

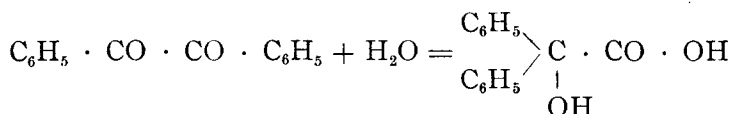
## ON THE OXIDATION OF DIACETYL.

BY HARRY F. KELLER AND PHILIP MAAS.

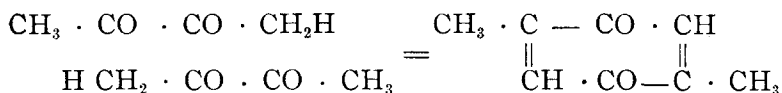
Diacetyl and benzile are the simplest representatives of the class of  $\alpha$ -diketones in the fatty and aromatic series, respectively.

Their constitutions may be regarded as definitely established, since it has been shown that they each contain *two* carbonyl groups, and that these are *directly* united.

But in spite of the close analogy expressed in their formulæ, diacetyl and dibenzoyl show some very remarkable differences in their chemical deportment. In accordance with the general rule, the aromatic compound is distinguished by the greater stability of its molecule. It is true that when treated with alkaline hydroxides, benzile takes up 1 molecule of water, and is transformed by molecular rearrangement into benzilic acid,



it does not, however, like diacetyl, appear capable of condensing into a quinogen or quinone.

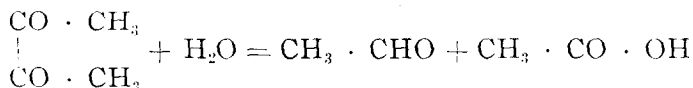


It is further well known that benzile resists the action of nearly all oxidising agents. Concentrated nitric acid and chlorine, for example, which are used in its preparation from benzoin, appear to be without action upon it. Chromic acid mixture converts it slowly into benzoic acid.

Diacetyl, on the other hand, is quite readily oxidised. The first observation in this direction was made by Fittig and one of us,<sup>1</sup> who found that, under certain conditions, this

<sup>1</sup> *Annalen*, **249**, 207.

body reduces silver solutions. To explain this, it was assumed that aldehyde and acetic acid are first formed by hydrolysis,



and the aldehyde further oxidised to acetic acid.



From the following experiments it will be seen that the oxidation of diacetyl into acetic acid is readily effected.

Two grams of diacetyl were dissolved in rather more than 25 c.c. of a 3 per cent. solution of hydrogen dioxide, and the mixture heated in a flask provided with an inverted condenser. Color and odor of the diketone soon disappeared, while the liquid acquired a strongly acid reaction. An excess of barium carbonate was now added, and, after warming for some time, the solution filtered off. The filtrate was evaporated to a small volume and then allowed to stand in a desiccator over sulphuric acid. At first, long needle-like crystals radiating from a common center separated, and, after evaporation to dryness, a crystalline mass weighing 6.2 grams remained. This is nearly the theoretical quantity—6.34 grams—required for  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2) + \text{H}_2\text{O}$ .

The salt gave all the reactions peculiar to acetates. Warmed with concentrated sulphuric acid, it emitted pungent fumes, and with alcohol and sulphuric acid, the fragrant odor of acetic ether. Ferric chloride produced a blood-red color in the aqueous solution.

The greater part of the barium salt was dissolved in water and precipitated with silver nitrate. Recrystallised from hot water, the silver salt formed the characteristic shining and flexible needles, darkening when exposed to daylight. It was analysed with the following results.

- I. .6075 gram yielded .3919 gram metallic silver.  
 II. .7234 " " .4671 " " "

Calculated for:		Found:	
		I.	II.
$\text{Ag} \cdot \text{C}_2\text{H}_3\text{O}_2$			
Ag . . . . .	64.59 per cent.	64.51 per cent.	64.57 per cent.

Hence, it follows that hydrogen dioxide quantitatively converts diacetyl into acetic acid.

*Permanganic acid* acts on diacetyl in an analogous manner. When a solution of potassium permanganate is added to diacetyl dissolved in water and acidified with sulphuric acid, the purple color is instantly discharged.

·5341 gram of the diketone was dissolved in water and sulphuric acid added: 92 c.c. of a permanganate solution of the standard 1 c.c. = ·0058 Fe., were decolorised by this liquid. This represents ·077 gram of oxygen, while theory would require ·098 gram.

In another experiment 3 grams of diacetyl were taken and 64 c.c. of a 2·5 per cent. solution of permanganate run in. This would correspond to ·405 gram of oxygen, instead of ·55 gram calculated.

That acetic acid is actually the main product of this oxidation, was proved by distilling the solution which resulted from the last experiment. By neutralising the distillate with barium carbonate, filtering and evaporating, about 4·5 grams of the acetate were obtained. It was tested in the manner already described.

Numerous experiments were made with nitric acid as the oxidising agent.

Having observed that, when highly concentrated, this acid acts upon diacetyl, even at ordinary temperatures, with formation of oxalic acid, we hoped to obtain intermediate products, perhaps ketonic acids, by working at low temperatures, and by diluting the nitric acid. These expectations have not been realised.

Five grams of diacetyl were mixed with nitric acid, specific gravity 1·48, in considerable excess. The temperature slowly rose to about 50°, when the action became exceedingly violent, torrents of red vapors being emitted. After the reaction ceased, the residue was dissolved in warm water; upon standing, a few tabular, rhombus-shaped crystals deposited. A larger crop of prismatic crystals formed after concentrating the solution, and these were easily recognised as oxalic acid. They melted at 100·5°, and their aqueous solution was precipitated by calcium chloride and silver nitrate. Weighed portions of the crystals required

the same quantities of standard solutions of caustic potash and permanganate as the same amounts of pure oxalic acid.

We are, at present, unable to say whether or not the tabular crystals first obtained were oxalic acid. Their total amount was less than a decigram. They blackened on heating, and repeated determinations of the melting point gave  $128^{\circ}$ . A weighed quantity was neutralised by one-fifth less of standard alkali than the same weight of oxalic acid. Otherwise, the reactions were like those of the latter acid.

In a second experiment, 2 grams of diacetyl were carefully poured on top of the nitric acid, so that the liquids could mix only by diffusion. The vessel was placed in cold water. After two weeks, the odor of diacetyl had disappeared, and the liquid was full of flat, prismatic crystals, which proved to be pure oxalic acid.

Ordinary nitric acid acts but slowly in the cold. At  $50^{\circ}$  to  $60^{\circ}$  the reaction becomes very violent, the sole product being oxalic acid. Similar observations were made when an acid diluted with its own volume of water was employed.<sup>2</sup>

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[ABSTRACT.]

A FERRUGINISED TREE.

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BY OSCAR C. S. CARTER.

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On the farm of Wm. Teas, situated about a mile from Three Tuns, Montgomery County, Pa., is a quarry of loose, disintegrating sandstone, of a light-yellow color. The first few feet of the surface is made up of loose sand, resulting from the decomposition of the underlying sandstone. Below the sand is the crumbling sandstone rock. This rock is made up of grains of sand bound together with a cement of feldspar. The feldspar is chalky-white in appearance, and is decomposing, which accounts for the crumbling

<sup>2</sup> Fileti and Ponzio (*Gazz. chim. ital.*, **25**, 233), in a paper on the oxidation of ketones, state that methyl-ethyl ketone, by warming with nitric acid, specific gravity 1.38, is converted into diacetyl. They also observed the destruction of this diketone by nitric acid, but do not appear to have examined the products.