not make a combustion with it. From the method of making it, and from its properties we suppose it to be dinitroacetic acid,  $\begin{matrix}O_2N\\O_2N\end{matrix}\!\!>CH{-}CO_2H$, and the explosive chrome yellow salt, probably one of the chromo isomers of dipotassium aci-dinitroacetate,



$$\begin{matrix}KO{-}\overset{O}{N}\\O_2N\end{matrix}\!\!>C{-}CO_2K.$$

Ethyl Dinitroacetate.—The free pseudo acid ester was obtained from its potassium salt as follows: 6.2 grams of the salt were powdered and suspended in 100 cc. of water and 10 cc. of ether. The theoretical amount of normal sulfuric acid was slowly dropped into it while it was agitated and kept below 0°. The ethereal solution containing the acid ester was washed with water, sodium carbonate, and again with water, to remove sulfuric acid, and dried over calcium chloride. The ether was evaporated in a vacuum desiccator and a limpid, nearly colorless oil remained. It smelled like willow and when treated with an alcoholic potassium hydroxide solution regenerates the original potassium salt from which it was made, m. p. 196–197°.

The purified oil stains the skin and nails yellow like strong nitric acid. While it is itself practically *colorless* and scarcely soluble in water, one drop of it will impart to several liters of water a decided *yellowish green* color. It slowly decomposes in the sunlight, giving off red oxides of nitrogen and nitric oxide. The free colorless acid ester thus made appears to be the leuco form of the pseudo acid, or its "aci form," which is slowly molecularly rearranged into one or more of the five chromo forms when acted on by water, but much more rapidly and intensely if a little alkali is present (see p. 965).

Salts.—When dry ammonia is passed through an ethereal solution of this acid oil an immediate precipitation occurs of a pale yellow ammonium salt. This salt is unstable. It is soluble in water with decomposition. It dissociates, giving ammonia gas, when boiled in absolute alcohol. By quick solution and cooling, the melting point was raised to 168–169°. The analysis showed it to be impure, however. When placed in a desiccator over caustic potash it slowly dissociates, and coats the sticks of alkali with a yellow film.

A beautiful silver salt may be obtained in yellowish green hexagonal plates by precipitating a concentrated solution of the potassium salt with a concentrated solution of silver nitrate. This silver salt is unstable and is reduced to metallic silver when heated or allowed to stand in the light for some time, or when its aqueous solution is warmed. The crystals melt around 160°.

Beautiful yellow crystallin salts were also formed with ethyl dinitroacetate and aniline, as well as hydrazine.

Potassium Ethyl Nitromalonate.—This potassium salt is contained in the crude potassium salts above mentioned and was obtained by evaporating the aqueous mother liquor from the potassium ethyl dinitroacetate (p. 967) to one-half volume. The crystals thus separated were filtered, washed with alcohol, and further purified by recrystallization from 95 per cent. alcohol. A constant melting point of 145–146° was obtained, but an analysis showed the salt to be impure. Seven grams of this salt were recrystallized four times from absolute alcohol. Three grams were thus obtained which melted at 154°. It was dried in a vacuum over sulfuric acid and analyzed.

Calculated for $C_7H_{10}NO_6K$: K, 16.04 ; N, 5.76 ; C, 34.52 ; H, 4.12.
Found: K, 16.02, 15.76; N, 6.02, 6.09; C, 34.47, 34.80; H, 4.09, 4.19.

A molecular weight determination on this salt in boiling acetone was made by Mr. Roarke but it did not give a constant value. It indicated some association, increasing with the concentration. The melting point of the salt recovered from the solvent showed that some decomposition had occurred.

	s. Gram.	S. Grams.	*r*.	Mol. wt.	Theory for $C_7H_{10}NO_6K$.
I.	0.3143	13.28	0.1340	294.9	205
II.	0.5535	13.28	0.1940	358.8	
III.	0.7865	13.28	0.2350	420.8	

Potassium ethyl nitromalonate crystallizes in bundles of needles or in beautiful hexagonal prisms of a dark canary-yellow color. Hantzsch[1] has obtained this salt in a pure white form by precipitating a solution of the colorless form of the ammonium salt, with potassium carbonate. It is extremely soluble in water, hot acetone, and hot 95 per cent. alcohol. It is fairly soluble in absolute alcohol, acetone, hot ethyl acetate, and methyl alcohol. It is insoluble in benzene, ligroin, carbon tetrachloride, chloroform, ether, and nearly so in cold ethyl acetate.

