

Contribution to our Knowledge
of
Acetylacetone

by Thomas Gray B.Sc.

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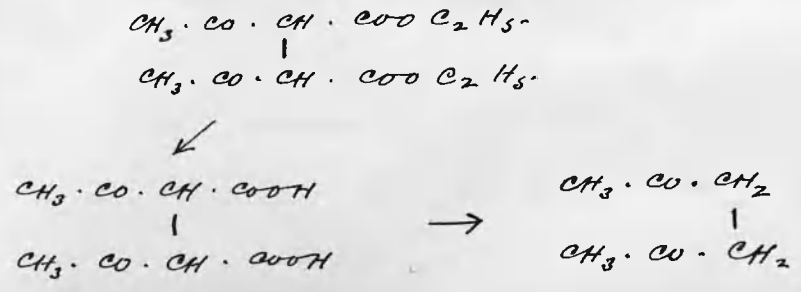
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Acetylacetone was first prepared by Paal (Ber. 17, 2765) by heating pyrotartaric acid with water to 150-160°. By this means he obtained a substance of the formula $C_6H_{10}O_2$, which he later, (Ber. 18, 58), recognized to be a double ketone having the constitution represented by the formula $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_3$. The formation of a diphenylhydrazone on treatment with phenylhydrazine, and of a diisnitroso compound by the action of hydroxylamine, served to establish the ketonic nature of the substance.

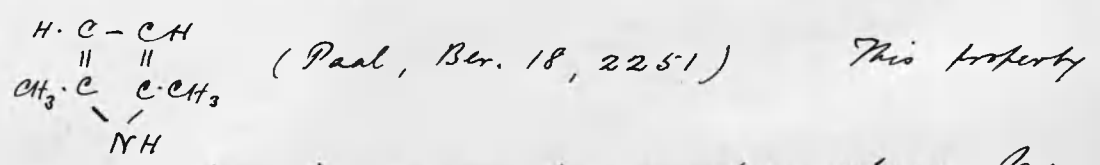
A much more convenient method of preparing the ketone was worked out by Knoor who used ethyl diacetylsuccinate as ~~was~~ his starting point. This ester on saponification with caustic soda solution (Ber. 22, 2, 2100), or with potassium acetate (Ber. 33, 1219) gives an almost quantitative yield of acetylacetone.



3.

The properties & reactions of acetylacetone have been very little investigated, probably on account of the difficulty attending the preparation of the substance in sufficient quantity. The compound however possesses a special interest, as it is the simplest representative of the class of γ -diketones; and as the work of Knorr had made it possible to prepare the ketone conveniently in quantity, it seemed desirable to determine its physical properties accurately & to study its chemical reactions more particularly. Before proceeding to give the results of my investigations it may be of interest to state shortly what has already been done on this subject.

The behaviour of acetylacetone towards ammonia and its derivatives has been fully investigated by Paal. The ketone reacts readily with ammonia with formation of 2,5-dimethylpyrrol

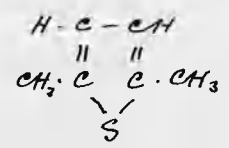


This property of reacting with ammonia has been shown by Knorr to be common to all substances of the

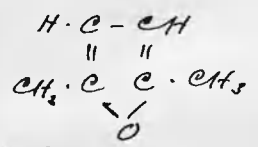
general formula $R_1 \cdot CO \cdot CHR_2 \cdot CHR_3 \cdot CO R_4$; and he has proposed the use of this reaction as a means of identifying γ -diketones. (Ber. 19, 46).

According to the researches of Paal & Schneider (Ber. 19, 558 & 3154) only those amido-compounds which possess ^{decidedly} strongly basic properties are capable of reacting with acetylacetone to form pyrrole derivatives. Thus ethylenediamine, trimethylene diamine, *m*-phenylenediamine, benzidine, amidobenzoic acid, *m*-amidobenzoic acid, *o*-amidophenol and amidoazobenzene were found to react whilst urea, oxamide, benzamide, *o*-nitraniline and sulphuric acid had no action on the ketone.

When acetylacetone is heated with phosphorus pentasulphide 2,5-dimethylthiophene



obtained (Paal, Ber. 18, 2251) and distillation of the ketone with zinc chloride results in the formation of the analogous oxygen derivative, dimethylfurfuran



(Paal & Dietrich Ber. 20, 1085)

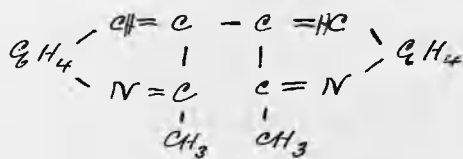
According to Angeli (Ber. 24, 1305), acetyl-

acetone is converted by the action of concentrated nitric acid into a crystalline substance having the empirical formula $C_6H_4N_2O_3$. Angeli proposes for this substance one of the two following structural formulae,



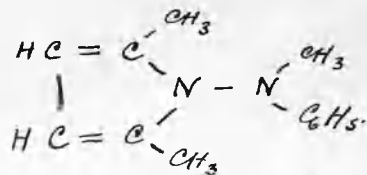
but as he does not bring forward experimental evidence in favour of either of these formulae, the constitution of the substance can not be regarded as having been established.

