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Oxidation of tetronic acids

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THE OXIDATION OF TETRONIC ACIDS

by

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I wish to thank Dr. Evans B. Reid without whose help this project would not have been possible.

ABSTRACT

The following paper contains a history of tetronic acids and includes a discussion on the methods of their synthesis, theoretical considerations concerning their unusual acidity, their oxidation, and the problem of their oxidative intermediate.

Two possible synthetic routes leading to the oxidative intermediate, α-alkyl-α-hydroxy tetronic acid, are proposed. Chemical and spectroscopic evidence is presented for the existence of α-ethyl-α-hydroxy tetronic acid obtained by one of the proposed synthetic methods. Actual proof for the existence of this compound awaits a quantitative chemical analysis.

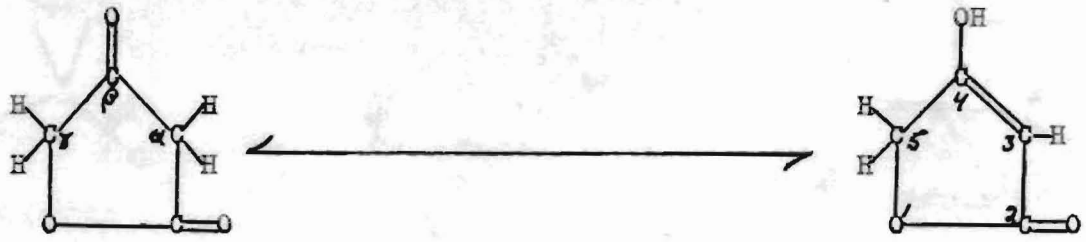
A further experiment is suggested which would answer the question of whether or not during the oxidation of tetronic acids the ring opens and splits out carbon dioxide before or after the formation of the diketones.

Table of Contents

The Oxidation of Tetronic Acids

HISTORICAL INTRODUCTION

Five membered heterocyclic systems "containing a lactone grouping with a carbonyl group in the position β to the lactone are known as tetronic acids."[1] Tetronic acid exists in tautomeric equilibrium between the keto (I) and the enol (II) forms.



I II

Nomenclature of such compounds usually follows the example in (I), although the nomenclature in (II) is also acceptable. There are an unlimited number of tetronic acids, since substitution is possible for either of the two hydrogens on both the α and the γ carbon.

Tetronic acids were first known synthetically as far back as 1880, when von Demarcay[2] synthesized the α-methyl and ethyl compounds. Synthesis of the unsubstituted parent tetronic acid eluded researchers until 1883 when Wedel[3] produced ethyl bromide and an unknown acid, (probably tetronic acid), by heating brominated acetoacetic ester. Wolff[4] finally made and isolated the parent tetronic acid in 1895 by heating dibromo acetoacetic ester to yield α-bromo tetronic acid and ethyl bromide. Wolff removed the bromine by using sodium amalgam.

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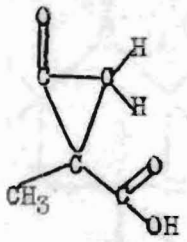
(1) Fortenbaugh, R. B., "Tetronic Acids" (unpublished Ph. D. dissertation, Dept. of Chemistry, The Johns Hopkins University, 1949), pp. 8-9.

(2) von Demarcay, M. Eug., A. Ch. (5), 20, 437 as noted in Beilstein, XVII, 412.

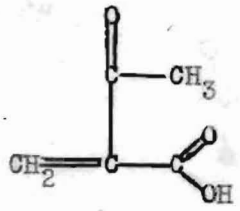
(3) Wedel, Wilh., Ann., 219, 105, (1883).

(4) Wolff, L., Ann., 288, 1, (1895).

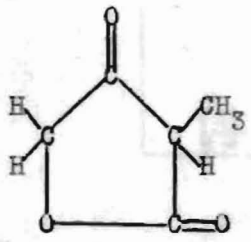
The structure of α-methyl tetronic acid, and thus tetronic acid itself, eluded researchers until Wolff's experiments in 1895. Until then there were several proposed structures, such as; Nef's lactide strucure which was proven wrong by a molecular weight



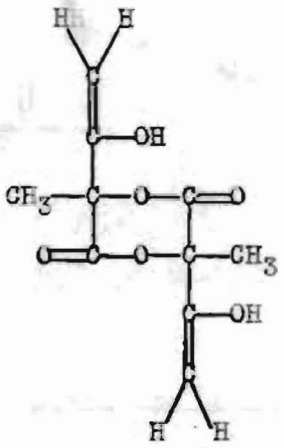
Wolff(4)



Pawlow(5)



Michael(6); Cornelius and Moscheles(7)



Nef(8)

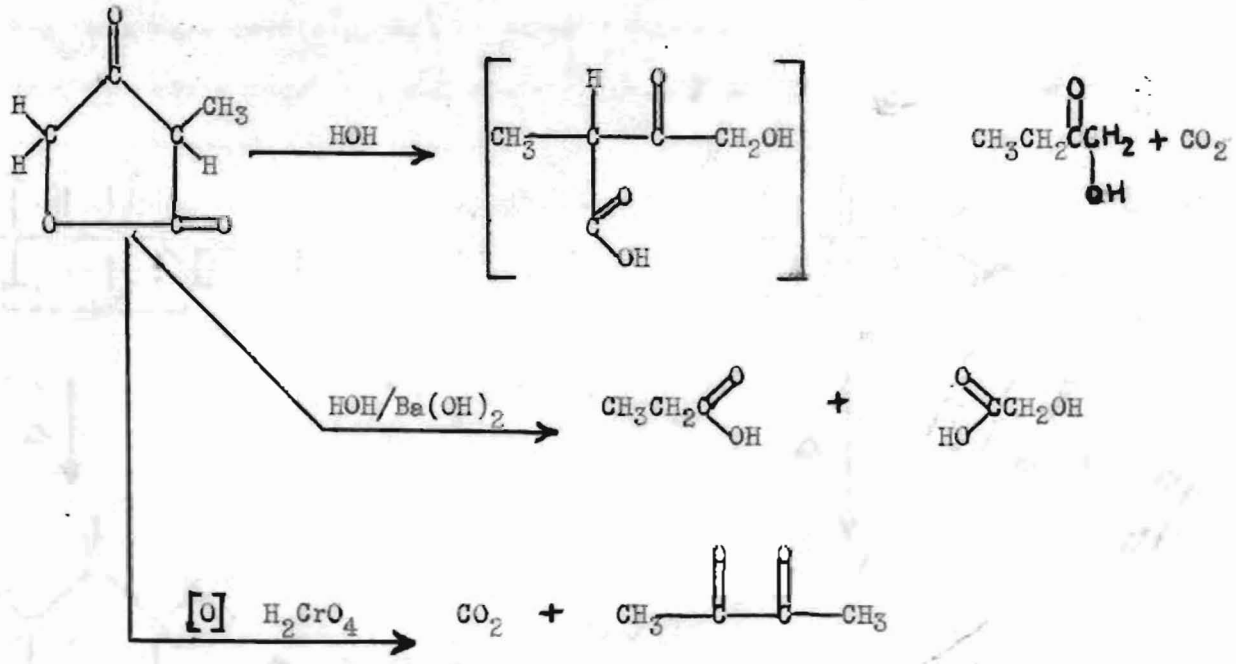
(5) Pawlow, W., Ber., 18 R, 182, (1885).

(6) Michael, J. F., Pract. Chem., 37, 502 as cited by Wolff, L., Ann., 288, 1, (1895).

(7) Moscheles, R. and Cornelius, H., Ber., 21, 2603, (1888).

(8) Nef, J., Ann., 266, 92, (1891).

determination, which showed the compound to be monomolecular. Wolff's hydrolysis and oxidative experiments established evidence in favor of the structure proposed by Michael and his contemporaries. His experiments [9] were;



Tetronic acids remained purely synthetic compounds until 1935, when Clutterbuck, Raistrick, Haworth, Smith and Stacey[10] were doing a study on the products of mold metabolism. In the course of this study tetronic acids were found to be the metabolic products of the two molds, Penicillium Charlesii and Penicillium Terrestre.

Through the years several methods of synthesizing the tetronic ring structure were developed. The real problem in such syntheses was getting the acyclic parent to undergo cyclization. Cannon and Jones[11] reported that cyclization was aided and that the final yields were improved by the use of concentrated sulfuric acid.

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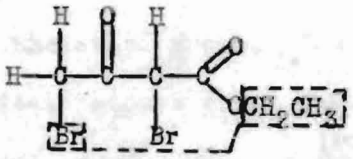
(9) Wolff, L., Ann., 291, 266, (1896).

(10) Clutterbuck, P., Haworth, W. N., Raistrick, H., Smith, G., and Stacey, M., Biochem. J., 28, 94, (1934).

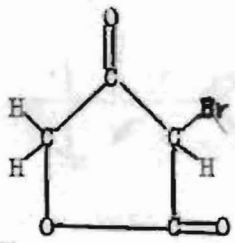
(11) Cannon, W. N. and Jones, R. G., J. Org. Chem., 23, 126, (1958).

Reid and Denny[12] later developed a method of ring closure using this information. Wolff was able to achieve ring closure of the dibromo acetoacetic ester (III) to obtain the α-bromo tetronic acid (IV). It is interesting to note that he was unable to obtain this same result by cyclization of the monobromo acetoacetic ester (V). At first this seemed peculiar, because it is the γ bromine and not the α bromine



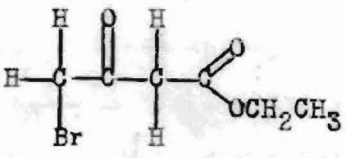
III

Δ



IV

+ CH_3CH_2Br

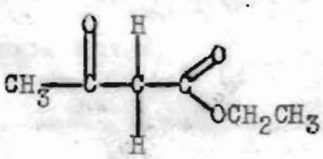


V

Δ

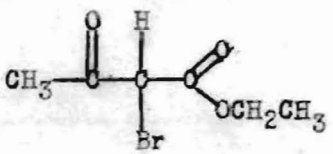
no ring closure

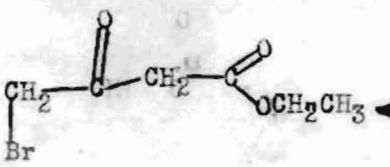
that splits out with the ethyl grouping to form ethyl bromide. Further research showed that acetoacetic ester (VI) on bromination yielded the α-bromo ester, which on standing rearranged to the γ-bromo ester (VII). This α-γ rearrangement occurred



VI

Br_2 → HBr +

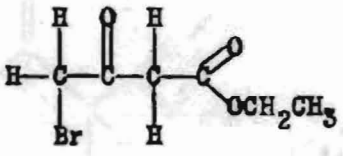




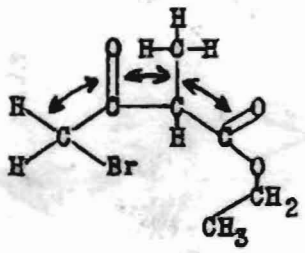
VII

(12) Reid, E.B., and Denny, G. H., J. Am. Chem. Soc., 81, 4632, (1959).

even when the α carbon was monosubstituted, and when the γ carbon was also substituted. It became evident that what was needed to accomplish cyclization of the bromo aceto-acetic ester was not necessarily another bromine atom in the α position; the requirement was instead to have at least one substituent group in the α position. This is a necessary requirement because without the substituted groups the spatial considerations are such that the γ bromine atom can not get within bond forming distance of the ethyl group. However, by substituting a group at the α carbon the steric effect becomes great enough to allow bond formation between the bromine atom and the ethyl group. This is followed by the subsequent splitting out of ethyl bromide and the closing of the tetronic ring system. The two situations are shown in (VIII) and (IX) respectively.



VIII



IX

Since the early work of Wolff other investigators have developed about five other basic methods of synthesizing the tetronic ring structure. The first of these, developed by Erich Benary,(13) involves the condensation of an α-halogenic acid halide with different condensing agents. The first of these agents is a sodio malonic ester.