Ethyl Nitromalonate from its Potassium Salt.—15 grams of finely powdered potassium ethyl nitromalonate were suspended in 15 cc. of ether and 10 cc. of water. The mixture was chilled in ice water and the theoretic amount, 3.24 grams of sulfuric acid in 50 cc. of water, was slowly dropped into it while the solution was continually shaken to remove the free aci-ester from the aqueous solution as fast as it was formed. The ethereal extract containing the acid oil was thoroughly washed with water, then with a little sodium carbonate solution, which imparts to the nearly colorless ethereal extract a golden yellow color. This coloration was due to the formation of a chromo form of the sodium salt of ethyl aci-nitromalonate. It was again washed with water and dried over anhydrous sodium sulfate for twelve hours. The ether was evaporated in a vacuum desiccator at diminished pressure. The nearly colorless oil which remained was immediately distilled *in vacuo*. The first fraction consisted of 0.5 g. of a colorless oil which boiled from 60°-145° at 33 mm. pressure. The chief product was in the second fraction, 6.5 g. of a colorless oil which boiled at 145-150.5° at the same pressure. The residue consisted of a small amount of yellow oil remaining in the flask.

Fraction two was redistilled and collected in the following fractions, all of which were colorless.

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[1] *Ber.*, 40, 1528.

Fraction No.	Boiling point.	Pressure.	Yield. Gram.
1	140–152°	37–38	1.5
2	152–153°	37–38	2.5
3	154–156.5°	37–38	1.4

A slight residue of yellow oil remained in the flask.

An analysis was made upon the oil of the second fraction with the following results:

Calculated for $O_2N—CH:(CO_2C_2H_5)_2$: C, 40.97 ; H, 5.36; N, 6.82.
Found: C, 41.45, 41.60; H, 5.87; N, 6.81, 6.85.

The product is a clear colorless liquid heavier than water, and possessing a fruit-like odor. While it is itself colorless and insoluble in water as such, a minute quantity of the oil will impart a yellowish green tinge to a large quantity of water. This is due to the molecular rearrangement of the pseudo-acid into a chromo-aci form.[1]

The Ammonium Salt of Ethyl Nitromalonate.—1.17 g. of the ethyl nitromalonate from fraction 2 in the last distillation were dissolved in 20 cc. of ether, and dry ammonia gas passed into it at —10°. An immediate precipitation of a light yellow salt was obtained, which weighed 1 gram. This was filtered off and washed with dry ether and twice recrystallized from hot absolute alcohol. This salt is unstable and ammonia dissociates from it when boiled with alcohol. The recrystallized product consisted of pale yellow, prismatic crystals and melted at 151°. Nitrogen was determined as follows:

Calculated for $NH_4O - \overset{O}{N} = C = (CO_2C_2H_5)_2$: N, 12.61. Found: 12.77.

A pure white sample of ammonium ethyl nitromalonate was obtained by recrystallizing the yellow salt, obtained as above, from its solution in cold absolute alcohol, by the addition of two volumes of ether. The colorless crystals are in the form of long needles that melt from 151.5–152°. This process of purification eliminates the decomposition that takes place when it is recrystallized from hot alcohol. The product was analyzed:

Calculated for $H_4NO—\overset{O}{N}=C=(CO_2C_2H_5)_2$: N, 12.61. Found: 12.80.

The ammonium salt decomposed when allowed to stand over sulfuric acid in a vacuum desiccator. The pure white salt dissolves in absolute alcohol or in water, to form a *yellow* solution. The color change is here due to a molecular rearrangement of the colorless salt to one of the isomeric chromo forms. The properties of the acid oil and its salts are here shown to be such as to prove their identity with ethyl nitromalonate and its salts.[2]

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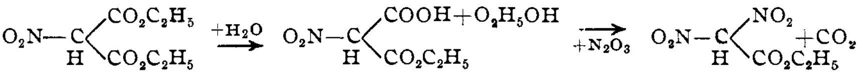
[1] Hantzsch, *Ber.*, 40, 1533.

[2] *Ibid.*, 40, 1528; Wohl, *Compt. rend.*, 132, 1052; Franchimont and Klobbie, *Rec. trav. chim.*, 8, 283.

Action of Red Oxides of Nitrogen on Ethyl Nitromalonate.—The red oxides of nitrogen prepared as described above were dried over phosphorus pentoxide and passed into 1.6 g. of ethyl nitromalonate at a temperature of —20°. The ethyl nitromalonate became green; the temperature rose rapidly but it was cooled below 0°. After a large excess of the gas had been condensed in the liquid it was packed in ice for twenty-four hours. The excess of oxides of nitrogen was removed by a current of dry air. The remaining liquid was distilled in a vacuum and passed over clear and colorless at 152° to 154° at 32 mm. This distillate gave a yellow potassium salt which proved to be potassium ethyl nitromalonate. The boiling point and the potassium salt identify this oil as unchanged ethyl nitromalonate. The red oxides of nitrogen when *thoroughly dry* do not, therefore, react with ethyl nitromalonate.