Acetylacetone, like acetone, condenses readily with o-amidobenzaldehyde (Eliasberg & Friedländer Ber. 25, 2, 1758) with the product of this reaction is dimethyl diquinolylin



The behaviour of acetylacetone towards methylphenylhydrazine has been studied by Kohlrausch (Ann. 253, 23) As a result of the action of methylphenylhydrazine on excess of the ketone he obtained an oily substance which gave up water at ordinary temperature, & passed into methyl-

Phenylamidodimethylpyrrol



From a study of the work on acetylacetone which had been previously published, & which is briefly discussed in the foregoing sketch, it appeared that the ketone still offered an excellent field for research. It seemed of special interest to determine whether acetylacetone would condense with aldehydes, & with the esters of various organic acids using the methods so successfully applied by Claisen in the case of other ketones. The possibility of preparing a number of complicated heterocyclic compounds by ^{the action} condensation of hydrazine hydrate, & of ammonia, on the condensation products was also indicated. These expectations have unfortunately not been realised owing to the great susceptibility of acetylacetone towards acids & alkalis - the presence of which is necessary to effect the condensations. As will be more particularly described in the experimental part of this paper, acetylacetone is quickly resinified by the action both of acids and of alkalis, and on this account most of the condensations

experiments resulted in the formation of brown resinous products, from which no substances of definite composition could be isolated. Thus attempts to condense the ketone with ethyl formate, ethyl succinate, ethyl acetate, and ethyl benzoate under varying conditions were unsuccessful. As a result of the condensation with ethylsuccinate a small quantity of ethyl succinylsuccinate was obtained. On the other hand it was found possible to bring the condensation with ethyl oxalate to a successful conclusion.

The results of a large number of condensation experiments with acetonylacetone lead me to conclude that the substance will not prove to be of general value as a synthetic agent.

Attempts to prepare the desmotropic forms of acetonylacetone were unsuccessful. The chemical properties, & the physical constants which were determined with a carefully purified ^{specimen,} ~~preparation~~ seem to prove that the preparation having the boiling point 191° consists of the double keto-form.

The absence of any colour reaction with ferric chloride, & the value of the molecular refraction, point to the keto-formula. Further purification of the ketone by conversion into the bisulphite compound, & subsequent isolation therefrom, had no ^{very} appreciable effect on the physical constants. The molecular refraction of the carefully purified, perfectly colourless, specimen obtained in this way was found to be slightly lower than that of the ketone prepared by distillation only. This might possibly indicate the presence of a small proportion of the Enol-form in the last-named preparation, but the difference in the two values is so small that this conclusion can scarcely be justified.

The experimental part of this paper, which follows, contains first a description of the methods of preparing acetylacetone, which is followed by a discussion of the properties & a statement of the physical constants of the ketone. The results of ^{the} condensation with hydrazine hydrate are then detailed & finally the product of the condensation of the ketone with ethyl oxalate,

as well as a number of pyrazol-derivatives, which have prepared from this condensation-product, are described.

Experimental.

Preparation of Acetylacetone.

The acetylacetone used in the following experiments was prepared by saponifying ethyl diacetylsuccinate by means of a 20% solution of potassium carbonate as recommended by Knorr (Ber. 33, 1219).

Saponification with a 3% solution of caustic soda was also carried out with the object of testing the ^{relative} efficiency of the two methods. The quantities of ketone obtained from 200 grs. of ethyl diacetylsuccinate were

| | | | |
|-------|-----------|--------|-------|
| using | K_2CO_3 | 68 gr. | = 77% |
| " | $NaOH$ | 67 gr. | = 76% |

The yields of ketone obtained by these two methods are practically identical, but the saponification with potassium carbonate is the more convenient.

In order to obtain the yields stated above it is

necessary to fractionate the first portions of the distillate carefully, as notwithstanding the high boiling point of the ketone a considerable quantity passes over with the alcohol & ether. With one distillation only 51-55 gr. of acetylacetone, boiling at 190-192, are obtained from 200 gr. of ethyl diacetyl succinate.

The acetylacetone obtained by distillation under atmospheric pressure had invariably a slightly yellow colour; but it was found possible to prepare a perfectly colourless specimen by distillation under reduced pressure. (300 mm.) The product however, on standing gradually acquired a yellow tinge.

When cooled in a freezing mixture the ketone solidified completely to a wax-like crystalline mass composed of leaflets. The melting point was $-9^{\circ}C$. The behaviour on cooling thus showed no evidence of the presence of two tautomeric forms of the substance.

The following physical constants were determined:-

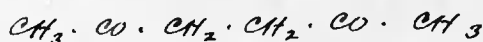
| B.P. | | Pressure |
|------|----|----------|
| 191° | at | 750 mm. |
| 178° | at | 500 " |
| 158° | at | 300 " |
| 137° | at | 150 " |

Spec. Grav. d_{4}^{20} 0.973

Refractive Index n_{D}^{20} 1.428

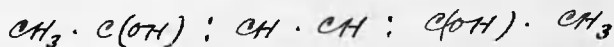
Molecular refraction M_{na} 30.14

Value calculated for the Keto-formula



30.10

Value calculated for the "Enol"-formula



31.98

The close agreement of the experimentally^{int.} determined value of the molecular refraction with the calculated number 30.10 points to the Keto-formula for acetylacetone; & this is confirmed by the fact that ferric chloride gives no coloration when added to the alcoholic solution of the substance.

As the acetylacetone which was used for the determination of the constants given above slowly developed a slightly yellow colour, a further purification of the ketone by conversion into the

Sodium bisulphite compound was effected.

Preparation of the Sodium bisulphite Compound of
Acetylacetone.

This compound was prepared in the usual way.

50 gr. of the ketone were added to 500 cc. Sodium bisulphite solution and the mixture was well shaken.

On a few minutes the whole solidified to a thick white crystalline mass. The substance was filtered off, washed with a small quantity of water, & dried by pressure between layers of filter paper in an hydraulic press.

As this substance had not previously been described an estimation of the Sodium was carried out.

0.5368 gr. Subs. gave 0.2222 gr. Na_2SO_4

Calculated for



Found

Na_2O 18.23 %

18.07 %

Acetylacetone was regenerated from this compound by heating it with potassium carbonate solution. The ketone was extracted with alcohol-free ether.

