

CLXXI.—*Derivatives of the Multiple Keten Group.*

By JOHN NORMAN COLLIE.

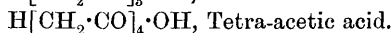
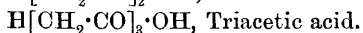
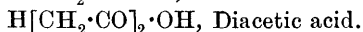
IN the present paper, the author wishes to call attention to the manner in which the group  $\cdot\text{CH}_2\cdot\text{CO}\cdot$  (a group which he wishes to call the "*Keten*" group) can be made to yield by means of the simplest reactions a very large number of interesting compounds; the chief point of interest being that these compounds belong to groups largely represented in plants.

The syntheses of organic compounds in the laboratory, as chemists know, are almost entirely different from those used by the living plant (compare Meldola, *Chemical Synthesis of Vital Products*, Vol. I., p. 7). Moreover, the photosyntheses which take place in plants have at present no parallel in the laboratory. Regarding the production of the chief compounds in plants, the celluloses, the starches, and the sugars, at present we know but little.

Usher and Priestley (*Proc. Roy. Soc.*, 1906, **77**, B, 369, and **78**, 318) have clearly shown that the action of light on carbon dioxide, together with water and chlorophyll, gives only hydrogen peroxide, formaldehyde, formic acid, and oxygen, but that in order to build up starches and celluloses from carbon dioxide and water, it is absolutely necessary that healthy protoplasm should also be present. If therefore living protoplasm is one of the factors necessary for this synthesis, then the ordinary synthetical operations used by the organic chemist never can be sufficient to produce starches and celluloses. Also it is probable that the simpler organic compounds found in plants are produced by a degradation of these starches and celluloses. Again, possibly the reactions which produce them are also as different from the ordinary reactions used by the organic chemist, as the production from dextrose on the one hand, of alcohol and carbon dioxide by means of yeast, and, on the other, of oxalic acid by means of nitric acid.

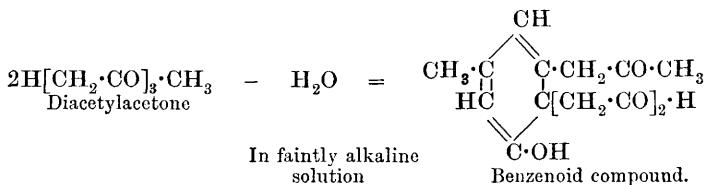
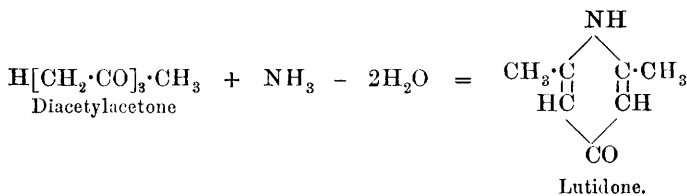
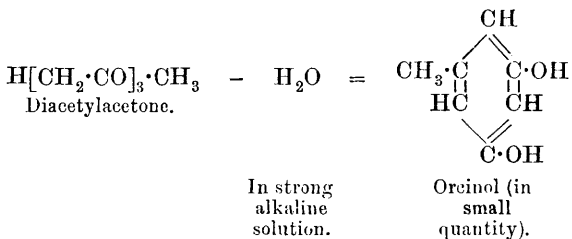
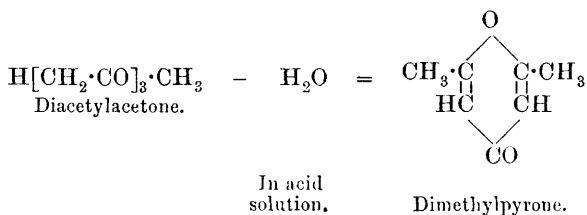
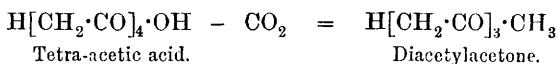
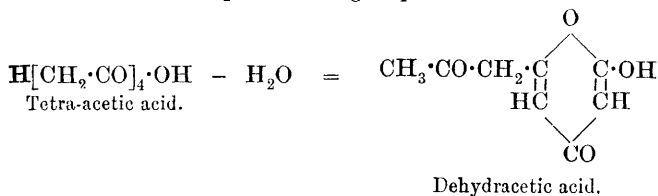
In plants, the initial reaction, brought about by the combined effect of light and living protoplasm, is firstly to build up molecules of the very highest molecular complexity, from which afterwards the simpler compounds can be formed. In the laboratory, the chemist starts with the same material, but is only able to ascend step by step towards these degradation products produced in the plants. Although, however, the actual reactions taking place in the plant are different from those in the laboratory, still much may be done by studying, in the laboratory, reactions which might quite conceivably occur in plants, such as those involving hydration, dehydration, oxidation, reduction, polymerisation, and condensation at as near the ordinary temperature as possible. Moreover, the effect on these reactions of faintly acid or alkaline solutions is worth while investigating.

