

LXXXV.—*Dimethyldiacetylacetone, Tetramethylpyrone,
and Orcinol Derivatives from Diacetylacetone.*

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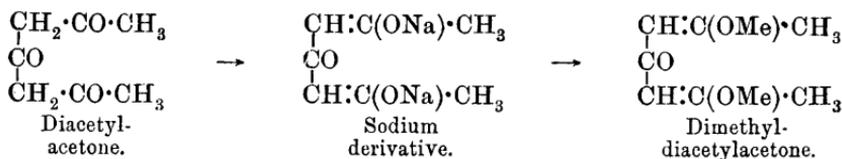
IN a paper published last year (Trans., 1899, 75, 710), one of us showed how dimethylpyrone was capable of acting as a basic substance, forming salts with various acids, and the idea was put forward that oxygen under certain conditions could replace phosphorus, nitrogen, sulphur,

or iodine in basic organic compounds owing to its quadrivalence, these compounds being supposed to be derived from the theoretical bases :

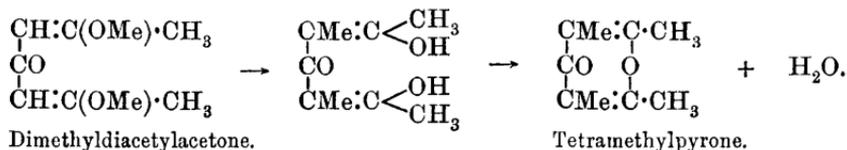


The present work was undertaken in order to see whether the property of forming these salts was peculiar to dimethylpyrone alone, or was shared by other pyrone compounds.

Diacetylacetone, when allowed to react with sodium ethoxide, at once yields a disodium derivative. This, when treated with methyl iodide, should yield dimethyldiacetylacetone, which should give tetramethylpyrone when boiled with acids or when heated :



The change undergone by dimethyldiacetylacetone when boiled with acids is due to molecular rearrangement and subsequent elimination of water :



This tetramethylpyrone should have properties closely resembling those of dimethylpyrone, and we expected that, owing to the greater number of methyl groups, it might form salts with even greater ease than the latter. We also hoped that the yield would be nearly quantitative. In both cases we were disappointed; the yield is by no means good, several other compounds being produced at the same time, and the basic properties of tetramethylpyrone do not seem to be so well marked as those of dimethylpyrone. The platinichloride separates at once when a moderately strong solution of platinic chloride is added to a solution of the base in hydrochloric acid, but with other acids crystallisable salts are not easily formed.

Although the original object of the investigation has not been attained to the extent that we had hoped, yet the side issues that have opened out are of considerable interest, and the other compounds produced by the reaction show how easily, by means of another kind of condensation, benzene and naphthalene derivatives can be formed.

The substances separated from the product after the action of methyl iodide on disodium diacetylacetone are the following :

- (1) Dimethyldiacetyl acetone, $\text{C}_9\text{H}_{14}\text{O}_3$, m. p. 86—87°.

- (2) Tetramethylpyrone, $C_9H_{12}O_2$, m. p. 92° .
- (3) Hydrate of tetramethylpyrone, $C_9H_{14}O_3$, m. p. $63-64^\circ$.
- (4) (3) Trimethyldihydroxybenzene, $C_9H_{12}O_2$, m. p. 150° .
- (5) (2) Trimethyldihydroxybenzene, $C_9H_{12}O_2$, m. p. $105-106^\circ$.
- (6) Trimethylpyrone, $C_8H_{10}O_2$, m. p. 78° .
- (7) Dimethylacetodihydroxynaphthalene, $C_{14}H_{14}O_3$, m. p. $183-184^\circ$.

The reaction is one, therefore, of some complexity, but is an excellent example of how simple condensation of molecules containing the complex $\cdot CH_2 \cdot CO \cdot$ or its enolic form $\cdot CH : C(OH) \cdot$ may be brought about in an alkaline solution.

EXPERIMENTAL.