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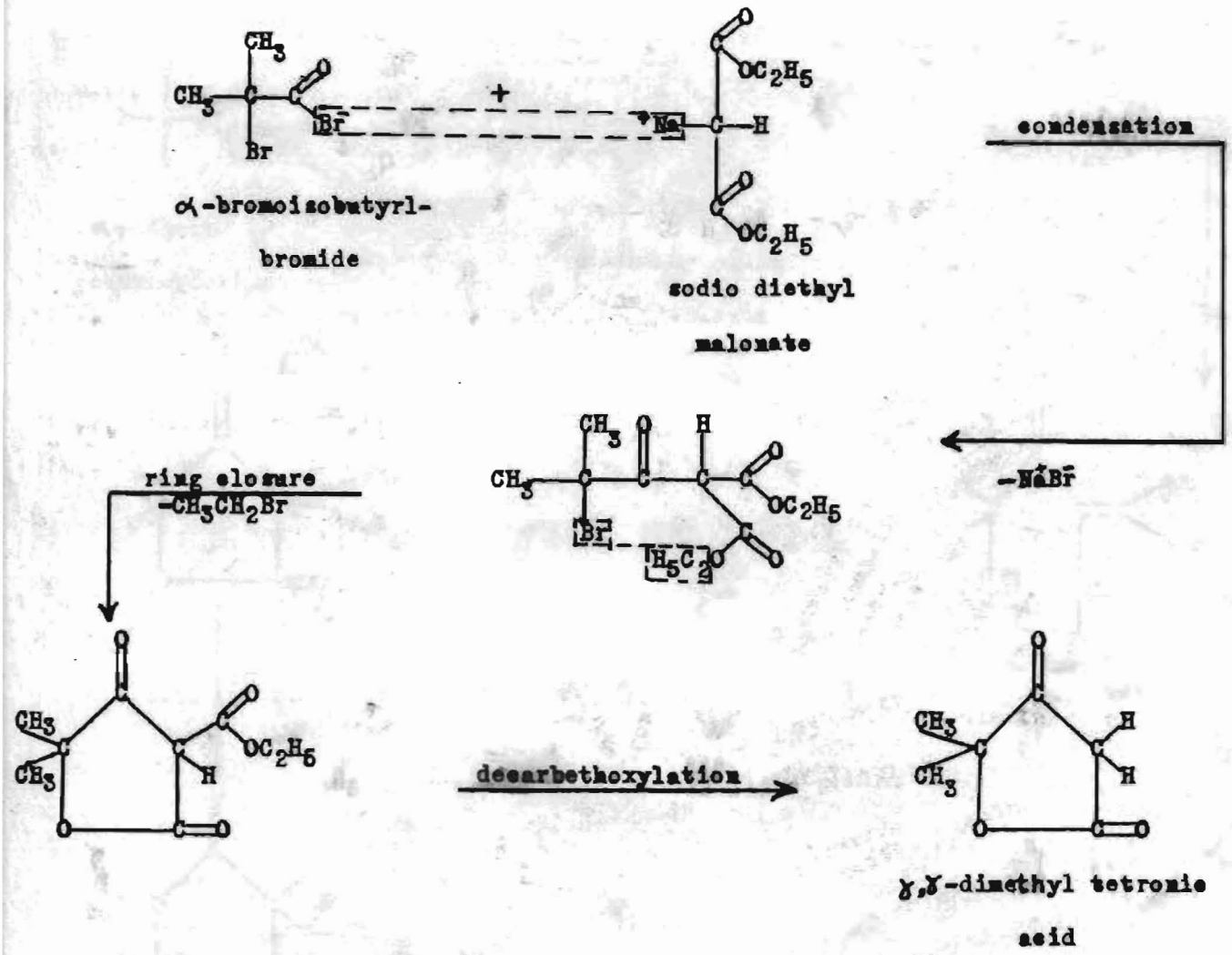
(13) Benary, E., Ber., 40, 1082, (1907).



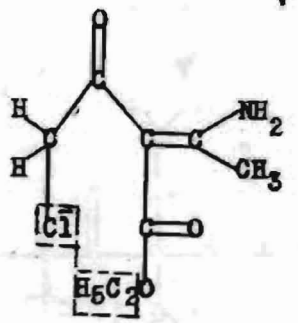
The second of the condensing agents is β-amino crotonate in the presence of pyridine. Once the tetronic ring structure was formed, Benary hydrolyzed it in alkaline solution to obtain an α substituted tetronic acid; instead of decarbethoxylating as in the first prosedure to give the γ,γ-substituted tetronic acid.

Another condensing agent experimented with by Benary was a sodio glutaric ester. The reaction sequences for these two condensations are shown in the order mentioned on the following two pages.

α-chloro acetylchloride

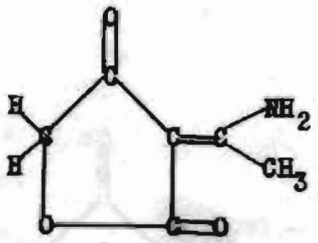
β-amino ethyl crotonate

condensation / pyridine

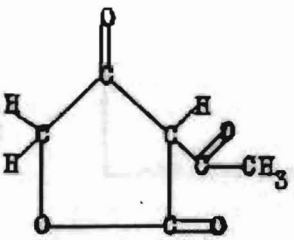


+ HCl

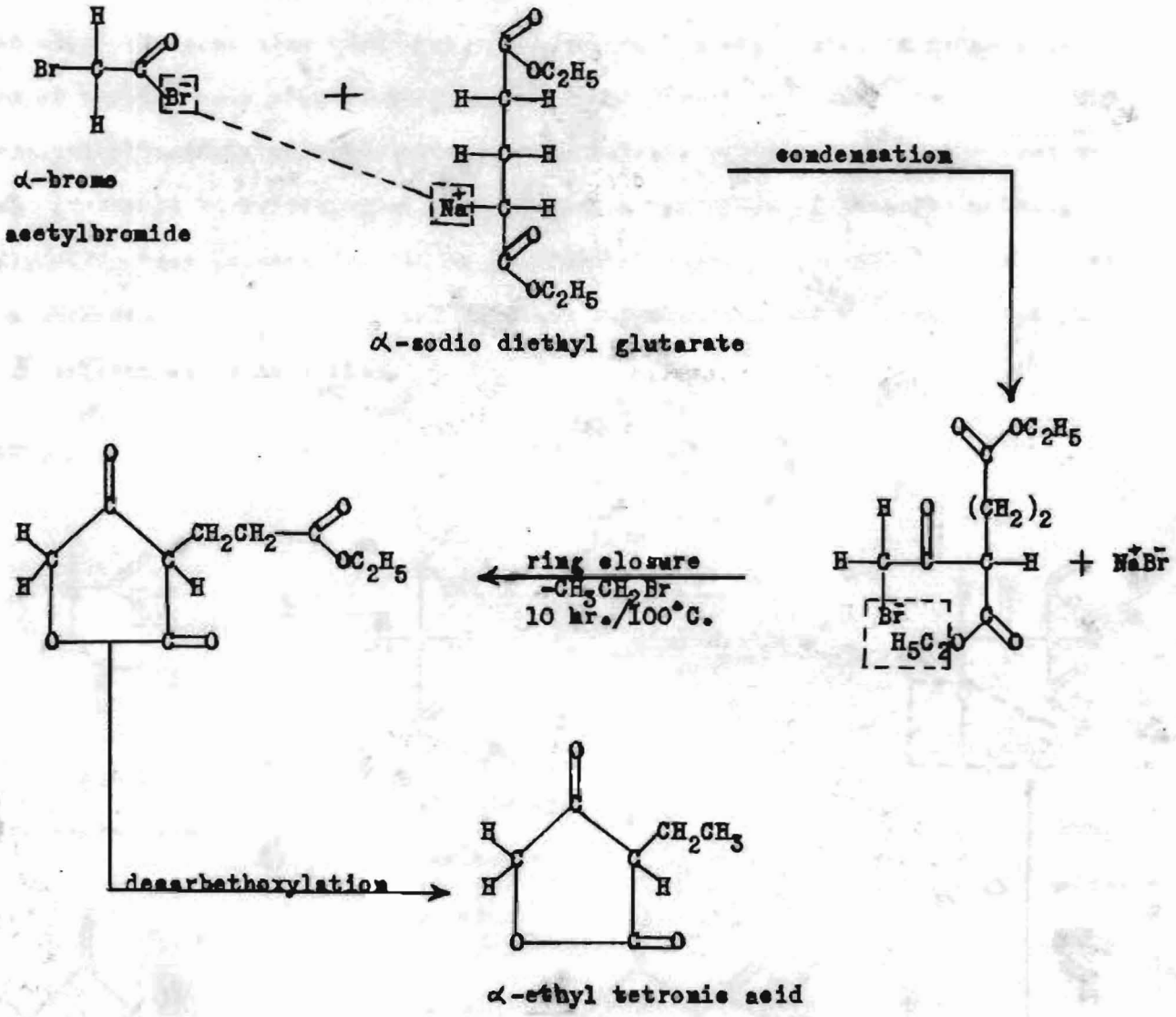
ring closure $-CH_3CH_2Cl$



$O\bar{H}$



α-acetyl tetronic acid

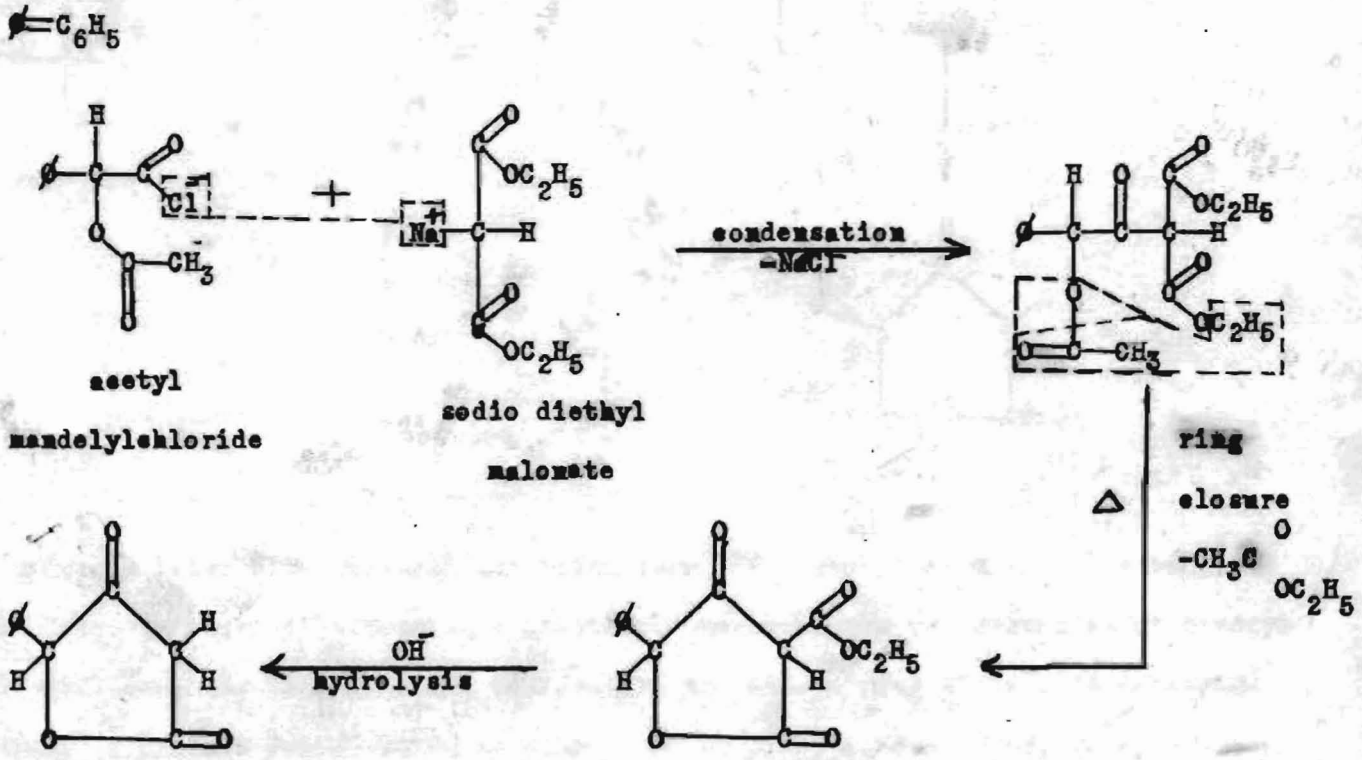


α-ethyl tetronic acid

It becomes obvious from Benary's experiments that the α or γ carbon that is to be substituted in the final product determines the initial reactants. That is to say that if the γ carbon were to be substituted in the final product, a substituted α halogenic acid halide must be used in the condensation. If a subsituted α carbon is desired then variations in the structure of the condensing agent are necessary, depending upon the amount of substitution desired. The only stipulation on the structure of the condensing agent is that the condensation must occur at the α carbon. For this to occur the metallic atom, for instance sodium, must be bonded

to this carbon in the original molecule.