For many years, the author has had this object in view, and he drew attention to some of these ideas fourteen years ago (*Trans.*, 1893, **63**, 329). The compounds which condense or polymerise most easily are the aldehydes and ketones, and by means of them carbon atoms can most easily be linked to carbon atoms. It was then pointed out "how easily the acetyl group condenses with itself" with the formation of such compounds as :



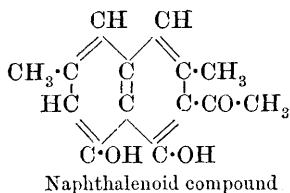
All these substances are compounds of the group  $\cdot\text{CH}_2\cdot\text{CO}\cdot$ , or keten group with water. It is these compounds and others which can be produced from them by addition or loss of water or of

carbon dioxide, or of a ketene group, that the author proposes to call derivatives of the "multiple keten" group. For instance:

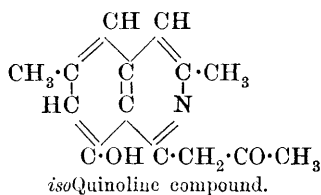


This benzenoid compound when dissolved in strong aqueous potass-

ium or sodium hydroxide loses another molecule of water, giving a naphthalene derivative :

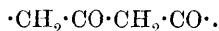


The benzenoid compound when treated with ammonia at the ordinary temperature gives an *isoquinoline* derivative :



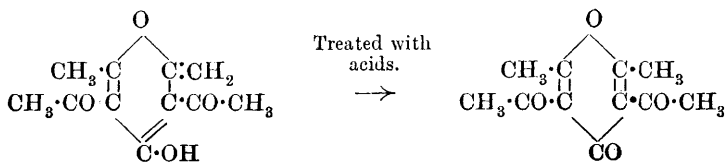
The ease with which all these condensations occur is most remarkable, as is also the diversity of the compounds produced.

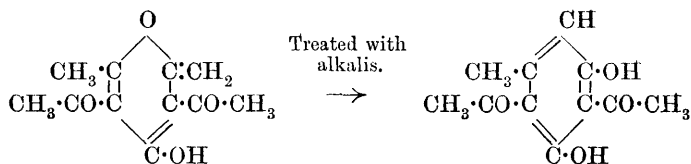
The chief reason for the chemical reactivity of these compounds and why they often give quite different condensation products in alkaline or in acid solution is that they all possess the grouping the properties of which are well exemplified in ethyl acetoacetate, namely,



According to circumstances, this group may react either in the ketonic or enolic condition, and acids and alkalis are the reagents which are best suited for bringing about this change in the molecular structure of the substance, a change which is usually expressed by a shifting in the position of the double bond.

Amongst the derivatives of the multiple keten group, an interesting example is to be found in the compound obtained by the action of acetyl chloride on the sodium salt of diacetylacetone (Trans., 1904, 85, 975). The substance is not a true pyrone derivative, neither is it a benzene compound, but hydrochloric acid converts it entirely into diacetyldimethylpyrone, whilst sodium hydroxide transforms it into diacetylorcinol.

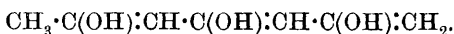




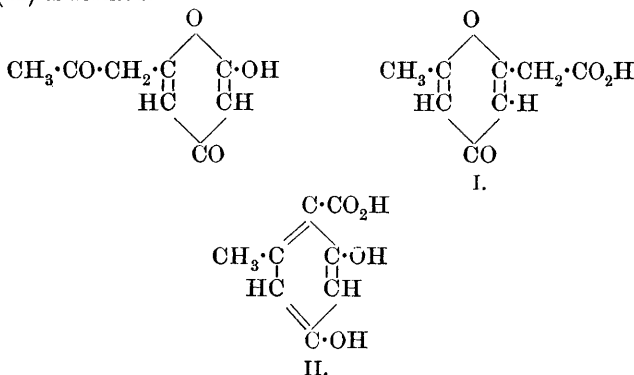
Several other instances might be given, for instance, diacetylacetone with acids gives dimethylpyrone, whilst with strong alkalis orcinol is formed in small quantity together with acetone and sodium acetate. The tendency of the acid is to produce :