When diacetylacetone is dissolved in absolute alcohol and a molecular equivalent of sodium ethoxide added, an insoluble salt is not obtained, but with more sodium ethoxide, a white, crystalline sodium compound separates. Fifty grams of diacetylacetone were dissolved in absolute alcohol, and sodium ethoxide made from 20 grams of sodium (calculated amount for $2Na = 16.2$ grams), dissolved also in absolute alcohol, was added. The sodium salt that crystallised out was washed and dried; when pure, it has a blue fluorescence. On analysis:

Found, $Na = 22.6$ and 22.8 . $C_7H_{10}O_4Na_2$ requires $Na = 22.5$ per cent.

This sodium salt was suspended in alcohol and boiled with 105 grams of methyl iodide (an excess of 5 grams) until the contents of the flask were neutral. The spirit was removed by distillation, and the residue treated with water and extracted with chloroform. After the chloroform had been distilled off in a water-bath, the residue was fractionated under $15-20$ mm. pressure. Several fractions were obtained; the bulk of the distillate ($25-30$ grams), however, was collected between 125° and 150° . This portion, on standing, became semi-solid. It was transferred to a porous plate, and the resulting crystals recrystallised from water. When pure, it melted at $86-87^\circ$, and boiled with much decomposition at $230-240^\circ$ under ordinary atmospheric pressure. On analysis, the substance proved to be dimethyldiacetylacetone:

Found $C = 63.1$; $H = 8.2$ per cent.

$C_9H_{14}O_3$ requires $C = 63.5$; $H = 8.2$ per cent.

The results of several other experiments were as follows: 10 grams of diacetylacetone gave 6 grams boiling at $120-150^\circ$ under reduced pressure; 30 grams gave 17 grams, and another 30 grams yielded 19 grams. During the reaction between methyl iodide and disodium diacetylacetone, it is absolutely necessary that the alcohol and other substances should be perfectly dry; if this is not the case, considerable quantities of a yellow resin, mainly dimethylacetodihydroxynaphthalene (Trans., 1893, 63, 334), are formed.

Dimethyldiacetylacetone is a white, crystalline substance melting at 86—87°. It can be recrystallised from water in groups of needles. With ferric chloride, it gives a purple coloration. Unlike diacetylacetone, it only gives a slight precipitate when boiled with barium hydroxide. When boiled, however, with caustic soda, decomposition occurs. Five grams of dimethyldiacetylacetone were boiled with rather more than 2 mols. of *N*-sodium hydroxide. From the residue were separated (1) a small amount of methyl alcohol and some sodium acetate, (2) about 0.5 gram of methyl ethyl ketone (b. p. 80—81°), (3) 1.5 grams of a substance crystallising in needles (m. p. 92°), which was readily volatile with steam, yielded a platinichloride, and proved to be tetramethylpyrone. The crystals were analysed:

Found C = 70.7; H = 7.9.

$C_9H_{12}O_2$ requires C = 71.0; H = 7.9 per cent.

From the action of sodium hydroxide on dimethyldiacetylacetone, it is evident that part of the latter exists in the form of a methoxy-compound, otherwise it is very unlikely that any methyl alcohol would be produced; a considerable portion, however, undergoes molecular change, water is eliminated, and tetramethylpyrone is formed. Dimethyldiacetylacetone, when boiled with hydrochloric acid, soon loses its power of giving a purple colour with ferric chloride. Tetramethylpyrone remains in the solution, and as this substance is volatile with steam, it is best to effect the change by digesting the diacetylacetone and acid in a flask connected with a reflux condenser. When the reaction is complete, the acid is nearly neutralised with soda and the liquid extracted with chloroform. The chloroform is removed by distillation, and the residue mixed with a little water and allowed to crystallise. A hydrate of tetramethylpyrone separates. This was recrystallised several times from water, and was then obtained in the form of colourless needles melting at 63—64°. On analysis:

Found C = 63.0; H = 8.3; also C = 63.3; H = 8.4.