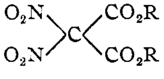
When ethyl malonate is treated with the red oxides of nitrogen to produce the mesoxalic ester, the crude acid oil, which has been the subject of this study, occurs as a by-product. We have frequently noticed when these oils are distilled that the yield of ethyl dinitroacetate is increased at the expense of the ethyl nitromalonate. This shows that under the conditions of the distillation, where water and N_2O_3 are present, ethyl nitromalonate is half saponified, and one carboxyl group is replaced by the NO_2 radical, yielding ethyl dinitroacetate.[1]



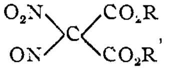
$$O_2N-\underset{H}{C}\begin{matrix}CO_2C_2H_5\\CO_2C_2H_5\end{matrix}\xrightarrow{+H_2O}O_2N-\underset{H}{C}\begin{matrix}COOH+O_2H_5OH\\CO_2C_2H_5\end{matrix}\xrightarrow[+N_2O_3]{}O_2N-\underset{H}{C}\begin{matrix}NO_2\\CO_2C_2H_5\end{matrix}+CO_2$$

We have also noticed that the ethyl nitromalonate largely disappears when the mixture of ethyl malonate, saturated with the red gases, warms up and a violent reaction causes it to "blow off" as frequently happens if not kept well packed in ice for the first ten of twelve hours after saturation.

When dry ammonia gas is passed into the crude oil dissolved in ether the salts of ethyl nitromalonate and ethyl dinitroacetate are first precipitated. At this point the ethereal filtrate should contain any *neutral* nitrogenous esters. An excess of ammonia added suddenly produced a deeper yellow color and soon an unstable red oil separated out. It is from such neutral esters as



and



which may be left in the ether at this point, that one might expect the production of oxomalonates, $O=C=(CO_2R)_2$, by elimination of the nitro, or nitroso groups in the presence of oxygen during the process of vacuum distillation. The presence of much free nitrogen gas, which was mentioned above as a product of the distillation of these crude oils, appears

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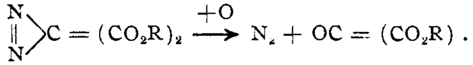
[1] See Bouveault and Wahl, *Compt. rend.*, 136, 159.

to be evidence of the presence of diazomalonic ester, which, with free oxygen, would give nitrogen gas and oxomalonates,



$$\mathrm{\overset{N}{\underset{N}{\|}}{>}C = (CO_2R)_2 \xrightarrow{+O} N_2 + OC = (CO_2R)}\ .$$

Diazomalonic ester has long been sought but without success. Our time was insufficient to investigate these neutral nitrogenous esters.

Mr. Roarke found that the ethereal filtrate, from the crude ammonium salts above mentioned, contains a substance which was obtained by the evaporation of the ether to dryness, and recrystallization of the yellow residue, from benzene-ligroin, and from carbon tetrachloride. The substance was obtained as flat, colorless needles, highly refractive, flexible and greasy to the touch. It melted at 50°, to a yellow liquid. The analysis follows:

C, 41.29, 41.35; H, 8.05, 8.60; N, 16.04, 16.14.

This same product was obtained, by distilling the "crude oils" washed with water, and was found in the fraction of b. p. 97° at 32–34 mm. (uncor.). It is easily soluble in ether, alcohol, acetone, carbon tetrachloride, chloroform, and fairly soluble in benzene and ligroin. It has not been further studied.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY, WORCESTER, MASS.]

THE PREPARATION OF ACETAMIDE.

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Methods Used Hitherto.—Acetamide has long been prepared by the action of aqueous ammonia upon ethyl acetate, as originally proposed by Dumas, Malaguti and Leblanc.[1] The reaction mixture has no effect upon iron, and so the process can be carried out on a considerable scale in iron autoclaves.

The preparation of amides from the ammonium salts of the corresponding acids was first introduced by Dumas.[2] The details of this method, as now generally employed for the preparation of acetamide on a laboratory scale, were worked out by Hofmann.[3] Hofmann sums up the condition of the preparative method at the time he undertook its amelioration, in the following words:

"If, however, the preparation of amides hy treating esters with ammonia leaves much to be desired, the yields obtained by the distillation of ammonium salts are even less satisfactory. Experiments on the prepara-

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[1] *Comptes rendus*, 25, 657 (1847).

[2] *Ann. chim. phys.*, [2] 44, 142, (1830).

[3] *Ber.*, 15, 977 (1882).