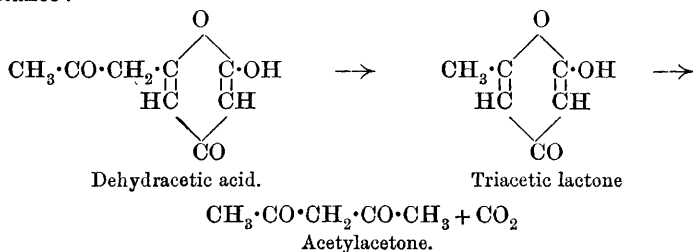
and of alkalis to give :



Dehydracetic acid also shows this difference. When treated with sulphuric acid (Trans., 1907, 91, 787), it partly changes to a pyrone-carboxylic acid (I), whilst with alkalis the isomeric orcinolcarboxylic acid (II) is formed.



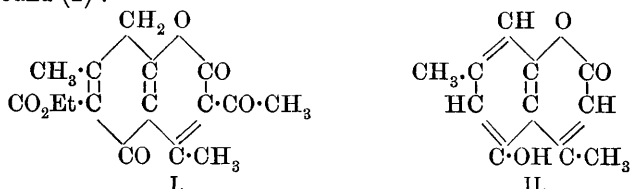
The chief action, however, of strong hydrating agents is to produce simpler substances. For instance, dehydracetic acid, diacetylacetone, dimethylpyrone, &c., give acetic acid and acetone when boiled with strong aqueous sodium hydroxide. But with different strengths of sulphuric acid, the down-grade hydrolysis can be better followed, for instance :



and finally the acetylacetone breaks down into acetone and acetic acid.

In the case where, however, there is a stable ring formation, such as in the diacetylorscinol mentioned above, strong hydrating agents merely split off the side keten groups and orscinol is left.

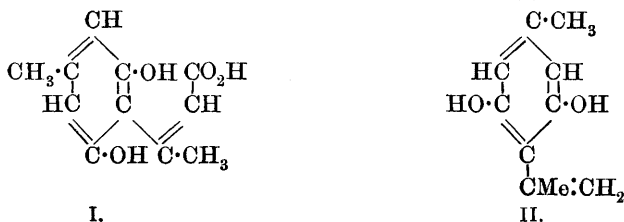
Another point of interest in these substances is the ease with which carbon dioxide is eliminated from them. The simplest case of this kind is, of course, acetoacetic acid. But dehydracetic acid also suffers this loss when converted into tetra-acetic acid by hydrolysis. The isomeric pyronecarboxylic acid decomposes so easily that considerable loss occurs during crystallisation, the solution effervescing through loss of carbon dioxide. Orcinolcarboxylic acid also is very unstable, easily losing carbon dioxide. It has already been shown how, from the combination of two molecules of diacetylacetone in concentrated or in slightly alkaline solution, more complicated derivatives of the multiple keten group can be produced. This is found to be the case also when the sodium salt of ethyl acetoacetate is heated (see preceding paper); the compound  $C_{16}H_{16}O_6$  being partly a benzenoid and partly a pyrone compound (I) :



It has also been pointed out how, when this substance is hydrolysed by heating with sulphuric acid, a simpler substance, dimethylumbelliferone (II), is produced.

The properties of this complex derivative (for the production of which from ethyl acetoacetate, only two simple reactions are needed) are of especial interest. Although colourless itself, with sodium hydroxide it gives a brilliant yellow compound. This is to be expected, as it is a "benzopyrone" compound, and therefore belongs to the same type as many of the yellow dyes.

Moreover, this brilliant yellow compound when warmed with more sodium hydroxide becomes nearly colourless, and the solution when acidified and extracted with ether gives the free acid (I) :



This acid undergoes two interesting changes :

(1) On heating, it yields carbon dioxide and a substance (II) which has an odour resembling that of thymol; also when heated with phosphorus and iodine in a sealed tube traces of cymene are formed.