$C_9H_{12}O_2 \cdot H_2O$ requires C = 63.5; H = 8.2 per cent.

This hydrate easily loses water if heated or left over sulphuric acid in a vacuum; it then melts at 92° and boils at 245°. On analysis:

Found C = 71.0; H = 8.0.

$C_9H_{12}O_2$ requires C = 71.0; H = 7.9 per cent.

The dehydration can also be effected by recrystallising the hydrate from light petroleum, when colourless, transparent plates melting at 92° are obtained. Also if the fused hydrate is kept for some time, and then allowed to cool and crystallise, the melting point is found to have risen to 92°. These crystals are changed back again to the original hydrate (m. p. 64°) when put into water. Another curious

change in melting point is shown by the tetramethylpyrone (m. p. 92°). If it is kept melted for a short time after crystallising, its melting point is found to be about 77° . This, however, may be due to partial decomposition.

Tetramethylpyrone easily dissolves in hydrochloric acid, and if platinic chloride is added to this solution a yellow platinichloride soon crystallises out. It was found best to recrystallise this salt by dissolving it in warm water and then allowing the aqueous solution to evaporate. Should the solution be boiled, decomposition occurs and a resinous material containing platinum separates. After two recrystallisations, it was considered to be pure, and was analysed :

Found C = 28.5 ; H = 4.0 ; Pt = 25.8 and 26.0.

$(C_9H_{12}O_2)_2, H_2PtCl_6, 2H_2O$ requires C = 28.8 ; H = 4.0 ; Pt = 26.0 per cent.

It was not found possible to estimate the water of crystallisation, for when heated, or even left in a vacuum desiccator, the double salt loses tetramethylpyrone as well as the water. That it did contain water of crystallisation was proved by heating some in a tube when water was driven off. This was found to be the case with tetramethylpyrone hydrate as well ; some of this compound (m. p. 64°), left in a vacuum over sulphuric acid for 24 hours, lost 13.6 per cent. of its weight, the calculated loss of weight being 10.6 per cent.

Tetramethylpyrone dissolves readily in water, and then the hydrate crystallises out. It differs in some respects from dimethylpyrone ; for instance, it does not give a precipitate with barium hydroxide, even after prolonged boiling, also it does not seem to form salts with mineral acids nearly so readily as dimethylpyrone. Potassium permanganate has no action on it in the cold, and it does not reduce silver nitrate solution. When warmed with strong sulphuric acid, it turns faintly yellow, and the aqueous solution gives a pink coloration with caustic soda. Ferric chloride gives no coloration.

Tetramethylpyrone hydrochloride is formed in long, needle-shaped crystals when a solution of the base is mixed with hydrochloric acid and allowed to evaporate. It is a very unstable salt, being instantly decomposed by water into tetramethylpyrone hydrate and hydrochloric acid. Also when left for a week in contact with air, nearly all the hydrogen chloride has evaporated away. Some was dried on a porous plate and analysed.

Found Cl = 9.0. $(C_9H_{12}O_2)_2, HCl, 2H_2O$ requires Cl = 9.4 per cent.

The substance, when heated, yields water, hydrogen chloride, and tetramethylpyrone.

Tetramethylpyrone hydriodide also can be obtained in the form of

needle-shaped crystals by the same method, but another crystalline compound is formed at the same time by the action of free iodine on the salt. This free iodine is produced by the decomposition of the excess of hydriodic acid.

An attempt to prepare the oxalate was made, but without success. The calculated quantity of oxalic acid was added to a solution of the base, and the whole allowed to slowly evaporate in a desiccator, but only tetramethylpyrone hydrate crystallised out.

The same result was obtained with a solution of the sulphate. When nitric or hydrobromic acids are added to the solid tetramethylpyrone, heat is evolved, but even after the solutions thus obtained had been left for several days in a vacuum over caustic soda no crystalline substance separated, the remaining salts consisting of syrupy solutions, which, when tested, were found to contain considerable amounts of the respective acids.