The ethereal solution was dried over potassium carbonate & fractionated at 300 mm. pressure. 30 gr. of the ketone were obtained. A determination of the index of refraction gave the value $n_D^{20} = 1.423$. The purity of the specimen thus obtained was established by redistilling the ketone, collecting the distillate in two fractions, & determining the refractive indices of these. The values obtained were :-

| | | |
|--------------------------|------------|---------|
| 1 st Fraction | n_D^{20} | 1.4230 |
| 2 nd Fraction | n_D^{20} | 1.4232. |

Physical Constants of acetylacetone prepared from its bisulphite compound.

| | | |
|-----------------------------------|---------------|--------|
| Spe. Grav. | d_4^{20} | 0.973 |
| Refractive Index | n_{Na}^{20} | 1.4232 |
| Molecular refraction | M_{Na} | 29.85 |
| Calculated for the "Keto" formula | | 30.10 |
| Calculated for the "Enol" formula | | 31.98 |

Behaviour of Acetylacetone towards caustic soda
and metallic sodium.

The susceptibility of acetylacetone towards caustic soda has already been referred to. The addition of a few drops of concentrated caustic soda solution produces a yellow colour in a few minutes. If allowed to stand for some days the liquid becomes quite black with separation of resinous products.

Metallic sodium was also found to have a resinifying action. An attempt was made to prepare the sodium salt of the "end" form. With this object the ketone was added to the calculated quantity of metallic sodium under dry ether. The reaction started immediately & the metal was gradually converted into a brown powder. This was dissolved in water & the solution was acidified & extracted with ether. A transparent brown resin remained after distilling off the ether.

The above observations explain the formation of uncrystallisable resinous substances in the attempted condensations of acetylacetone with various ethereal salts.

Action of hydrochloric & sulphuric acids on
Acetylacetone.

These experiments were conducted with the object of preparing condensation products analogous to those obtained in the case of acetone.

Dry hydrochloric acid gas was passed into well cooled acetylacetone and the solution was allowed to stand at ordinary temperatures. The ketone immediately assumed a reddish-brown colour & was converted after some days into a black semi-solid mass. On

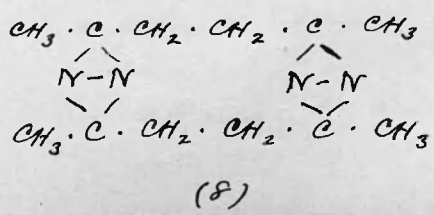
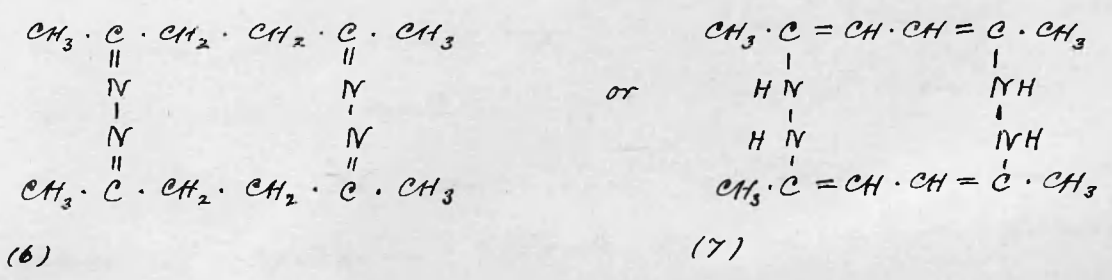
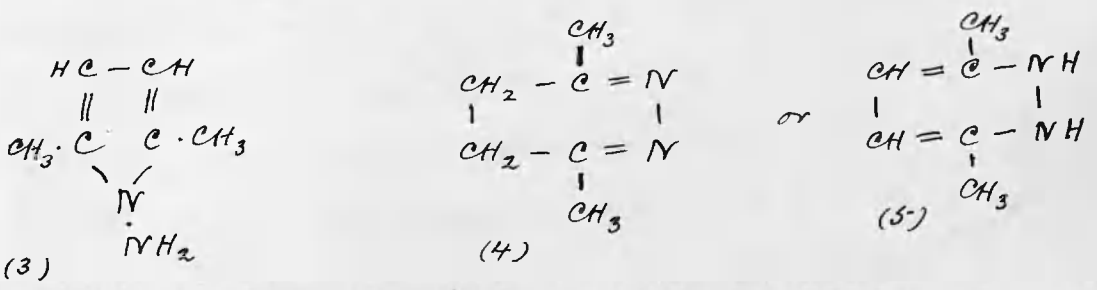
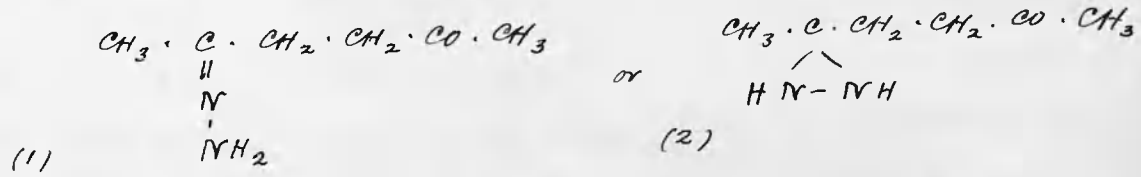
addition of water a black mass resembling charcoal was obtained, & from this on treatment with alcohol a small quantity of a brownish-yellow solid was extracted. This substance was readily soluble in ether & in benzene, but as it could not be obtained in a crystalline condition it was not further examined.

The action of concentrated sulphuric acid was found to be similar to that of hydrochloric acid gas. In this case the brownish-yellow solid, referred to above, was also separated from the charred mass.

Condensation of acetylacetone with Hydrazine hydrate.

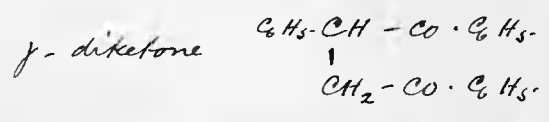
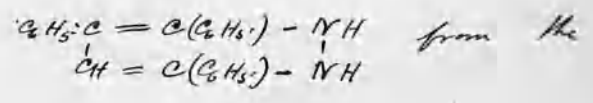
This condensation takes place readily. Two products are obtained; one of these is formed when hydrazine hydrate is added to excess of acetylacetone and the other if the hydrazine hydrate is in excess.