At about the same time that Benary was developing his synthetic methods of preparation of the tetronic ring system, Anschütz and Böeker[14] found that they could condense acetyl mandelylchloride with a sodio malonic ester to obtain the tetronic system. It should be evident that this is just a variation of Benary's method. The only difference between the two is that acetyl mandelylchloride is used instead of an α-halogeno acid halide. Thus the same stipulations about substitution on the α or γ carbons apply here also.



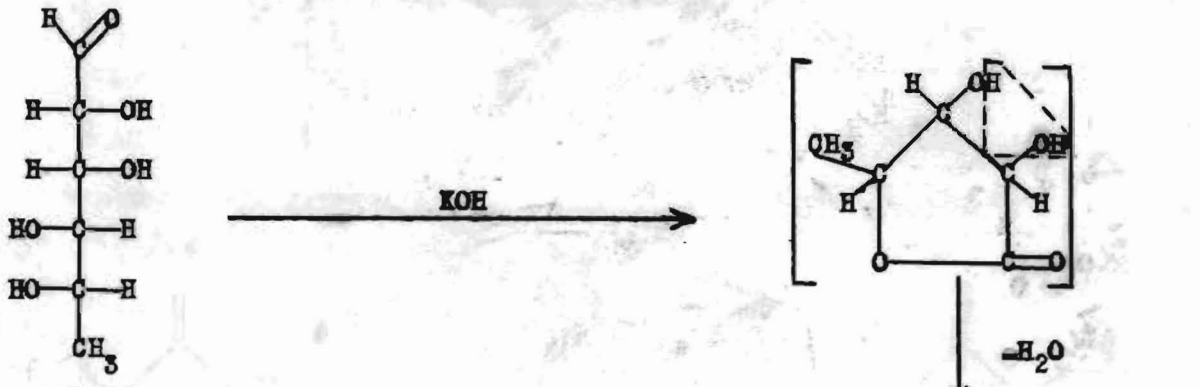
acetyl mandelylchloride

sodio diethyl malonate

γ-phenyl tetronic acid

(14) Anschütz, R., and Böeker, R., Ann., 368, 53, (1909).

In the early 1920's Hudson and Chernoff[15] took advantage of the fact that oxidation of pentoses results in a lactone structure. Since tetronic acids are variations of a β keto γ lactone, these two men proposed that by oxidizing rhamnose they would obtain γ-methyl tetronic acid, and they did.



rhamnose

γ-methyl tetronic acid

A decade later Fritz Micheel and Fritz Jung[16] synthesized α-hydroxy tetronic acid. They did this by performing a Claisen condensation on two molecules of benzoyl ethyl glycolate, and then inducing the product to undergo ring closure in potassium ethoxide. A Claisen condensation is similar to an aldol condensation, except that it is a condensation between two esters, each having a carbonyl group with hydrogens on the carbon α to it.. The best yields are obtained when two of the same ester

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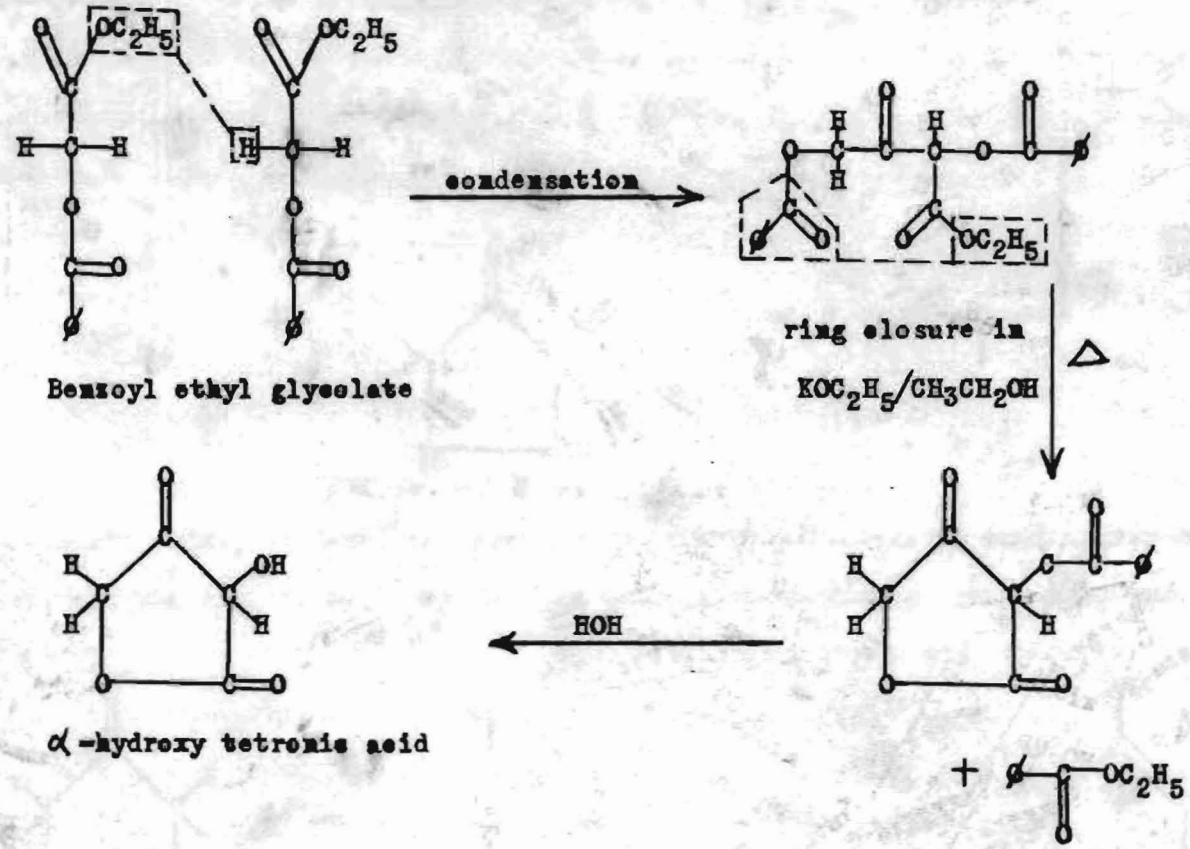
(15) Hudson, C. S. and Chernoff, C. H., J. Am. Chem. Soc., 40, 1006, (1918).

(16) Micheel, F. and Jung, F., Ber., 66B, 1291, (1933).

molecules having two ∝ hydrogens apiece are condensed.



Benzoyl ethyl glycolate

∝-hydroxy tetronic acid

In 1954 Lacey,[17] using a form of a Claisen condensation called a Dieckmann cyclization, developed a new method of synthesizing ∝-acetyl tetronic acids directly from the acetoacetates of ∝-hydroxy esters. The difference between a Claisen condensation and the Dieckmann cyclization is that the latter is a special case of the former, in which the condensation is usually between diesters or ketoesters and usually results in a cyclic structure as shown on the following page.

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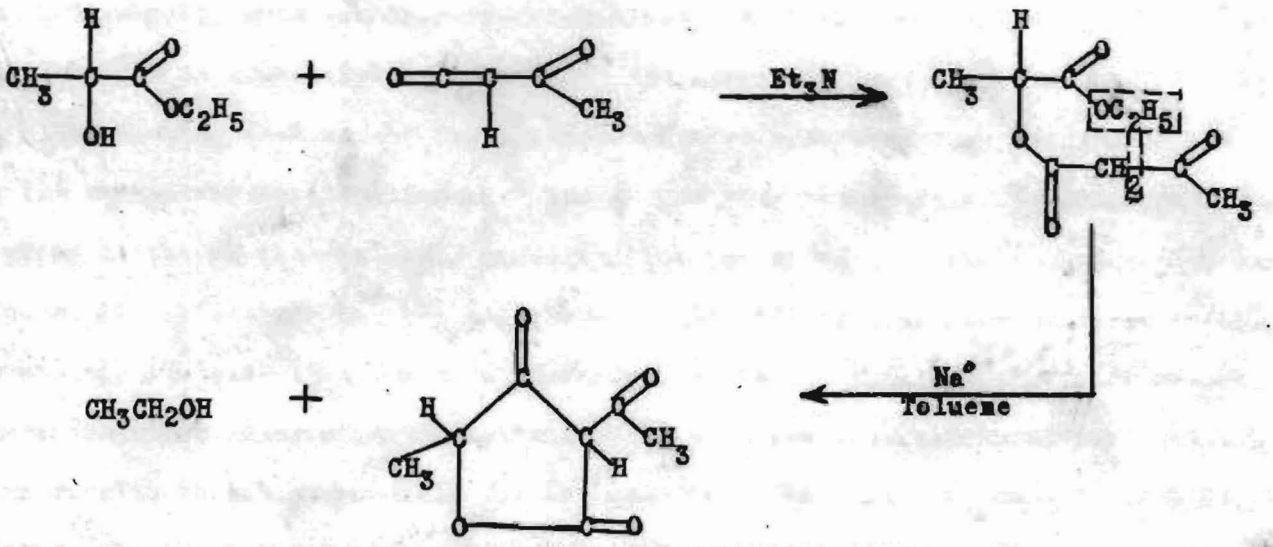
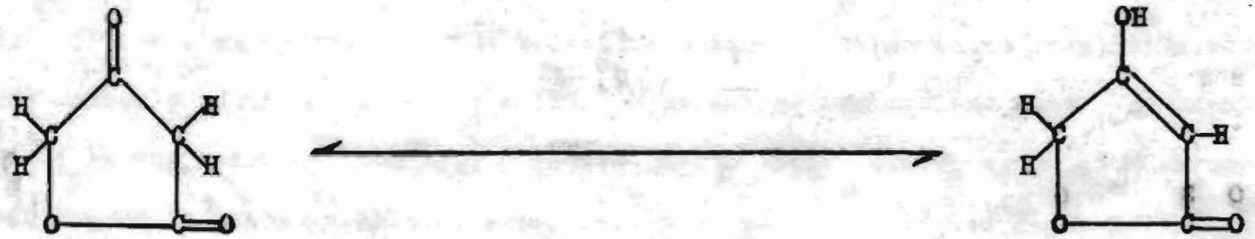
(17) Lacey, R. N., J. Chem. Soc., 832, (1954).



∝-acetyl-δ-methyl tetronic acid

Tetronic acids, as mentioned previously, exist in tautomeric equilibrium between the keto and the enol forms. Why is such an organic structure, which does not contain



an organic acid grouping, an acid? The acidity of the tetronic acids is due to the easily ionizable hydrogen of the enol form, especially since most tetronic ring systems exist mainly in the enol form. The ionization proceeds to such an extent that tetronic acid is comparable in strength to several carboxylic acids.(18)

Other systems have enolizable hydrogens and yet their acid strength may be no where near that of tetronic acid, why then is the tetronic acid system so strongly acid? According to Kumler(18) there are three possible reasons explaining the strong acidity. These are (1) the ring structure of tetronic acid enables a group to set

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(18) Kumler, W. D., J. Am. Chem. Soc., 60, 859, (1938).

on the ionizable hydrogen from two directions, (2) the ring could open and the acidity could be due to a carboxyl hydrogen, (3) resonance considerations.

Considering each one of these effects Kumler concludes that the answer lies in the resonance stabilizations. Although the ring structure of tetronic acid enables a group to act on the ionizable hydrogen from two directions and although this increases the acid strength, the magnitude of this effect could not be large enough to explain the exceptional acidic character of the tetronic system. Furthermore, there are three lines of evidence indicating that the possibility of the lactone ring opening is not responsible for the acidity. The first of these is that if the ring opened two dissociation constants would be expected, one due to the carboxyl group and one due to the enol hydrogen of the hydroxyl group; but research has shown only one dissociation constant. Secondly, evidence was obtained for the existence of ions of the sodium salts of tetronic, α-bromo tetronic and α-iodo tetronic acids. If the ring opened then the molecular weight of these salts should increase by one molecule of water, however, molecular weight determinations showed no such increase in the weight of the ions. Lastly, the p-nitro benzyl ester of α-bromo tetronic acid is not a carboxylic ester, which it should be if the lactone ring opened. This eliminates all explanations of the acid strength of tetronic acid except that one dealing with resonance stabilizations.