(2) When it is allowed to remain in a faintly alkaline solution in contact with air, the solution gradually absorbs oxygen, becoming a dark cherry-red. This is due to the formation of a dye which possesses properties similar to brazilin. The dye may be obtained from the acidified solution by extraction with ether, in which it is soluble. It then consists of a yellowish-red powder, but it could not be obtained pure owing to the fact that it could not be made to crystallise. Like brazilin, it dissolves in water with a yellow colour, which is at once changed to cherry-red by alkalis. It is decolorised by sodium hydroxide and zinc dust, but the colour is at once restored by shaking the colourless solution with air. Analysis gave :

$$C = 57.2 ; H = 4.5.$$

A molecular weight determination gave M.W. = 470.

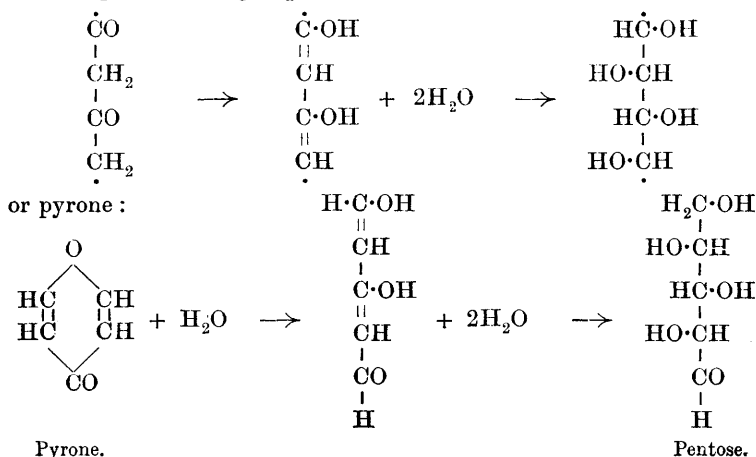
$$C_{22}H_{22}O_{11} \text{ requires } C = 57.3 ; H = 4.7 \text{ per cent. } M.W. = 462.$$

Silk and cotton can only be dyed by this substance after mordanting; with alum, a brownish-red colour is produced.

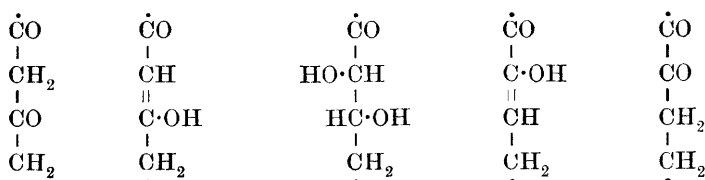
Whether the substance has a molecular structure similar to brazilin has not yet been ascertained, but it is not difficult to account for such a substance either on the lines of the formula of Kostanecki or that of Perkin.

In conclusion, the close relationship of these pyrone or keten compounds to the sugars, and through them to the starches and celluloses, might be pointed out. The whole question is one of hydrolysis.

Taking two keten groups :



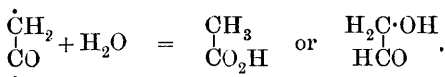
whilst if the hydration were to take place in another way :



then, in a long chain of keten groups, or hydrated keten groups (such as are undoubtedly present in the starches and celluloses), there would be an accumulation of oxygen towards one end of the chain, that is, carbon dioxide would be evolved; whilst at the other end, hydrogen or  $\cdot\text{CH}_2\cdot$  groups would predominate.

This might be offered as an explanation of the formation of fats and oils, and the production of carbon dioxide. That some such change can occur is plainly seen by the formation of alcohol, carbon dioxide, succinic acid, and glycerol from dextrose by fermentation. It is the living ferment that can effect this particular kind of hydrolysis.

Free keten reacting with water gives acetic acid, but perhaps under the influence of healthy protoplasm, glycollaldehyde and its polymerides might be produced :



It has already been pointed out by the author (Trans., 1905, 87, 1548) that when  $\cdot\text{CH}_2\cdot$  groups are combined with carbon monoxide by means of the silent electric discharge, combination occurs and a keten group results. Moreover, that the  $\cdot\text{CH}_2\cdot$  group easily combines with itself forming complex chains of  $\cdot\text{CH}_2\cdot$  groups was also noticed, and what was of considerable interest was the fact that certain definite nuclei of these  $\cdot\text{CH}_2\cdot$  groups appeared to be more stable than others. These nuclei are represented by  $\text{C}_{10}$  and  $\text{C}_{15}$  or  $\text{C}_{16}$ . Such nuclei are found in the terpenes and in the fatty acids.

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