The reaction between molecular quantities of the two substances may theoretically take place in a variety of ways: the possibility exists of the formation of substances having the following structural formulae:-



The analysis of the product of the reaction proved the absence of oxygen and consequently excluded the formulae 1 & 2. Of the remaining formulae 3, & 5, seemed the most probable in view of the ease with which the formation of pentatomic & hexatomic ring complexes takes place.

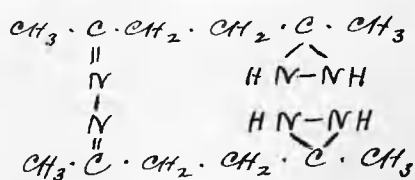
This view received support from the observation of Knorr that phenylhydrazine forms with acetylacetone phenylamido-dimethylpyrrol, and also from the formation triphenyldihydropyrazine



A number of determinations of the molecular weight of the substances according to the method of depression of freezing point in benzene & in aqueous solution, as well as by the elevation of the boiling point in ethereal solution, gave values slightly above 220. These results dispose of formulae 3, 4, & 5, & of the three remaining these formulae 7 seems to me the most probable on account of the fact that the substance reacts readily with benzoyl chloride.

The condensation of acetylacetone with excess of hydrazine hydrate resulted in the formation of a crystalline substance having the empirical formula $\text{C}_{12}\text{H}_{24}\text{N}_6$. An attempt to determine the molecular

weight of the product by the boiling point method in methyl alcoholic solution failed, owing to decomposition of the substance. The sparing solubility of the product in water & in benzene, and its instability in presence of the other liquids commonly used as solvents, precluded the possibility of determining the molecular weight by the freezing point method. The formula



Satisfactorily expresses the composition & properties of the substance, though it cannot be regarded as having been definitely established.

Condensation of acetylacetone with hydrazine hydrate
in molecular proportions. 1 M : 1 M,

15 grs. hydrazine hydrate were slowly added to 34.2 grs. acetylacetone cooled in water. The reaction proceeded with evolution of heat. The mixture was allowed to stand for about an hour and afterwards dissolved in dry ether. The ethereal solution was dried over potassium carbonate, the ether was distilled off and the residue was distilled under diminished pressure in hydrogen gas. The bulk of the product (24.5 grs.) distilled over between 160° & 175° at a pressure of 20 mm. This was rectified by distillation

and a pure product, boiling at $157-158^\circ$ under 13 mm. pressure, was obtained. The distillate solidified in the condensing tube at the beginning of the distillation, but after it had been melted it remained liquid for several days. The substance thus prepared was a slightly yellow, highly viscous oil, which, after having stood for over a week at ordinary temperatures, began to crystallize and was slowly converted into a solid white crystalline mass composed of rhombohedral crystals.

Analyses:

| | | | | |
|----|-----------------------|--------------------------|----------|---------------------------------|
| I | 0.2168 gr. subs. gave | 0.5192 gr. CO_2 | ∇ | 0.1702 gr. H_2O |
| II | 0.2156 " " " | 0.5160 " " " | " | 0.1796 " " " |

| | | | | | |
|-------|----|---|-------|---|------|
| Found | I | C | 65.31 | H | 8.72 |
| | II | " | 65.27 | " | 9.25 |

Calculated for $\text{C}_{12}\text{H}_{20}\text{N}_4$ C 65.45 H 9.09

0.1784 gr. subs. gave 38.6 cc. N at 15° ∇ 757 mm.

Found N 25.24 %

Calculated for $\text{C}_{12}\text{H}_{20}\text{N}_4$ " 25.45 %

Determination of Molecular Weight of Base.

0.3468 gr. subs. in 12.98 gr. Benzene gave depression of freezing point 0.64° .

Found $M = 208$

I 0.2344 gr. subs. in 14.67 gr. water depression Freezing Pt. 0.13°
 II 0.5164 - - - - - - - - - - - - - 0.29°

Found m. I 227 II 224.

Results obtained using the method of Landsberger as modified by Walker & Lumden (Journ. Chem. Soc. 1898, 502)

| Wt. of subs. | Elevation of B.P. | Vol. of sol ⁿ | Mol. weight |
|--------------|-------------------|--------------------------|-------------|
| 0.6586 gr. | 0.65° | 11 cc. | (279) |
| | 0.55° | 16.3 " | 222 |
| | 0.45° | 19.5 " | 227 |
| | 0.45° | 22.1 " | 200 |

Summary of results.

| In | Benzene | Water | Ether | Calculate for $C_{12}H_{20}N_4$ |
|----|---------|-------|-------|---------------------------------|
| | 208 | 227 | 222 | 220. |
| | | 224 | 227 | |
| | | | 200 | |

The base is easily soluble in water, alcohol, ether & benzene. It rapidly absorbs oxygen from the air becoming dark brown in colour, & possesses reducing properties. No immediate change is observed on adding the aqueous solution to silver nitrate or Fehling's solution, but on boiling, reduction takes place with precipitation of metallic silver & cuprous oxide. The aqueous solution is neutral to litmus, but the substance possesses basic properties. On addition of an ethereal solution of the substance to excess of an ethereal solution of

hydrochloric acid gas, a white crystalline precipitate of the hydrochloride is obtained. The salt prepared in this way was washed with dry ether, & dried in vacuo first over concentrated sulphuric acid, & finally over Soda lime to remove any excess of hydrochloric acid. It was found to be highly deliquescent & very soluble in water.

Analyses.

I 0.5166 gr. hydrochloride gave 0.5073 gr. AgCl
 II 0.4258 " " " 0.4185 " "

| | | |
|---|-------------|----------|
| Found | HCl I 24.97 | II 24.99 |
| Calculated for $C_{12}H_{20}N_4 \cdot 2HCl$ | " | 24.91 |

The base forms a sparingly soluble chloroplatinate which is obtained as a yellow precipitate on adding chloroplatinic acid solution to an aqueous solution of the hydrochloride.