The yield of dimethyldiacetylacetone from disodium diacetylacetone and methyl iodide is never greater than 50 per cent. of the theoretical; the residues, after extraction with chloroform, were therefore examined. When shaken out with ether, small quantities of a substance melting at 150° were obtained; then on extraction with benzene another compound was separated, which, after recrystallisation from light petroleum, melted at 78° . The aqueous residue, chiefly consisting of sodium iodide, was evaporated to dryness and distilled in a vacuum, a crystalline sublimate was obtained, which, after recrystallisation, melted at 150° , and was identical with the compound extracted in small quantities from the aqueous solution by means of ether.

The compound melting at 150° gave, with ferric chloride, a green coloration rapidly turning to a grey precipitate, whilst that melting at 78° gave no reaction with ferric chloride, but formed a crystalline platinichloride with platinic chloride solution.

Compound melting at 78° . Trimethylpyrone, $C_8H_{10}O_2$.

Unfortunately, only a very small quantity of this substance was obtained. It is very soluble in water, but eventually was found to crystallise in well-defined prisms from light petroleum. On analysis :

Found C = 69.3 ; H = 7.5.

$C_8H_{10}O_2$ requires C = 69.5 ; H = 7.3 per cent.

That it possesses basic properties is proved by the existence of the platinichloride, which was also analysed.

Found C = 26.6 ; H = 3.6 ; Pt = 27.0.

$(C_8H_{10}O_2)_2, H_2PtCl_6, 2H_2O$ requires C = 26.6 ; H = 3.6 ; Pt = 27.0 per cent.

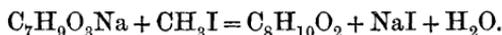
As such a very small quantity of this substance had been obtained by extracting the aqueous residues with benzene, it was thought that possibly it might be found in the first portion of the distillate, before dimethyldiacetylacetone had distilled over. The fraction boiling between 115° and 120° under 15—20 mm. pressure was examined, and from it a small quantity of a platinichloride was produced, which, after recrystallisation, was analysed.

Found C = 27.4 ; H = 3.7 ; Pt = 26.7.

$(C_8H_{10}O_2)_2, H_2PtCl_6, 2H_2O$ requires C = 26.6 ; H = 3.6 ; Pt = 27.0 per cent.

The quantity obtained, however, was very small, and as the analysis showed that the platinum salt was contaminated with one of a higher molecular weight, presumably that of tetramethylpyrone, the investigation was not carried further.

This trimethylpyrone had evidently been produced by the action of methyl iodide on a monosodium derivative of diacetylacetone,



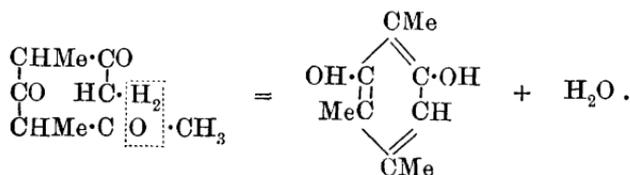
Compound melting at 150° . Trimethyldihydroxybenzene (?)

This substance was purified by several recrystallisations from water, and after the melting point had risen to 150° several further recrystallisations did not change it. On analysis :

Found C = 70.8 and 71.0 H = 8.1 and 8.0.

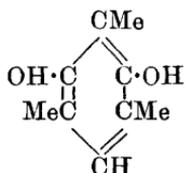
$(CH_3)_3C_6H(OH)_2$ requires C = 71.0 ; H = 7.9 per cent.