In considering resonance as a factor in increasing the acid strength of the tetronic ring system, it is difficult to see why such a system is more acidic in character than similar systems such as diethyl dihydroxy malonate or acetoacetic ester. However, according to Micheel and Schulte[19] there is some doubt as to whether the hydroxyl group in α-hydroxy tetronic acid is on the α or β carbon. According to the acylous or negative character of the nearby groups, the hydroxyl

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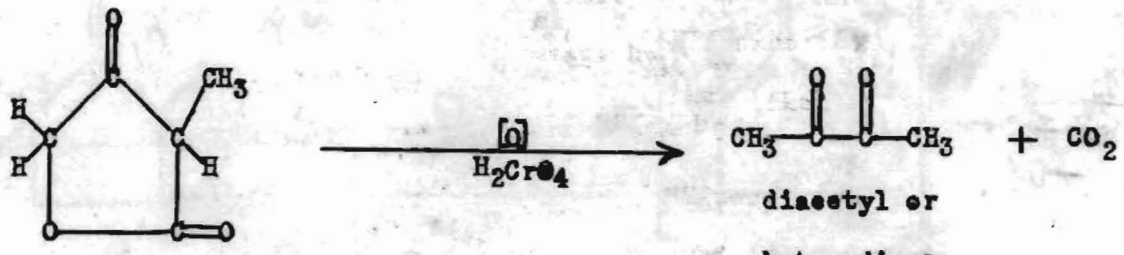
[19] Micheel, F. and Schulte, W., Ann., 519, 70, (1935).

group if it was on the α carbon would be a strong acid, since it would have acylous groups on either side of it. However, if the hydroxyl group was on the β carbon then there would be a negative grouping on one side only, and thus this structure would be a weaker acid. This problem, of where the hydroxyl group actually is, when looked at with resonance in mind gives a different answer. If the hydroxy group was on the α carbon then the resonance structures possible would be highly improbable. If the hydroxy group was on the β carbon then there are two possible resonance structures as a result of the dissociation of the hydrogen. These structures would stabilize the negative charge of the ion about evenly between the two oxygen atoms, and thus make the β hydroxy structure the more acidic form. Although there seems to be some controversy, resonance appears to be the most logical explanation of the unusual acidity of the tetronic acids.

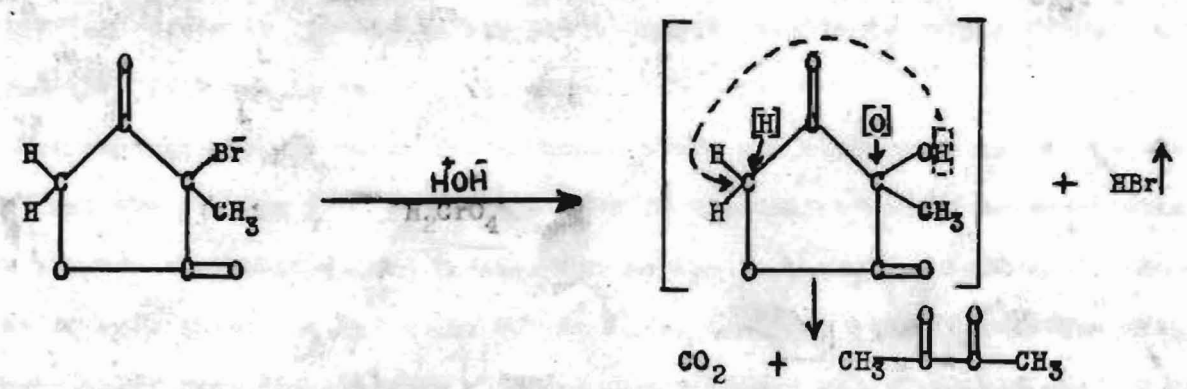
It was mentioned earlier that the proof of the tetronic acid structure was largely due to Wolff's experiments. One of the experiments he performed was the oxidation of the acid ring. If a closer look is taken at this reaction it is not



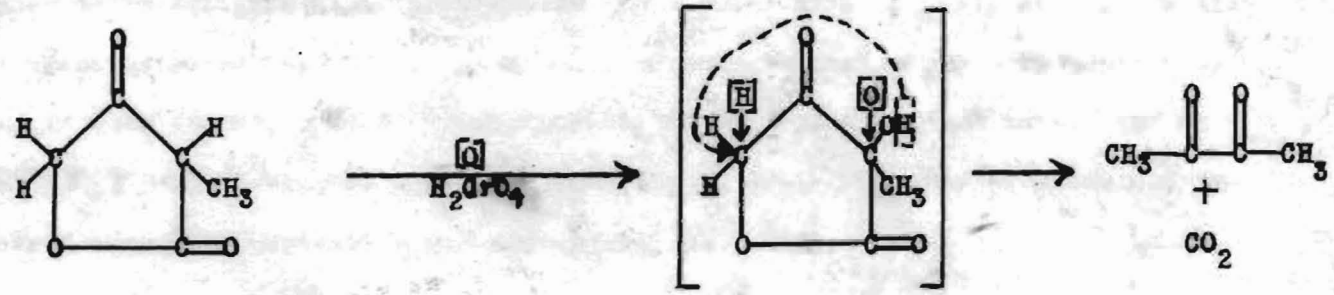
α-methyl tetronic acid

diacetyl or butanedione

all so simple as it seems. In order for diacetyl to be liberated from the tetronic ring, somehow the $-CH_2-O-$ grouping must be reduced to a CH_3 group, and the hydrogen on the α carbon atom must be oxidized to a carbonyl group $\rightarrow C=O$. In other words oxidation must occur at the α carbon while reduction occurs at the γ carbon, thus splitting out carbon dioxide when the ring opens. Wolff found this peculiar oxidation mechanism difficult to explain. However, he noticed that the α -bromo-α-methyl tetronic acid on oxidation and acidification yielded the same products as the α -methyl tetronic acid. He further observed that the bromo derivative on standing in water liberated hydrogen bromide. He proposed that a hydroxyl group, OH^-, took the place of the bromine atom, and then the hydrogen of the hydroxyl group rearranged to the γ carbon. Thus when the ring opened carbon dioxide and diacetyl were liberated. Wolff proposed that the oxidation of α -methyl tetronic acid was



entirely analogous to the above mechanism.



After Wolff's work, which was a good proposal, but failed to prove anything, hardly anyone did any research on this oxidative mechanistic problem until the late 1940's and early 50's. The first real work on this peculiar mechanism was done by Patterson.[20] She synthesized α,γ -dimethyl tetronic acid and oxidized it with chromic acid. The products were those predicted by Wolff's theory of α oxidation and γ reduction. However, the same products would have resulted if the γ carbon was oxidized and the α carbon was reduced. Consequently she synthesized α-ethyl tetronic acid and oxidized it to obtain the products, which were again in agreement with Wolff's proposal. Her work provided general evidence for Wolff's idea, but as she pointed out, "Further work is necessary before any final mechanism can be proposed for this remarkable oxidation. It seems probable that there must be some sort of prototropic shift in the molecule to account for the reduction of the —CH_2O— group, but how the oxygen is removed before the hydrogen goes in is very difficult to explain."[20] This was indeed a problem.

Fortenbaugh took up where Patterson left off and elaborated on the problem. He defined the problem as "(1) to show that in the oxidation of these tetronic acids there are two simultaneous and independent mechanisms, (2) to discover if the oxidation of the α carbon and the reduction of the γ carbon is a general reaction when tetronic acids are oxidized with chromium trioxide and sulfuric acid, and (3) to investigate the mechanism of the reaction whereby carbon dioxide is eliminated."[1] In order to investigate these problems he synthesized nine tetronic acids. He prepared these acids so that he had an α-mono substituted, an α,α -disubstituted, a γ -mono substituted, a γ,γ -disubstituted, an α,γ -mono substituted, and an α-mono-γ,γ -disubstituted acid. He was able to prove that two separate and independent reactions, oxidation and hydrolysis, did exist.

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[20] Patterson, H. R., "Some α-Halo-β-Keto Esters and Their Derived Tetronic Acids" (unpublished Master's dissertation, Middlebury College, 1946), p.28.

In a paper by Reid, Fortenbaugh, and Patterson[21] a substantiated explanation for the oxidation of tetronic acids was put forth. There are in fact three types of tetronic acids; those being substituted only on the α carbon, those substituted only on the γ carbon, and those being substituted on both the α and the γ carbons. From the oxidation products of these three types of tetronic structures it becomes evident that the formation of diketones, such as butanedione, is not a general reaction. The first requirement for the production of α diketones is the presence of an enolizable hydrogen. When the α carbon is monosubstituted, oxidation occurs at the α carbon and reduction at the γ carbon and α diketones are produced. When the α carbon is disubstituted there is no enolizable hydrogen present, and a deep seated degradation occurs and the products are those of the hydrolysis reaction. When the γ carbon is monosubstituted then oxidation takes place at the γ carbon and reduction at the α carbon, thus α diketones are the products of the reaction. When the carbon is disubstituted a degradation occurs and α diketones are not produced. When both the α and the γ carbons are substituted, then, no matter what the substitution at the γ carbon as long as the α carbon is monosubstituted, α diketones will be produced by oxidation. When disubstitution occurs at both the α and γ carbons, there is no enolizable hydrogen available and a deep set degradation producing products other than α diketones would be expected. Furthermore, by using a neopentyl rearrangement, Fortenbaugh[1] was able to show that the elimination of carbon dioxide does not occur by means of an ionic mechanism, but does probably occur by means of a free radical mechanism. If the loss of carbon dioxide occurred by a radical mechanism, then the oxidative intermediate (X) should occur before the ring is broken to split out carbon dioxide and the α diketone. (See the following page for the structure of the intermediate.)

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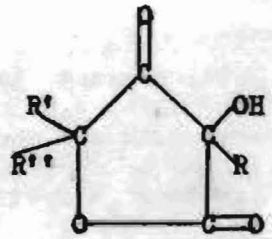
(21) Reid, E. B., Fortenbaugh, R. B., and Patterson, H. R., J. Org. Chem., 15, 572, (1950).



X

where R, R', and R'' do not have to the same, and R does not equal a hydrogen

Reid, Atwater, and Gompf[22] later worked on Wolff's idea of the similarity of the oxidation of tetronic acids to that of the bromo tetronic acids. They found the oxidation of the bromo derivatives to be completely analogous to that of the tetronic acids, just as Wolff suggested.

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[22] Reid, E. B., Atwater, N. W., and Gompf, T. E., J. Org. Chem., 16, 1566, (1951).

PRESENT INVESTIGATION

The foregoing research helps to clarify the mechanism of the oxidation of tetronic acids, but the oxidative intermediate(X) has never been proven to exist. Circumstantial evidence, however, does point strongly towards its existence. This investigation is concerned with the possibility of synthesizing and isolating this general oxidative intermediate, for if this α-hydroxy compound could be isolated and then oxidized the products of the reaction would either substantiate or refute the present postulated mechanism. If the products of such a reaction were carbon dioxide and an α diketone, then the existence of the hydroxy compound as the intermediate would be proven. If other products were obtained from the oxidation, then the this compound would not very likely be the oxidative intermediate. In either case something positive is gained towards a definite answer to the question.

It was mentioned previously that α-hydroxy tetronic acid had been synthesized, however, no oxidation products were reported by Micheel and Jung.[23] Since this particular acid contains neither α or γ alkyl substitution, which is the basis for the theory proposed by Reid et. al.;[21] oxidation of it would neither confirm nor disprove their theory. There is as yet no mention in the literature of an α or γ substituted-α-hydroxy tetronic acid.

For this investigation two different synthetic routes leading to an α-alkyl-α-hydroxy tetronic acid were established. A third method, using sodium triphenyl as a condensing agent for two molecules of ethyl-α- benzoxy-α-methyl acetate, was discarded because according to Micheel and Jung[16] this condensation will not occur when sodium is used. It might be possible to use metallic pottssium as the condensing agent, but then the reaction takes on an explosive nature.