The base reacts readily with benzoyl chloride, is dissolved in benzene, as well as in aqueous solution according to the method of Schotten-Baumann. The benzoyl-derivative is a white solid which melts at 235 to 236°. The analysis of this substance is not yet completed.

Condensation of acetylacetone with excess of hydrazine hydrate.

6.3 gr. Acetylacetone were gradually added to 6 gr. hydrazine hydrate cooled in water. Separation of crystals started almost immediately & the mixture solidified in a few minutes to a white crystalline mass. This was pressed dry on a porous plate & purified by crystallisation from methyl alcohol. The substance was found to undergo slight decomposition in the operation of crystallising and a product with a perfectly sharp melting point could therefore not be obtained. In order to establish the unitary nature of the compound it was recrystallised several times, & each of the product of each crystallisation was analysed.

Analyses.

I Substance once crystallised

0.1630 gr. Subs. gave 48.3 cc. N at 23° & 748 mm.

II After two crystallisations.

0.1420 gr. subs. gave 42.2 cc. N at 22° & 743 mm.

0.1840 gr. " " 0.3840 gr. CO₂ & 0.1562 gr. H₂O

After four crystallisations.

III 0.1382 gr. Subs. gave 40.4 cc. N at 22° & 755 mm.

0.1830 " " " 0.3836 gr. CO₂ & 0.1564 gr. H₂O

| | Found | | | Calculated for |
|---|-------|-------|-------|-------------------|
| | I | II | III | $C_{12}H_{24}N_6$ |
| C | - | 56.91 | 57.16 | 57.14 |
| H | - | 9.43 | 9.49 | 9.52 |
| N | 33.15 | 33.19 | 33.18 | 33.33 |

The substance separated from its solution in methyl alcohol in the form of prismatic crystals m.p. 130-132°. It is very sparingly soluble in water, benzene and ether. When exposed to air the substance gradually becomes yellow & slowly decomposed, and even in absence of air it undergoes gradual decomposition.

The aqueous solution of the substance possesses powerful ^{reducing} properties. Addition of platinum chloride causes an immediate evolution of nitrogen with formation of platinumous chloride. Gold chloride is quickly reduced with precipitation of the metal. Silver nitrate gives no immediate precipitate but reduction to metal takes place on standing in the cold. Fehling's solution is also reduced in the cold. If mercuric oxide is added to a solution of the substance in methyl alcohol rapid oxidation takes place with brisk evolution of nitrogen.

The great instability of the condensation product in presence of acids is worthy of note. Even such feeble acids as picric & picrolonic acids decompose it with formation of the respective hydrazine salts. The salt obtained on addition of picric acid was identified as hydrazine picrate by its crystalline form, its decomposition temperature (189-190°) and its percentage of nitrogen.

By adding an alcoholic solution of picrolonic acid to a solution of the condensation product in alcohol a yellow crystalline precipitate was obtained. This proved on analysis to be the hitherto unknown hydrazine picrolonate.

Analysis.

0.1580 gr. subs. gave 0.2334 gr. CO₂ & 0.0548 gr. H₂O
 0.1376 gr. subs. gave 34.6 cc. N at 22° & 750 mm.

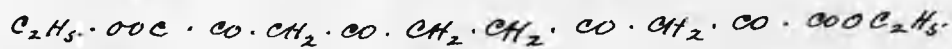
| | Found | Calculated for N ₂ H ₄ · C ₁₀ H ₈ N ₄ O ₅ |
|---|-------|--|
| C | 40.29 | 40.54 |
| H | 3.85 | 4.05 |
| N | 28.35 | 28.38 |

Hydrazine picrolonate was prepared for the purpose

of comparison, from hydrazine hydrate. The salt crystallises from alcohol or water in the form of characteristic bow-shaped prisms or needles which decompose at 262° . It is very sparingly soluble in alcohol & dissolves somewhat more easily in water.

Condensation of Acetylacetone with Ethyl oxalate.

Diethyl acetylacetonediocxalate.



Ethyl oxalate condenses readily with acetylacetone using metallic sodium as the condensing agent.

An experiment conducted with sodium ethoxide in alcoholic solution gave no satisfactory result.

The best results were obtained using the following method :-

A mixture of 73 gr. Ethyl oxalate and 28.5 gr. acetylacetone was added to 11.5 gr. sodium wire, covered with 500 cc. dry ether well cooled in a freezing mixture. The mixture was allowed to stand for some time in the

freezing mixture & allowed to stand over night at ordinary temperature. On the following morning the mixture was heated for about an hour on the water-bath to complete the reaction, the contents being well shaken to break up any crusts of salt, & to expose unchanged metal. The sodium salt, after filtration & washing with dry ether, was dissolved in ice-cold water & decomposed by dilute sulphuric acid. The condensation product was thus precipitated as a slightly yellowish colored solid which ~~may~~ ^{was} be obtained by recrystallising from alcohol in nearly colourless, lustrous, rhombohedral leaflets melting at 100-101°.

The yield was 18 - 20 gr.

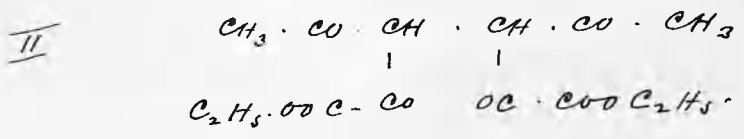
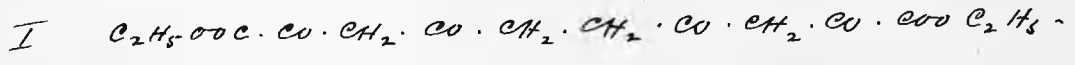
Analysis.