When heated, it sublimes. It is neutral to litmus paper. With ferric chloride, it gives first a green colour, then a grey precipitate. In all these properties, and also in its melting point, it exactly resembles mesorcinol, but its acetyl derivative melts at 73° , whilst diacetylmesorcinol melts at 63° ; the boiling point of this substance (m. p. 150°) seems to differ from that of mesorcinol, being somewhere near 290° , but with such small quantities as could be used the boiling point could not be determined with accuracy. Mesorcinol is said to boil about 275° . When heated with caustic soda, alcohol, and chloroform, it at once gives a deep red colour, and the aqueous solution has a green fluorescence. Left in contact with ammonia vapour, it becomes a deep red colour. When oxidised with ferric chloride and then distilled, a yellow quinone in the distillate gives the reaction first noticed by Fittig, namely, a purple colour with alkalis which is discharged by acids. Mesorcinol is said to give this last reaction as well, but in spite of all these resemblances to mesorcinol, it is not evident how such a substance could be produced from dimethyldiacetylacetone by condensation :

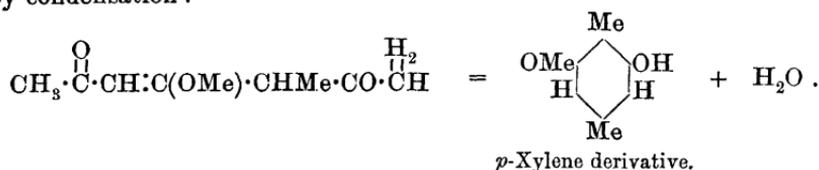


Dimethyldiacetylacetone. 1 : 2 : 4-Trimethyl-3 : 5-dihydroxybenzene.

Mesorcinol is undoubtedly a mesitylene derivative, and therefore can only have the following formula :



Still, it is said to give a quinone on oxidation with ferric chloride, although all the ortho- and para-positions are already occupied by methyl groups. Moreover, to make it more confusing, Kraus (*Monatsh.*, 1891, 12, 203) has prepared a trimethylresorcinol, which he says is the 1 : 2 : 4-trimethyl-3 : 5-dihydroxybenzene, and melts at 156°. The substance obtained from the residues in the preparation of tetramethylpyrone undoubtedly melts at 150°, and in every respect, with the exception of the boiling point and the melting point of the acetate, resembles mesorcinol. An attempt was therefore made to prepare mesitylene from it by heating with zinc dust, and 1.5 grams thus treated gave about 1 c.c. of a hydrocarbon which was found to boil at 137—138°. As mesitylene boils at 163°, it could not be that substance. *m*- and *p*-Xylene, however, boil at about 137°. An attempt was made to prepare from this small quantity of hydrocarbon the trinitro-*m*-xylene melting at 176°, but without success, and it is doubtful which of these two hydrocarbons it was. It is not probable that either *m*- or *p*-xylene could be obtained from a mesitylene derivative, but from a dimethylmethoxyhydroxybenzene such substances are to be expected. The formation of such a substance from diacetylacetone could either take place by the production of orcinol first (*Trans.*, 1893, 63, 122), and subsequent methylation, or directly from dimethyldiacetylacetone by condensation :



Under no conditions, however, could the methyl groups be found in the

meta-position as they are supposed to be in mesorcinol. It is also difficult to understand how isoxyloquinone can be produced from mesorcinol by boiling with ferric chloride, although Knecht states such to be the case (*Annalen*, 1882, 215, 100). The above *p*-xylene derivative, however, would at once give such a compound. The presence of a methoxy-group in the compound melting at 150° is, however, doubtful, for it can be boiled with fuming hydriodic acid without any change being effected, the original compound being recovered.

Compound melting at 105°. Trimethyldihydroxybenzene (?).

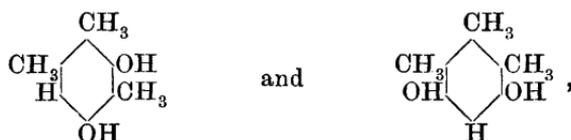
During one experiment in the preparation of dimethyldiacetylacetone, an attempt was made to prepare tetramethylpyrone directly from the product of the action of methyl iodide on disodium diacetylacetone. After the spirit had been evaporated off, the residue, consisting of sodium iodide and presumably dimethyldiacetylacetone, was treated with hydrochloric acid and boiled. Instead of obtaining tetramethylpyrone hydrate, an oil separated, from which a crystalline substance melting at 105—106° was obtained. This experiment was repeated with the same result. On analysis :

Found C = 71.1. C = 8.15.