The first of the synthetic approaches involves the synthesis of α-ethyl tetronic

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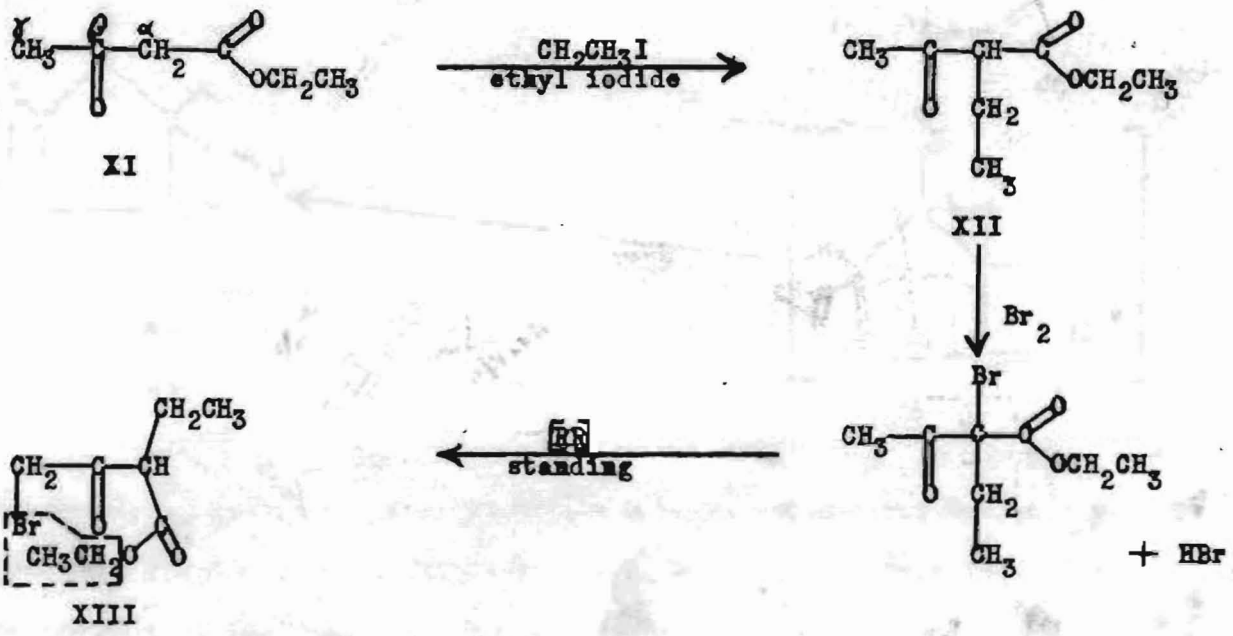
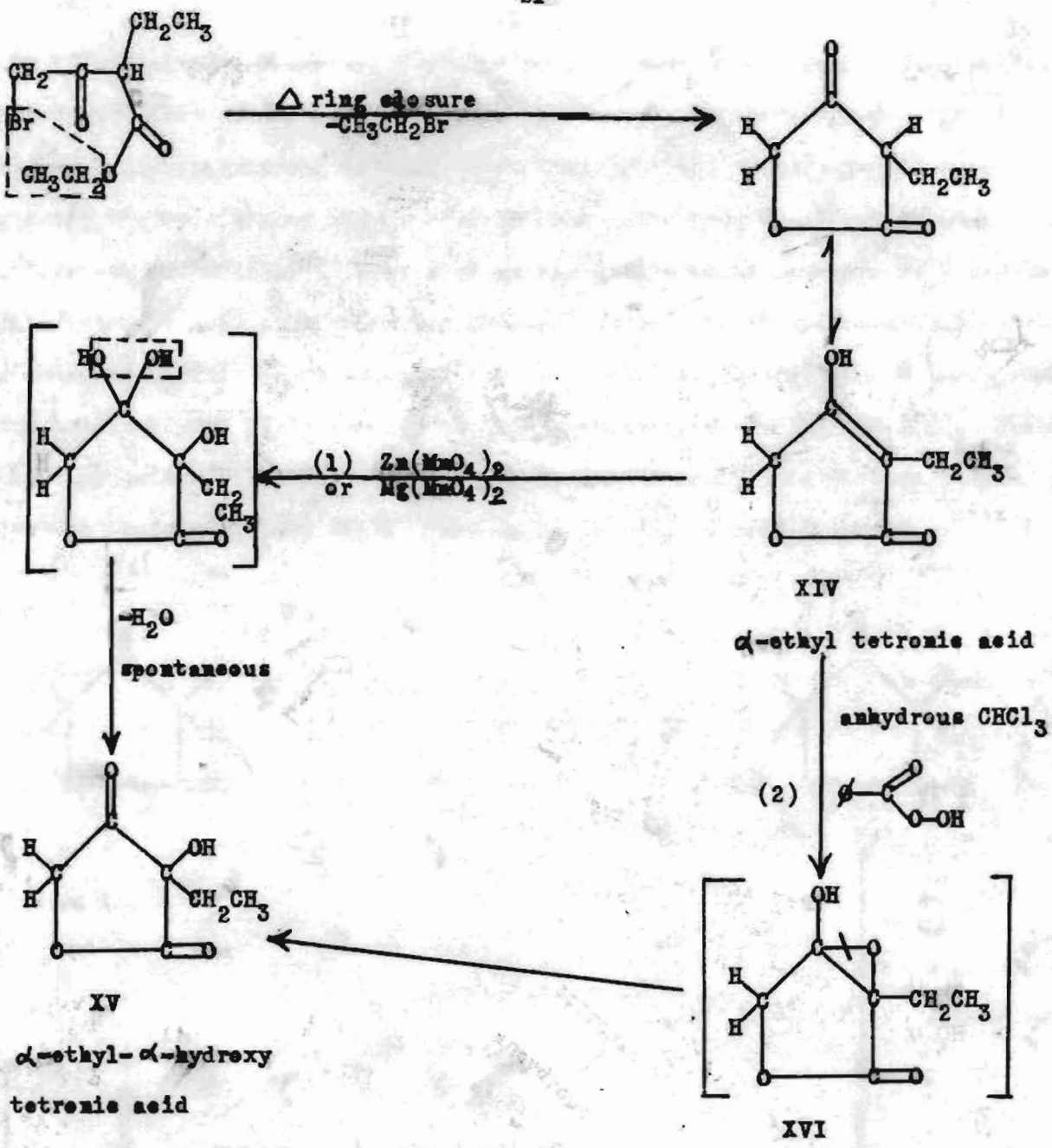
(23) Micheel, F. and Jung, F., Ber., 67 B, 1660, (1934).

acid. This is a standard synthesis in which ethyl acetoacetate (XI) is alkylated in the α position using ethyl iodide. The α-ethyl product (XII) is then brominated in the α position and allowed to stand so that the bromine will undergo rearrangement to the δ position to yield α-ethyl-δ-bromo acetacetic ester (XIII). This product undergoes cyclization when heated, to give α-ethyl tetronic acid (XIV). Using this product, two possibilities exist for obtaining the sought after α-ethyl-α-hydroxy tetronic acid (XV). The first involves the use of zinc or magnesium permanganate to hydroxylate α-ethyl tetronic acid. The zinc or magnesium used would form zinc or magnesium hydroxide, thus preventing the hydrolysis of the tetronic acid to 2,3-pentanedione. The second possibility lies in the reaction of perbenzoic acid in anhydrous chloroform with the above mentioned product (XIV). This reaction might result in an ethylene oxide structure (XVI) involving the α and β carbons of tetronic acid. This would subsequently break open to yield the α-ethyl-α-hydroxy tetronic acid (XV).



XI XII XIII



XIV

α-ethyl tetronic acid

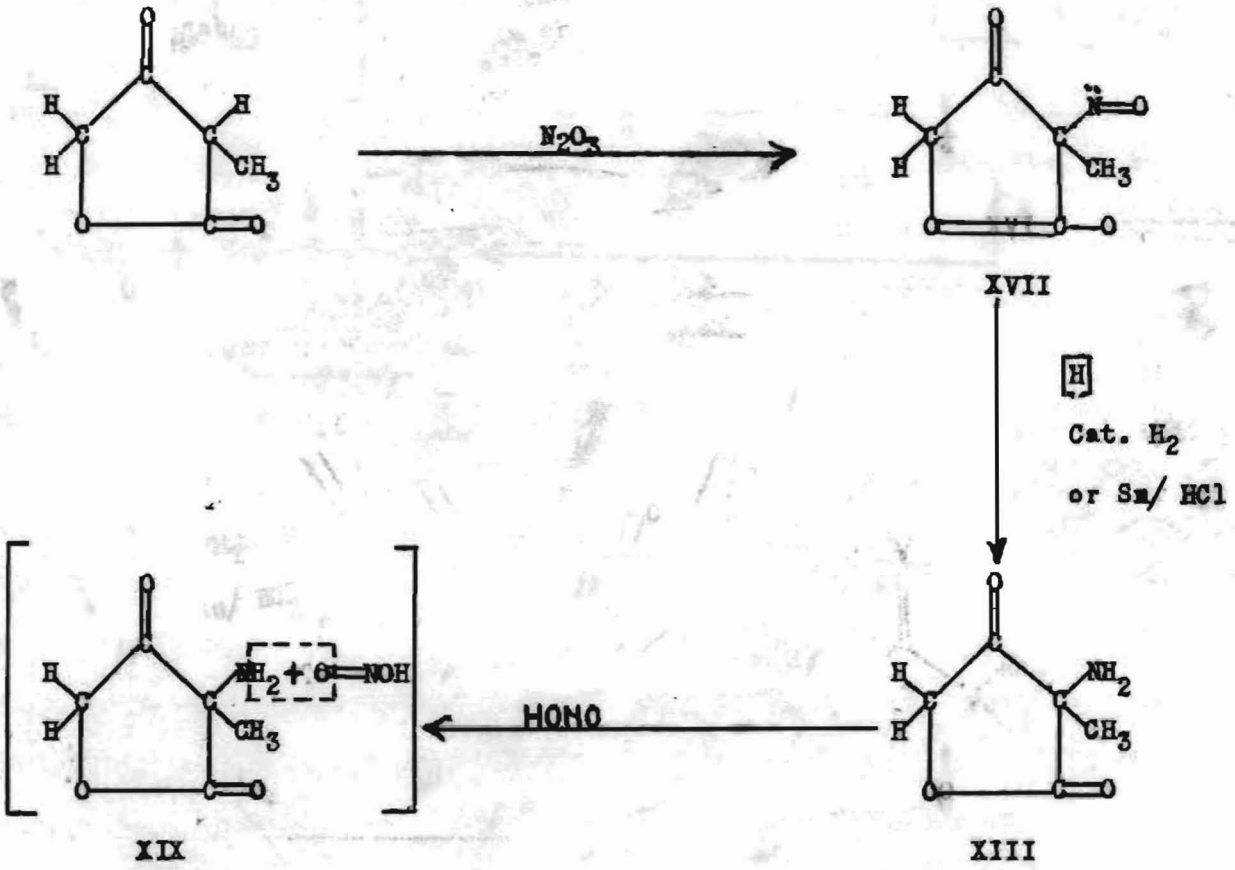
XV

α-ethyl-α-hydroxy tetronic acid

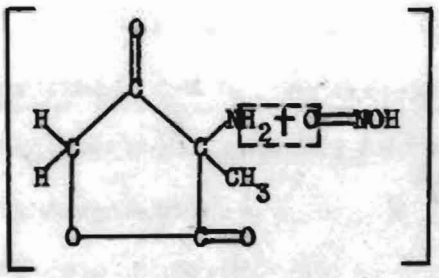
XVI

The remaining possible synthesis of the α-alkyl-α-hydroxy tetronic acid is described here for the sake of future research, although due to a lack of time, no work was done on it.

In this synthesis α-methyl tetronic acid is made in the same manner as α-ethyl tetronic acid described previously. It is then reacted with nitrogen trioxide to give α-methyl-α-nitroso tetronic acid (XVII). This product on hydrogenation using catalytic hydrogen or tin in hydrochloric acid gives α-methyl-α-amino tetronic acid. Micheel and Mittag[24] have also prepared this amino compound by reducing α-nitro tetronic acid with molecular hydrogen using palladium as a catalyst. The amino compound (XVIII) on reaction with nitrous acid should give the α-methyl-α-hydroxy tetronic acid (XXI) through the intermediate steps (XIX) and (XX). Whether this hydroxy acid will be isolateable in this acid solution, or whether it will be oxidized to the α diketone (XXII) remains to be seen on experimentation.

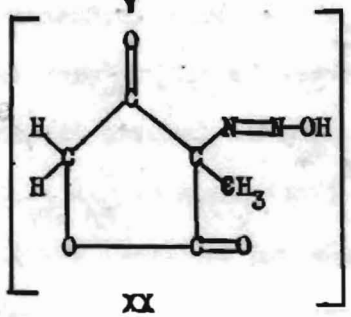


(24) Micheel, F. and Mittag, R., Z. Physiol. Chem., 247, 34, (1937).



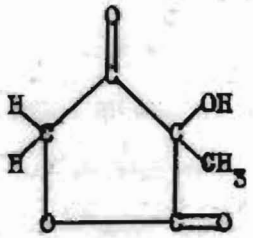
XIX

$-H_2O$



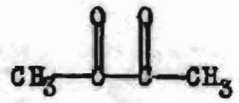
XX

$-N_2$



XXI

(isolate?)