0.1534 gr. subs. gave 0.3020 gr. CO₂ & 0.0776 gr. H₂O

| | Found | Calc. for C ₁₄ H ₁₈ O ₈ |
|---|-------|--|
| C | 53.69 | 53.50 |
| H | 5.62 | 5.73 |

The results of the analysis thus prove that the product is diethyl acetylacetonate dioxalate. Leaving

the various tautomeric forms out of consideration, and assuming the keto-formula for the sake of simplicity in the formulation, the following two formulae remain to be considered as representing the constitution of the product :-

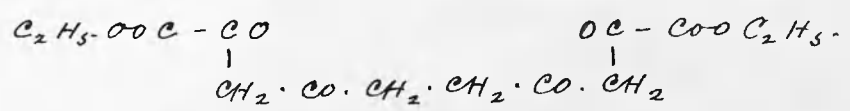


A substance possessing the formula I would be formed by condensation of ethyl oxalate with the methyl group of the ketone, whilst reaction with hydrogen of the methylene group would result in the formation of

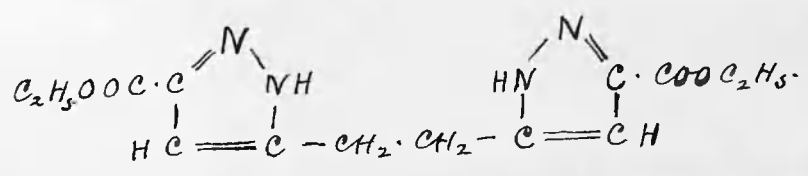
II. A study of the pyrazol derivatives of the condensation product proved the validity of formula

I. Hydrazine hydrate reacted very readily with the product with formation of an ethereal salt belonging to the pyrazol group. By saponifying this ester the corresponding acid was obtained, & this acid on oxidation with potassium permanganate yielded pyrazole-3:5-

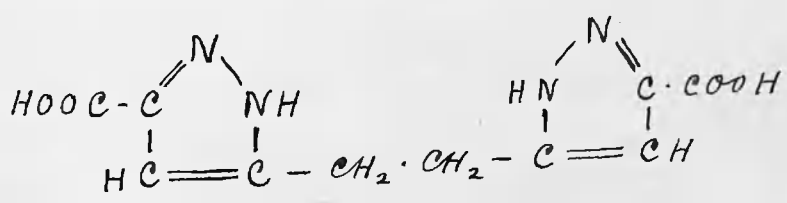
dicarboxylic acid. The last named was identified by conversion into Pyrazole. The formation of these substances prove the correctness of formula I as will be evident from the following formulation of the various stages of the process :-



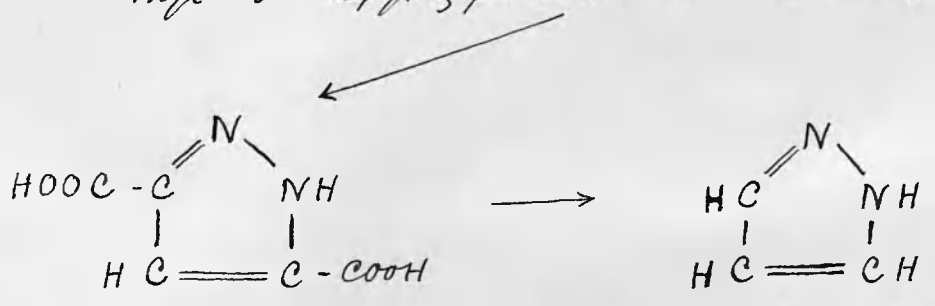
diethyl acetylacetonedioxalate
↓



ethyl 5-dipyrazolethane-3-dicarboxylate
↓



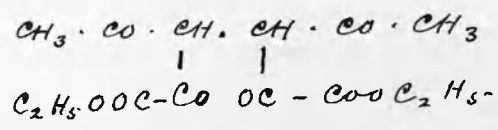
ethyl 5-dipyrazolethane-3-dicarboxylic acid



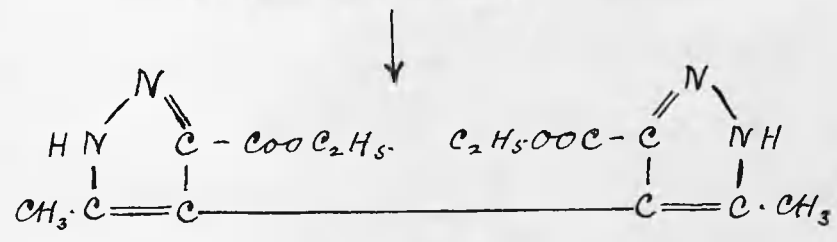
pyrazol-3,5-dicarboxylic acid

pyrazole

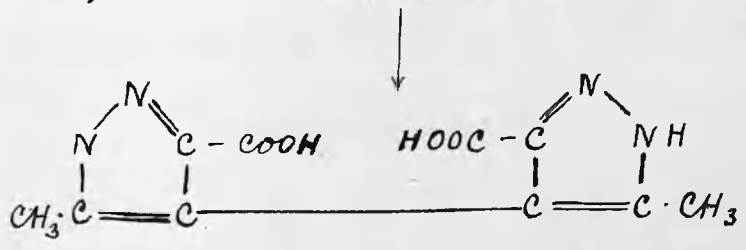
$\frac{2}{7}$ A substance possessing the structure represented by formula II, if similarly treated, would be expected to yield a tetracarboxylic acid as shown by the following scheme :-



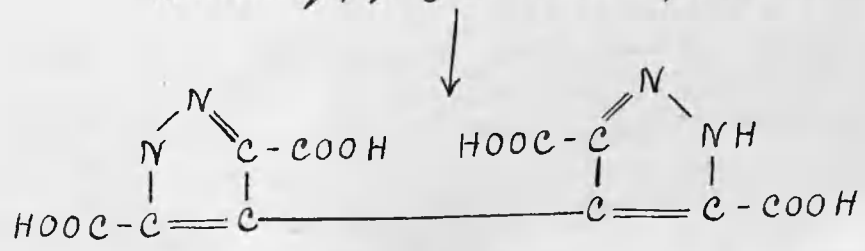
Condensation - product



Ethyl bis-methylpyrazole-dicarboxylate.