$C_9H_{12}O_2$ requires C = 71.0 ; H = 7.9 per cent.

Although this substance is identical in its composition with tetramethylpyrone, $C_9H_{12}O_2$, yet in properties it is entirely different from it. That it is a benzene derivative is evident from various reactions. With ferric chloride, it gives a grey precipitate ; with caustic soda, a pink solution after warming ; with caustic soda, alcohol, and chloroform, a red solution, which on diluting shows a brilliant green fluorescence. Strong sulphuric acid gives first a green coloration, then yellow ; on adding water, a precipitate forms, which dissolves in soda to a bright red, and the solution shows a green fluorescence. In all these tests, it resembles the substance melting at 150°. An attempt was made to convert it into that compound by boiling with hydrochloric acid, but without success, the original substance melting at 105° being recovered. A small amount was boiled with acetyl chloride and a drop of sulphuric acid, and an acetyl compound melting at 70° was obtained. The quantity of substance, however, was so small that no further experiments could be tried with it. Hydriodic acid has no action on it when the two are boiled together, and the original substance (m. p. 105—106°) was recovered. As this compound resembles the compound melting at 150° so closely in all its reactions, the two must be similarly constituted, and both are derivatives of orcinol. From diacetylacetone, sodium ethoxide, and

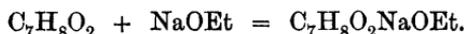
methyl iodide, only two trimethyldihydroxybenzenes are likely to be formed :



but whether the two compounds melting at 150° and 105° respectively are these substances, it is at present impossible to say.

Ethyldiacetylacetonone (?).

Dimethylpyrone, when dissolved in absolutely dry alcohol, reacts with sodium ethoxide to form an additive product, which is soluble in hot alcohol, but crystallises out again on cooling.



If the alcohol is not dry, then the disodium derivative of diacetylacetonone is produced, which is almost insoluble in boiling alcohol. The sodium salt was analysed :

Found Na = 12.5. $\text{C}_7\text{H}_8\text{O}_2\text{NaOEt}$ requires Na = 12.0 per cent.

When this salt is dissolved in water and dilute acid added, a white, crystalline substance separates, which gives a blue colour with ferric chloride. It was recrystallised from light petroleum, and melts at $57-58^\circ$. On analysis :

Found C = 63.5. H = 8.3.

$\text{C}_9\text{H}_{14}\text{O}_3$ requires C = 63.5 and H = 8.2 per cent.

On warming with dilute hydrochloric acid, this substance, instead of being converted into dimethylethylpyrone, loses alcohol and gives dimethylpyrone. The dimethylpyrone was extracted by chloroform, converted into the platinichloride, and analysed. Three separate fractions of this salt gave the following numbers :

Found Pt = 29.6, 29.9 and 29.8.

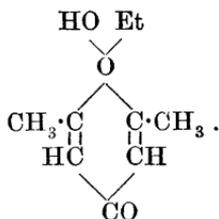
$(\text{C}_7\text{H}_8\text{O}_2)_2, \text{H}_2\text{PtCl}_6$ requires Pt = 29.4 per cent.

The melting point of the dimethylpyrone was also determined, and found to be 132° .

The substance $\text{C}_7\text{H}_8\text{O}_2\text{EtOH}$, when heated, decomposes almost entirely into dimethylpyrone and alcohol. The dimethylpyrone was recognised by its boiling point, 249° , and melting point, 132° . An analysis of its platinichloride was also made. Found Pt = 29.8 per cent.

From the curious behaviour of this substance, and the ease with

which it decomposes, it seems possible that it may have its molecular structure expressed by the following graphic formula :



That it is not dimethylpyrone with alcohol of crystallisation is proved by the blue colour it produces with ferric chloride, and by the fact that it may be recrystallised from water or light petroleum; also it cannot be ethoxydiacetylacetone, as this, like acetylacetone and diacetylacetone, would probably give a blood red colour with ferric chloride.

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