CO_2 + 

XXII

butanedione

EXPERIMENTAL PROCEDURE AND OBSERVATIONS

1-Preparation of α-ethyl acetoacetic ester

Patterson's[24] adaptation of the method given in Organic Syntheses[25] was used in this preparation.

40 gms. of freshly cut sodium is placed in a 3-neck, 2-liter, round bottom flask, which is fitted with a mechanical stirrer, a dropping funnel, and a reflux condenser with a $CaCl_2$ drying tube at the top. Since the reaction is exothermic, all connections must be air tight to avert the possibility of a hydrogen explosion. The stirrer is started and kept running for the duration of the reaction, and 600 ml. of absolute alcohol is added slowly over a 20 minute period. The flask is kept cooled in an ice bath until the initial reaction has subsided. It was necessary to heat the flask on the steam bath in order to effect complete dissolution of the sodium. The sodium does not dissolve completely by itself due to the coating of sodium ethoxide which is formed on it, thus preventing it from further reaction. It might be possible to avoid this difficulty by slicing the sodium into thin strips.

After all of the sodium has dissolved, 221 gms. of ethyl acetoacetate (b.p. 102-103°C), diluted with alcohol, is added to the solution slowly from the dropping funnel. Again the flask must be cooled due to the exothermic nature of the reaction. After this addition is complete, 265 gms. of ethyl iodide are added over a 30 minute period to the reaction mixture from the dropping funnel. Once this addition has been completed, the mixture is refluxed until it is neutral to litmus (about 3½ hrs.).

At the end of this time the reflux condenser is replaced by distilling apparatus, and the excess ethyl alcohol (about 300 ml.) is distilled over from the orange sol solution. The residue is decanted from the precipitated sodium iodide into a

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(25) Organic Syntheses, Coll. Vol. I, John Wiley and Sons, Inc., New York, 248, (1941).

separate flask. The sodium iodide is rinsed once with some cold distilled water and the wash combined with the decanted liquid. Two layers are formed, a dark orange brown upper layer containing the α -ethyl ester and a light orange aqueous layer.

The two layers are separated and the aqueous layer is extracted three times with equal portions of benzene. The volume used per extraction is equal to about one third of the total volume of the aqueous layer. The benzene extracts are combined with the α -ethyl ester layer, and this solution is extracted with portions of water equal to one third of the total volume of the solution. The extractions are continued until a negative silver nitrate test is obtained on the solution. This indicates the absence of any sodium iodide.

The Beilstein test for halogen was found to be inapplicable for this purpose. Evidently it is specific for halo-organic compounds, but not for halo-inorganic salts.

The benzene, water, and α -ethyl ester mixture; which is now a greenish yellow and has a cheesy odor, is fractionally distilled under a vacuum produced by a water aspirator. Three fractions were collected. The first fraction, containing benzene, water, and unalkylated acetoacetic ester, was collected over a distilling temperature range of up to 45°C at 66 mm. pressure over an oil bath. The second fraction, cont. containing the α -ethyl ester was collected over the distilling temperature range 118-126°C at 66 mm. pressure, and an oil bath temperature range of 145-160°C. The distillate was colorless and had a distinct odor, but not the cheesy odor observed previously. The dialkylated acetoacetic ester was collected in the final fraction over the distilling temperature range 124-126°C at 66 mm. pressure and an oil bath temperature of 160-200°C.

Weight of the α -ethyl ester - 210.3 gms. Yield - 78%. B.p. 118-126°C at 66 mm. pressure. The product was colorless.

2-Bromination of α -ethyl acetoacetic ester

The α -ethyl acetoacetic ester obtained above was assumed to be 95% pure, and on this basis complete bromination would ensue if 200 gms. of bromine were added to the ester.

The α-ethyl ester was dissolved in an equal volume of chloroform and cooled in the refrigerator. This cooled flask was then placed in a $CaCl_2$ salt bath, and 200 gms. of bromine, diluted to four times its initial volume with chloroform, were added dropwise with stirring. After the addition is complete, stirring is continued until no more hydrogen bromide is evolved. The product is then washed three times with an equal volume of water to remove any dissolved hydrogen bromide. The α -bromo-α -ethyl ester is placed in the refrigerator overnight so that the bromine will rearrange to the γ position. The presence of the γ -bromo-α-ethyl ester can be detected easily due to its lachrymatory nature.

3-Preparation of α -ethyl tetronic acid

The chloroform solution of γ -bromo-α-ethyl acetoacetic ester, obtained from the preceeding procedure, was placed in a vacuum distillation apparatus and all of the chloroform possible distilled off at 61°C and 1 atmosphere pressure. This distillation caused the solution to turn red. The remaining chloroform was distilled over at 30°C and 92 mm. pressure over an oil bath at 70°C. At the end of this distillation the solution had turned a dark orange brown, indicating the splitting out of ethyl bromide and cyclization of the ester to form the tetronic acid.

After all of the chloroform and probably some ethyl bromide had been distilled over, the oil bath was raised to 175°C and the distillation continued at 86.5°C; there was no readable pressure. The distillation was continued until there was no more ethyl bromide distilling over. Even though the receiving vessel was immersed in an icebath, all most all of the ethyl bromide was vaporized by the suction and

very little ethyl bromide was actually collected. The residue remaining after this distillation was a brownish-black, lachrymatory tar, which solidified on standing.

The mass was broken up, dissolved in hot chloroform, and norite added. The solution was filtered by suction, but inspite of repeated treatments with norite, it remained contaminated with the tar. Crystalization of the tetronic acid from this solution was possible only after most of the chloroform was evaporated and the solution seeded. Under these conditions, the crystals were highly contaminated with tar.

Several solvents were tested as to their ability to remove the tar from the tetronic acid. Carbon tetrachloride, a mixture of carbon tetrachloride and chloroform, and sodium carbonate were all tested. The tar proved to be acidic and thus the sodium carbonate was ineffective as a differential solvent. Chloroform proved to be the solvent best suited for the removal of the tar.

Finally, Patterson's method of extracting the acid from the tar with water was resorted to. This meant a reduction in the yield due to hydrolysis of the acid by water. In this extraction procedure the tar is dissolved in a two fold volume of chloroform, 100 ml. of distilled water is added to this solution, and the mixture is refluxed for 10 minutes at constant boiling. The time should be watched carefully, since extensive hydrolysis occurs if a longer reflux period is used. After the mixture cools down, the layers are separated and the aqueous layer is allowed to stand overnight in the refrigerator until crystallization has occurred.

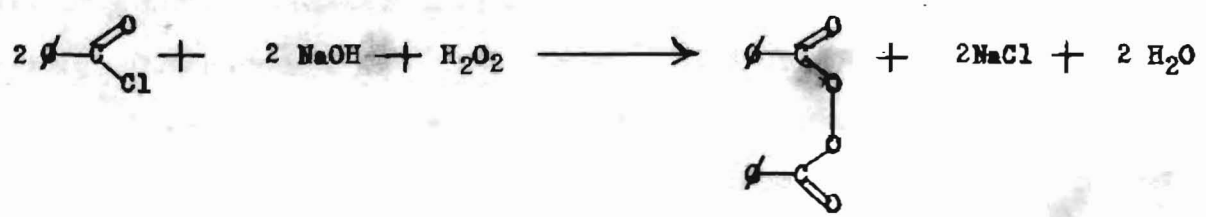
The whitish-tan crystals obtained from this layer can be recrystallized from a small volume of hot water, using norite and performing a hot suction filtration. The filtrate is then cooled immediately, but some hydrolysis to the α diketone does occur. An infrared spectrum was run on this tetronic acid for future identification purposes.

Weight of α -ethyl tetronic acid - 23.85 gms. Yield - 14.80%. M.p. 127-129°C. The pure product is obtained as white, crystalline plates.

The yield of α -ethyl tetronic acid is quite low, especially when compared with Patterson's yield of 50%. The low yield can be accounted for in part by the hydrolysis of the acid by water. This hydrolysis was observed in both the refluxing and recrystallization procedures. However, the main cause for the reduction in yield undoubtably lies in the amount of tar produced as a contaminant of the acid. This tar, although not identified, is probably a polymer of either α -bromo or γ -bromo-γ-ethyle acetoacetic ester. The tar retained its lachrymatory properties, but repeated attempts to cause further cyclization of it failed. The amount of tar produced is quite likely a function of the rate of addition of bromine to the unhalogenated α-ethyl acetoacetic ester, and the presence of some tar is inevitable. However, if the bromine is added very slowly, with constant stirring over a period in excess of 30 minutes, the production of the tar will probably be held to a minimum. Consequently the yield of the tetronic acid would be increased.

4-Preparation of Benzoyl Peroxide

The method given by Hickinbottom[26] is given here with a few minor adaptations. The equation for this synthetic reaction is:



200 ml. of 10% H_2O_2 is placed in a 3-neck, 1-liter, round bottom flask, which

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[26]Hickinbottom, W. J., Reactions of Organic Compounds, Longmans, Green and Co., New York, 231, (1946).

is fitted with two burets, a mechanical stirrer, and is cooled in an external ice bath. The mechanical stirrer is started and kept at high speed while 58 gms. of benzoyl chloride and 152 ml. of 15% sodium hydroxide are added from the burets at such a rate that both additions are completed simultaneously. The reaction mixture should be kept faintly alkaline through out the entire reaction. Under these conditions the white flocculent benzoyl peroxide forms immediately.

On completion of the reaction the mother liquor in the flask is decanted, filtered by suction and the filtrate discarded. The flask is placed on a steam bath and the benzoyl peroxide dissolved in a small amount of boiling ethanol. After the product has been removed, the flask is rinsed several times with hot alcohol. The alcoholic solution is then placed in the refrigerator overnight and the benzoyl peroxide allowed to crystallize.

The alcoholic solution containing the crystalline product is filtered, washed with cold water, and dried by suction. An increased yield of the peroxide can be obtained by concentrating the filtrate, however, evaporation of such a filtrate can lead to an explosion especially in the presence of halogen. The explosive nature of this evaporation can be circumvented by adding 100 ml. of distilled water to the alcoholic filtrate. The alcohol is then evaporated under suction and the benzoyl peroxide, which is insoluble in water, precipitates out and can be recovered by filtration.

Weight of benzoyl peroxide -34.79 gms. Yield -69.60% m.p. 102-104°C. Purity as ascertained by titration with 0.1 N sodium thiosulfate on two separate samples; 126.7%, 77.9%. The benzoyl peroxide is obtained as white, crystalline needles.

This particular synthesis of benzoyl peroxide is a perfectly good one, however, due to difficulties encountered in ascertaining the purity of the product, commercial benzoyl peroxide was used in the subsequent synthesis of perbenzoic acid.

Purity of commercial benzoyl peroxide as determined by titration with 0.1 N sodium thiosulfate 157%, 168%; m.p. 104-106°C.

5-Procedure for determining the purity of benzoyl peroxide

The procedure described here is the same as that described in Organic Syntheses(27)

0.5 gms. of benzoyl peroxide is dissolved in 15 ml. of chloroform in a 300 ml. Erlenmeyer flask. The flask and its contents are cooled to -5°C. in an ice salt bath and 25 ml. of 0.1 N ice cold sodium methoxide solution is added at once with cooling and shaking. The solution is allowed to stand at -5°C. for 5 minutes, and then 100 ml. of ice water, 5 ml. of 10% sulfuric acid, and 2 gms. of potassium iodide in 20 ml. of 10% sulfuric acid are added in that order with vigorous and continuous stirring by a mag-mix. The solution is titrated with 0.1 N sodium thiosulfate to the disappearance of the iodine color.

6-Preparation and standardization of 0.1 N sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$)

The procedure outlined here can be found in Quantitative Chemical Analysis(28) with a more detailed discussion.

1200 ml. of distilled water is boiled in a 2-liter Erlenmeyer flask and then cooled with running tap water. 200 ml. of the boiled water is used in two separate portions to wash out a previously rinsed 1-liter volumetric flask. 25 gms. of sodium thiosulfate is dissolved in the remaining liter of boiled water and the solution transferred to the volumetric flask. The sodium thiosulfate should be

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(27) Organic Syntheses, Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, 431, (1956).