Bismethylpyrazol dicarboxylic acid



Bispyrazol tetracarboxylic acid.

Bisethyl acetylacetonedioxalate m.p. 100-107° may there-

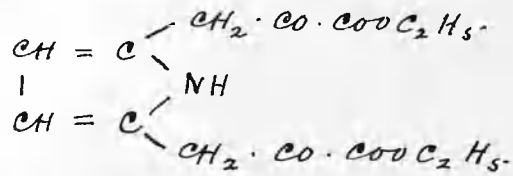
fore be regarded as an oxidation product of decane and, may according to the newer nomenclature, may be termed diethyl decane-2,4,7,9-tetrone-1,10-dicarboxylate.

The ester dissolves in ether and alcohol & is sparingly soluble in water. The solutions become yellow when boiled. On addition of ferric chloride to any of these solutions an intense cherry-red colouration is produced, & on this account the ester should probably be represented by the "Enol" formula. It dissolves easily in caustic soda or potassium carbonate solutions, & is reprecipitated therefrom on neutralising with acids. Prolonged contact with caustic soda solution in the cold effects saponification of the ester.

The ester is readily decomposed by chemical reagents. In contact with concentrated sulphuric acid it gradually blackens even at ordinary temperatures, with formation of noxious products.

A quantity of the ester dissolved in glacial acetic acid was warmed with ammonia, with a view

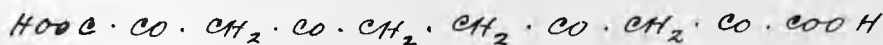
to preparing a pyrrolderivative having the formula -



The ester was however quickly resinified and the attempt was consequently unsuccessful.

Action of Nitric acid on
Diethyl acetylacetonate dioxalate.

Decane - 2, 4, 7, 9 - tetrone - 1, 10 - dicarboxylic acid.



Approximately 10 gr. of the ester were dissolved in the smallest possible quantity of concentrated nitric acid at ordinary temperature, & afterwards placed in an ice cupboard. After three days the brownish yellow solid which had separated out was filtered off, washed with water, and crystallised from acetone. The crystals, which were still slightly brown in colour, were washed with ether and thus obtained in the form of white prisms. The substance was finally crystallised, as quickly as possible, from hot water.

In this operation the substance developed a faint yellow colour, indicating a slight decomposition. The substance was dried in vacuo over sulphuric acid & analysed.

Analysis.

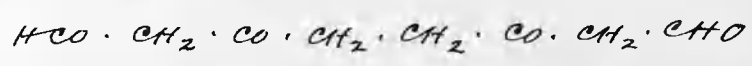
0.1472 gr. subs. gave 0.2484 gr. CO_2 & 0.0464 gr. H_2O

| | Calculated for | Found |
|---|--|-------|
| | $\text{C}_{10}\text{H}_{10}\text{O}_8$ | |
| C | 46.51 | 46.02 |
| H | 3.87 | 3.50 |

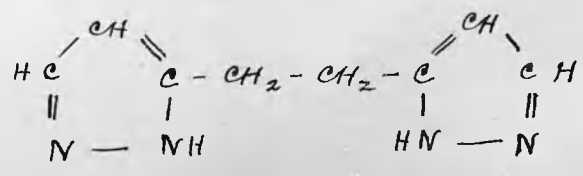
Considering the difficulty attending the purification of this product owing to its highly unstable nature, the analysis agrees sufficiently well with the assumption that the substance is Decane-2,4,7,9-tetrone-1,10-dicarboxylic acid. The first action of nitric acid ^{there} consists in a saponification. Prolonged action of the acid at ordinary temperatures resulted in the formation of oxalic acid by oxidation.

When heated to between 150° & 160° the acid becomes brown, & decomposes at 171° with evolution

of gas. It is easily soluble in alcohol & acetone, very sparingly soluble in ether, and almost insoluble in benzene & in ligroine. When the aqueous solution of the acid is boiled a distinct gas evolution takes place, & the acid gradually resinifies. The decomposition of this acid might be expected to yield the interesting double aldehyde octane-3,6-dione-dial



through loss of CO_2 . Attempts to prove the formation of this substance were unsuccessful: ^{on} evaporation of the aqueous solution of the acid ~~left~~ a resinous mass remained. As a double aldehyde of the above formula would probably be highly unstable, & consequently completely destroyed in the operation of evaporation, its presence in the liquid was tested for by addition of pyrazene hydrate to a solution of the acid which had been heated till the gas evolution had ceased. If the double aldehyde had been present the formation of dipyrazylethane



should have been observed. The

(see page 36)

result was again negative.

Condensation of Diethyl acetylacetonedioxalate with
Hydrazine hydrate.

Ethyl 5-dipyrazolethane-3-dicarboxylate.



6 gr. of hydrazine hydrate were gradually added to a hot solution of 17 gr. diethyl acetylacetonedioxalate in 100 cc. alcohol. Separation of crystals began in a few minutes. The solution was boiled for about half an hour to complete the reaction. 14 gr. of the crystalline condensation product separated out on cooling. The pyrazol derivative was recrystallized from alcohol, from which it separated in the form of characteristic rhombohedral plates with rounded corners, as indicated in sketch.



It melts at 198-199°

and is sparingly soluble in the ordinary organic solvents.

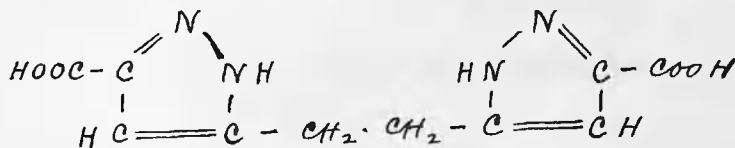
Analyses.