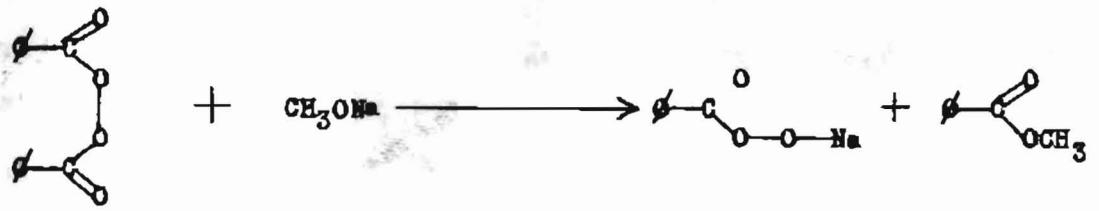
(28) Hamilton, Leicester F., and Simpson, Stephen G., UQuantitative Chemical Analysis, 12th ed., The Macmillan Company, New York, 263, (1959).

neutral or slightly alkaline; if it is not, then small increments totaling up to 0.1 gm. of sodium carbonate is dissolved in the solution to bring it to a neutral pH.

The sodium thiosulfate is then standardized against potassium iodate as follows. Duplicate 0.1000 gm. samples of pure potassium iodate, that has been dried at 100°C. for an hour are weighed out into 250 ml. beakers. The samples are dissolved in 50 ml. of distilled water and 10 ml. of a 30% potassium iodide solution are added to the samples. This is followed by the addition of 20 ml. of 6N sulfuric acid. The solution is allowed to stand for three minutes in the dark, and then diluted to 150 ml. with distilled water. Sodium thiosulfate is added from a buret until the iodine color has almost been dissipated. 5 ml. of starch indicator are added and the titration completed by the addition of titrant until the color of the indicator has just disappeared. The normality of the thiosulfate is calculated from the weight of the sample and the volume of sodium thiosulfate added.

7-Preparation of perbenzoic acid

The synthesis, as reported in Organic Syntheses,[27] proceeds as shown by the following equations.



2.6 gms. of sodium is dissolved in 50 ml. of absolute methanol in a 300 ml. Erlenmeyer flask with moderate cooling. The resulting sodium methoxide solution is cooled to -5°C. in an ice salt bath. 25 gms. of the pure benzoyl peroxide prepared

above is then dissolved in 100 ml. of chloroform and this solution cooled to 0°C. After the benzoyl peroxide attains this temperature it is added immediately to the sodium methoxide solution with constant shaking and cooling so that the temperature does not exceed 0°C. A milky white solution results, and contrary to Organic Syntheses turns into a white slush. This slush is transferred to a 500 ml. separatory funnel where it is extracted with 250 ml. of cold water containing chopped ice.. Two layers result and the chloroform layer is removed. The remaining aqueous layer is extracted twice with 50 ml. portions of chloroform in order to remove the methyl benzoate in solution. Perbenzoic acid, present in the aqueous solution as its sodium salt, is liberated by the addition of 113 ml. of cold 1N sulfuric acid. The white flocculent precipitate which results is extracted three times with 50 ml. portions of chloroform, which dissolves the perbenzoic acid. The chloroform extracts are united and washed twice with 25 ml. portions of water. Two, 3 ml. portions of the moist chloroform solution are taken for duplicate active oxygen determinations and the remainder of the perbenzoic acid solution is transferred to a dark bottle and stored in the freezer.

The active oxygen determination is carried out by dissolving 2 gms. of sodium iodide in 50 ml. of water. 5 ml. of both glacial acetic acid and chloroform are added to this solution followed by the addition of 3 ml. of the chloroform solution containing the perbenzoic acid. The solution is stirred vigorously with a magnetic stirrer and the iodine liberated titrated with 0.1N sodium thiosulfate solution to the complete disappearance of the iodine color. 1 ml. of the sodium thiosulfate solution is equivalent to 0.0069 gm. of perbenzoic acid and according to Organic Syntheses 1 ml. of the perbenzoic acid solution requires about 13 ml. of titrant.

The perbenzoic acid solution prepared from the previously synthesized benzoyl peroxide required 2.67 ml. and 2.61 ml. of titrant per milliliter. The synthesis was repeated using commercial benzoyl peroxide as the starting material, but again the ratio of titrant to perbenzoic acid solution was extremely low. A review of the literature for another method of synthesizing perbenzoic acid led to the

disclosure that while the method described above yields perbenzoic acid, it is a difficult method to reproduce and the yields are low. Due to this latter reason the decision was made to attempt the synthesis of α-ethyl-α-hydroxy tetronic acid by means of the magnesium permanganate method.

8-Oxidation of α-ethyl tetronic acid with magnesium permanganate

The reaction as formulated proceeds according to the following equation.

$$\alpha\text{-ethyl tetronic acid} + Mg(MnO_4)_2 + H_2O \longrightarrow \alpha\text{-ethyl-}\alpha\text{-hydroxy tetronic acid} + MnO_2 + Mg(OH)_2$$

3.00 gms. of magnesium permanganate, which represents a 10% excess of the stoichiometric amount required for the reaction, is dissolved in 30 ml. of distilled water which has been boiled to remove the dissolved carbon dioxide. 4 gms. of α-ethyl tetronic acid is dissolved without heating in an excess of distilled water which has also been treated to remove the dissolved carbon dioxide. The solution of tetronic acid is transferred to an 800 ml. beaker and cooled to 0°C. in an ice salt bath and the stirrer is started. Magnesium permanganate is added dropwise from a buret to this solution. Each succeeding drop is added only after the characteristic permanganate $\overset{\text{color}}{\wedge}$ of the previous drop has been dissipated. After the stoichiometric amount of permanganate has been added the titration is stopped and the reaction mixture filtered by suction to remove the precipitated manganese dioxide. The titration is then continued dropwise until further addition of permanganate gives the solution a faint pink color which persists for a minute or more. The solution is then filtered by suction and placed in an evaporating dish in the air.

The initial aqueous solution of tetronic acid is acidic, pH≅ 2, but as the magnesium hydroxide is formed in solution the pH rises rapidly to 5 and the manganese dioxide which is quite insoluble precipitates out. However, there is only a very slow rise in pH with further addition of permanganate and the final pH≅ 6. Once a neutral pH is reached any further addition of permanganate should make the

solution alkaline and the magnesium hydroxide should precipitate. However, no magnesium hydroxide was observed to precipitate and its contaminating presence was indicated later by an ignition test on an oil recovered from the oxidation solution by evaporation.

9-Isolation of the oxidation products.

5 ml. of the oxidized solution were evaporated on a steam bath to yield a small amount of yellow oil with a distinct caramel odor. This oil was solidified by covering it with petroleum ether; as the ether evaporates it exerts a cooling effect on the oil which along with scratching produces solidification. The solid was also yellow in color and maintained its caramel odor. An ignition test on this solid indicated the presence of magnesium, but it was believed that its presence would not interfere with the infrared spectrum which was subsequently run on the material. The solid formed a phenylhydrazone which decomposed at 76-77°C. and which on recrystallization from ethyl alcohol formed a tar.

The large scale evaporation in air produced a substantial amount of the same yellow, caramel smelling oil. On further standing this oil became tacky and started to solidify. As the solidification proceeded bubbles began appearing in this amorphous substance. These bubbles were attributed to the decarboxylation of the substance. The resulting decarboxylation product was yellow, brittle and flaky as well as having a slight caramel odor. The substance did not form a dinitro phenyl-hydrazone so an infrared spectrum was run on this product for comparison purposes.

A second permanganate oxidation was performed on another 4 gm. sample of α-ethyl tetronic acid. However, this time 300 ml. of the final oxidized solution was taken and a constant ether extraction was performed in order to obtain some of the product free from magnesium. The ether was placed in a three neck flask and distilled into a second three neck flask containing the material to be extracted. The resulting solution was stirred and as the ether filled the second flask, a

point was reached where the ether layer began to flow from the second vessel through some tubing back into the first vessel. The ether which flowed back would then be distilled through the same cycle again, but the material extracted by the ether would not volatilize with it and consequently was collected in the first flask. After the extraction had been run for some time it was stopped and the ether layer in the second flask separated from the aqueous layer and combined with the ether in the first flask. This ether solution was then evaporated in the air as was the aqueous layer. The evaporation of the ether solution yielded a dark yellow oil with a slight caramel odor. This oil, however, did not undergo solidification or decarboxylation on standing. The oil boiled between 108-112°C. as determined by a micro boiling point determination. It apparently did not form a dinitro phenylhydrazone. An infrared spectrum was run on this oil for comparison purposes.

CONCLUSION

Possible Compounds for the Unknown Products and Spectra Analysis

It is quite probable that the reaction of α-ethyl tetronic acid with magnesium permanganate yields the desired α-ethyl-α-hydroxy tetronic acid. However, the problem is still one of isolating this compound in sufficient quantity for a chemical analysis. The problem is complicated by the ease with which this compound reacts to yield the corresponding diketone as well as by its apparent decarboxylation as it is concentrated in almost neutral solution. The yellow, caramel smelling oil is believed to be the desired α-ethyl-α-hydroxy tetronic acid and its spectrum is presented on plate 2.

The spectrum of α-ethyl tetronic acid, plate 1, is characterized by the broad absorption region between 3 and 4 μ, the slight sharp dip at 5.8 μ followed by the absorption area at 6.1-6.5 μ, the upside down "W" absorption at 13.7-13.9 μ which appears on all of the spectra and may be attributed to the polyethylene film used. The presence of so many peaks and valleys in this and subsequent spectra is due to the fact that there are several absorbing groups present in each molecule and these interact to give overtones and a general "fuzziness" to the spectra.

The first absorption region for α-ethyl tetronic acid, 3-4 μ, is due to the tautomeric secondary alcohol group. That this absorption region is shifted from its normal 2.75-3.25 μ region is a result of the fact that it is in tautomeric equilibrium. The slight dip at 5.8 μ is characteristic of the carbonyl group and its weakness is possibly explained by the fact that the carbonyl group is also involved in the tautomeric equilibrium. The broad absorption band from 6.1 to 6.5 μ is interesting because it is due to the equilibrium which exists between the enol and the keto forms of α-ethyl tetronic acid. In this respect the absorption

here is in agreement with those values reported by Rasmussen, Tunnicliff, and Brattain.[29]

Spectrum number 2, which is believed to be that of the α-ethyl-α-hydroxy tetronic acid is characterized by absorption regions at 3.5 μ, 5.8 μ, 7.8 and 8.9 μ, and 9.3 μ and 13.8-13.5 μ. The last two regions are in all likelihood due to ring strain and the various rocking and bending motions of the molecule. The absorption at 3.5 μ is probably due to the new tertiary hydroxyl group on the α carbon, but it is shifted from its normal wavelength probably because of the absorbing environment of the carbonyl groups on either side of it. The absorption regions at 7.8 μ and 8.9 μ are overtones of this same tertiary hydroxyl group, and these wavelengths are also slightly shifted from their normal values. The absorption at 5.8 μ is quite strong and characteristic of the carbonyl group. It is important to note that the enol-keto absorption region, 6.1-6.5 μ, is missing. This observation is in complete accord with the fact that the α-ethyl-α-hydroxy tetronic acid is incapable of this type of tautomeric equilibrium.

The absorption spectra of the unknown solid and the decarboxylation product are believed to represent the same compound. This compound is believed to be 1,3-dihydroxy-2-pentanone and would arise from a neutral solution of the α-ethyl-α-hydroxy tetronic acid upon heating, in which case the decarboxylation would not be noticed, or upon decarboxylation on standing. The decarboxylation occurs due to the inherent instability of the tetronic acids which is further increased by the presence of the hydroxyl group on the α carbon.