0.1440 gr. subst. gave 0.2894 gr. CO_2 \vee 0.0786 gr. H_2O

0.1398 gr. Subs. gave 22.35 cc. N at 21° & 754 mm.

| | Calculated for | Found |
|---|----------------------|-------|
| | $C_{14}H_{18}N_4O_4$ | |
| C | 54.90 | 54.81 |
| H | 5.88 | 6.06 |
| N | 18.30 | 18.19 |

5-dipyrazylethane-3-dicarboxylic acid.



The ester is easily saponified by boiling with caustic soda solution & the acid is precipitated from the solution by addition of acid. The acid is obtained free from potassium by recrystallisation from 30% hydrochloric acid.

It is soluble ^{very sparingly} in alcohol & glacial acetic acid and insoluble in ether, benzene & water.

It melts with gas evolution at 309-310°.

Analysis.

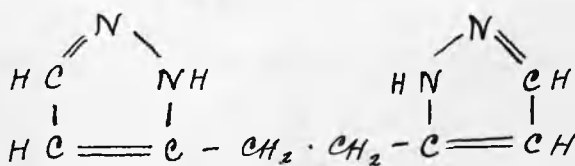
0.1544 gr. Subs. gave 0.2710 gr. CO_2 & 0.0572 gr. H_2O

0.1476 " " " 29.3 cc. N at 23° & 743 mm.

Calculated for
 $C_{10}H_{10}N_4O_4$

| | Calculated for $C_{10}H_{10}N_4O_4$ | Found |
|---|--|-------|
| C | 48.00 | 47.87 |
| H | 4.00 | 4.11 |
| N | 22.40 | 22.03 |

5-dipyrazylethane.



10 gr. of the acid described above were heated till the evolution of carbon dioxide ceased, and the 5-dipyrazylethane was extracted from the flux by means of alcohol. The alcoholic solution was decolourised by boiling with animal charcoal & evaporated to dryness. The residue was crystallised from dilute alcohol.

The substance was thus obtained in the form of spindle-shaped crystals melting at 150-151°. It crystallises from water in the form of prismatic crystals. It is easily soluble in hot water, alcohol & benzene, dissolves sparingly in

benzene and ether, and is almost insoluble in ligroin.

Analysis.

0.1516 gr. subs. gave 0.3282 gr. CO₂ & 0.0854 gr. H₂O
0.1428 " " " 44.1 cc. N at 26° & 754 mm.

| | Calculated for | Found. |
|---|---|--------|
| | C ₈ H ₁₀ N ₄ | |
| C | 59.26 | 59.04 |
| H | 6.17 | 6.26 |
| N | 34.57 | 34.40 |

Oxidation of 5-dipyrazylethane-3-dicarboxylic acid

3.37 gr. of the acid were boiled with 140 cc. $\frac{1}{10}$ normal caustic potash solution, and 8.52 gr. powdered potassium permanganate were gradually added. After boiling for half an hour the solution was filtered from the precipitated manganese dioxide, & hydrochloric acid was added. The crystalline precipitate was crystallized from 30% hydrochloric acid & dried at 120°. The yield was approximately 3 gr.

The oxidation product proved to pyrazol-3-5-dicarboxylic acid. It decomposed on heating at 289° , which is the value observed by Knorr & Macdonald (Ann. d. Chem. 279, 218)

Analysis.

0.1504 gr. subs. gave 0.2122 gr. CO_2 & 0.0366 gr. H_2O
 0.1420 " " " 22.9 cc. N at 24° & 747 mm.

| | Calculated for | Found |
|---|--|-------|
| | $\text{C}_5\text{H}_4\text{N}_2\text{O}_4$ | |
| C | 38.46 | 38.48 |
| H | 2.56 | 2.70 |
| N | 17.95 | 17.94 |

In order to further establish the identity of the substance the difficultly soluble ^{acid} potassium salt was prepared. For this purpose the acid was dissolved in caustic potash solution and excess of glacial acetic acid was added.

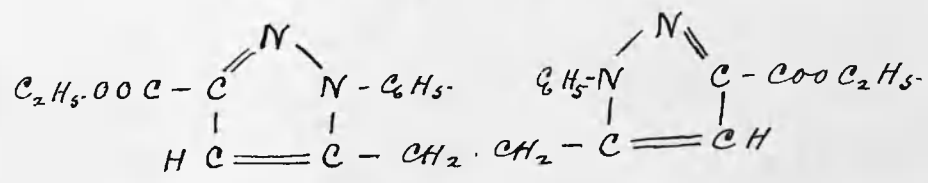
Analysis.

0.2648 gr. salt gave 0.1164 gr. K_2SO_4

| | Calculated for | Found |
|---|--|-------|
| | $\text{C}_5\text{H}_3\text{N}_2\text{O}_4\text{K}$ | |
| K | 20.10 | 19.74 |

A quantity of the acid was finally subjected to dry distillation. The distillate was crystallized from ligroin and thus obtained in the form of long thin needles melting at 70° . From this a picrate melting at $159-160^\circ$ was prepared. These values are identical with those of pyrazol & its picrate & serve to identify the substances.

Condensation of diethyl acetoacetylacetonedioxalate
with phenyl hydrazine.



2.16 gr. phenyl hydrazine were added to a hot solution of 3.14 gr. diethyl acetoacetylacetonedioxalate in 20 cc. alcohol. Crystals began to separate after a few minutes but the solution was boiled for half an hour to complete the reaction.

2.3 gr. of crystals separated from the solution.

By recrystallization from alcohol the pyrazol derivative was obtained in the form of white

Rhombohedral plates melting at 201° .

The substance dissolves in benzene, is easily soluble in glacial acetic acid, sparingly soluble in alcohol and almost insoluble in ether.

Analysis.

0.1522 gr. subs. gave 0.3784 gr. CO_2 & 0.0772 gr. H_2O

0.1794 " " " 19.1 cc. N at 17° & 751 mm.

| | Calculated for | Found |
|---|---|-------|
| | $\text{C}_{26} \text{H}_{26} \text{N}_4 \text{O}_4$ | |
| C | 68.12 | 67.80 |
| H | 5.68 | 5.63 |
| N | 12.23 | 12.21 |