If the compound is indeed 1,3-dihydroxy-3-pentanone the question of whether the diketones formed in acid solution from tetronic acids (reaction 1) arise before or after the breaking of the ring to liberate carbon dioxide could be answered. If in acid solution

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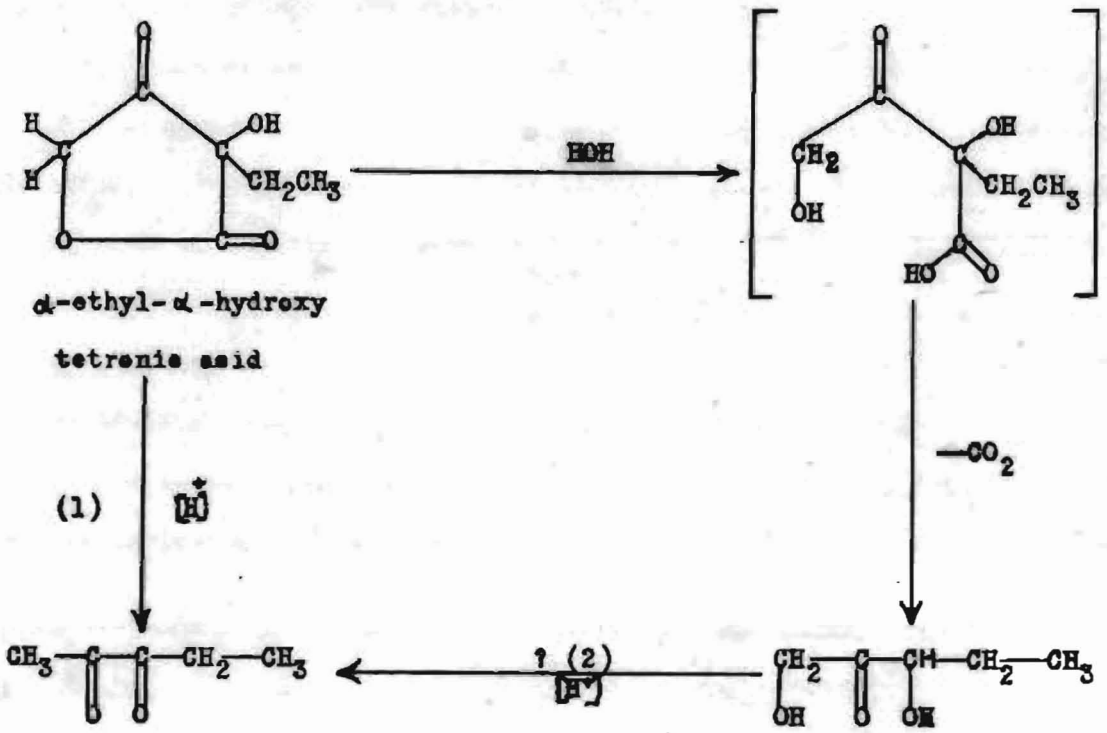
[29] Rasmussen, R.S., Tunnicliff, D.D., and Brattain, R.R., J. Am. Chem. Soc., 71, 1068, (1949).

the 1,3-dihydroxy-2-pentanone yields 2,3-pentanedione (reaction 2) then isolation of the former compound proves that the tetronic ring must open and carbon dioxide must be liberated before the diketone is formed. The mechanism for the above reactions is shown below.



In comparing the spectra of the unknown solid and the decarboxylation product (spectra numbers 3 and 4 respectively) it is immediately obvious that while the spectra are quite similar they are not superimposable. The difference between the two spectra can most likely be explained by the fact that there are probably two absorbing species present. This would be the case if the decarboxylation reaction did not go to completion. If this were the case then it is likely that there would be different concentrations of the two active species in each sample on which the

infrared spectrum was run. The infracord would sum the absorption of each species to give in each case a slightly different spectrum.

The pertinent absorption areas in each of these two spectra are those occurring in both cases from 2.7 to 3.7 μ and from 5.8 to 6.5 μ. The first area of absorption is probably due to the primary and secondary hydroxyl groups in 1,3-dihydroxy-2-pentanone. The region of absorption is again shifted from its reported normal value. In the case of the secondary hydroxyl group this is most likely due to the tautomeric equilibrium which exists between it and the carbonyl group. The second area of absorption contains no distinct carbonyl absorption valley at 5.8 μ, but the absorption valley does extend to 6.5 μ indicating that the presence of the carbonyl group has been masked by the tautomeric equilibrium between the enol and keto forms which give the characteristic absorption region at 6.1 to 6.5 μ.

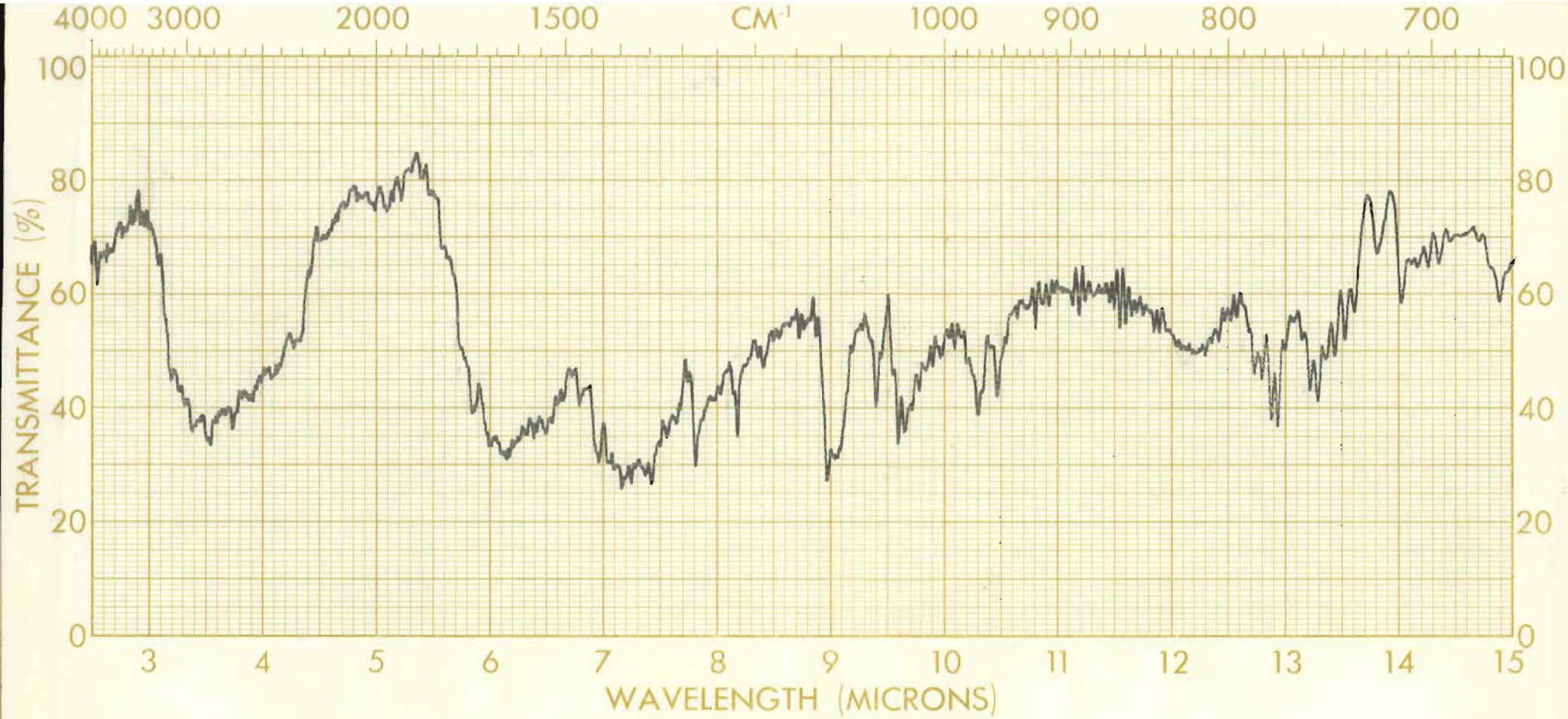
The enol keto equilibrium, represented below, is interesting and serves to explain another curiosity of the tentatively identified compound. The structure

of 1,3-dihydroxy-2-pentanone is similar to the structure of a carbohydrate as is the structure of α-ethyl-α-hydroxy tetronic acid, hence the caramel odor. Of further interest is the fact that dihydroxy acetone also has this caramel odor.

Since the unknown compound had not been rigorously proved to be the dihydroxy pentanone, it was desirable to compare the spectrum of the unknown with that of a known compound of similar structure. For this purpose only one other compound was known and that was dihydroxy acetone (spectrum number 5). At first glance there is no apparent similarity between the spectra of the purported dihydroxy pentanone and dihydroxy acetone. However, a closer look reveals that aside from the width of the

hydroxyl absorption region of the latter (3-3.6 μ as compared with 2.7-3.7 μ for the former) and the existence of a peak at 5.9-6.5 μ where the former has a valley, the spectra are quite similar. The reduction in the width of the hydroxyl absorption region is due to the fact that in dihydroxy acetone both hydroxyl groups are primary. At 5.8 μ the characteristic carbonyl absorption occurs. Between 5.9 and 6.5 μ there is a peak where the enol-keto equilibrium absorbs. This difference between the spectra of dihydroxy pentanone and dihydroxy acetone is explained by the fact that in the latter this tautomeric equilibrium does not occur, because the methylene groups on either side of the carbonyl group are not activated. Thus the spectra of the two compounds do in fact have a similarity.

The above discussion is in many cases speculative, but the circumstantial evidence presented does point to the existence of the α-alkyl-α-hydroxy tetronic acid as the oxidative intermediate in the oxidation of tetronic acids. Actual confirmation of this fact awaits a chemical analysis of the yellow oil believed to be the hydroxy tetronic acid.



SPECTRUM NO. 1	ORIGIN Synthesis	LEGEND	REMARKS
SAMPLE		1.	Run at fast speed
d Ethyl Tetronic Acid	PURITY Recrystallized	2.	
	PHASE Nujol Mull	DATE May 6, 1966	
	THICKNESS	OPERATOR Peter Dansen	

SPECTRUM NO. 1
SAMPLE d Ethyl Tetronic Acid

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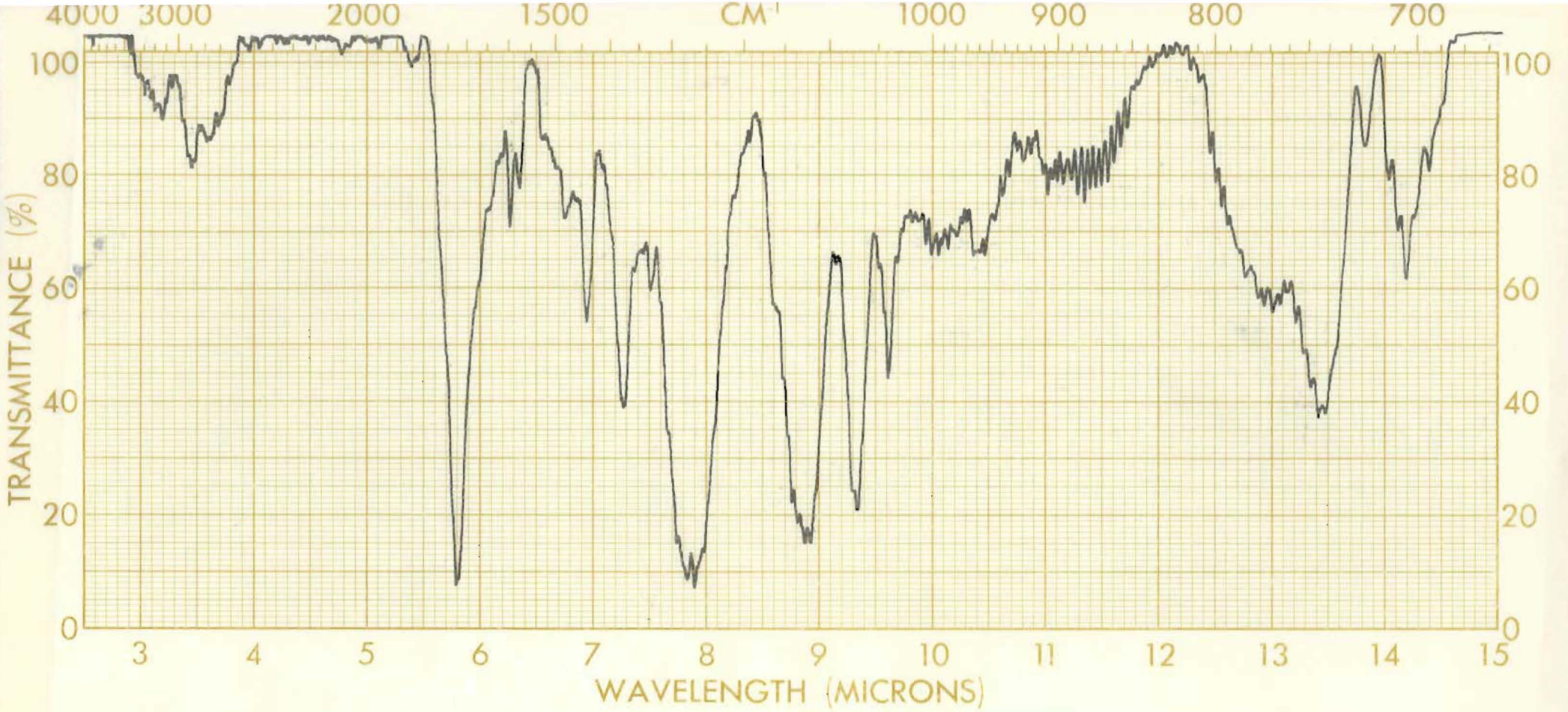
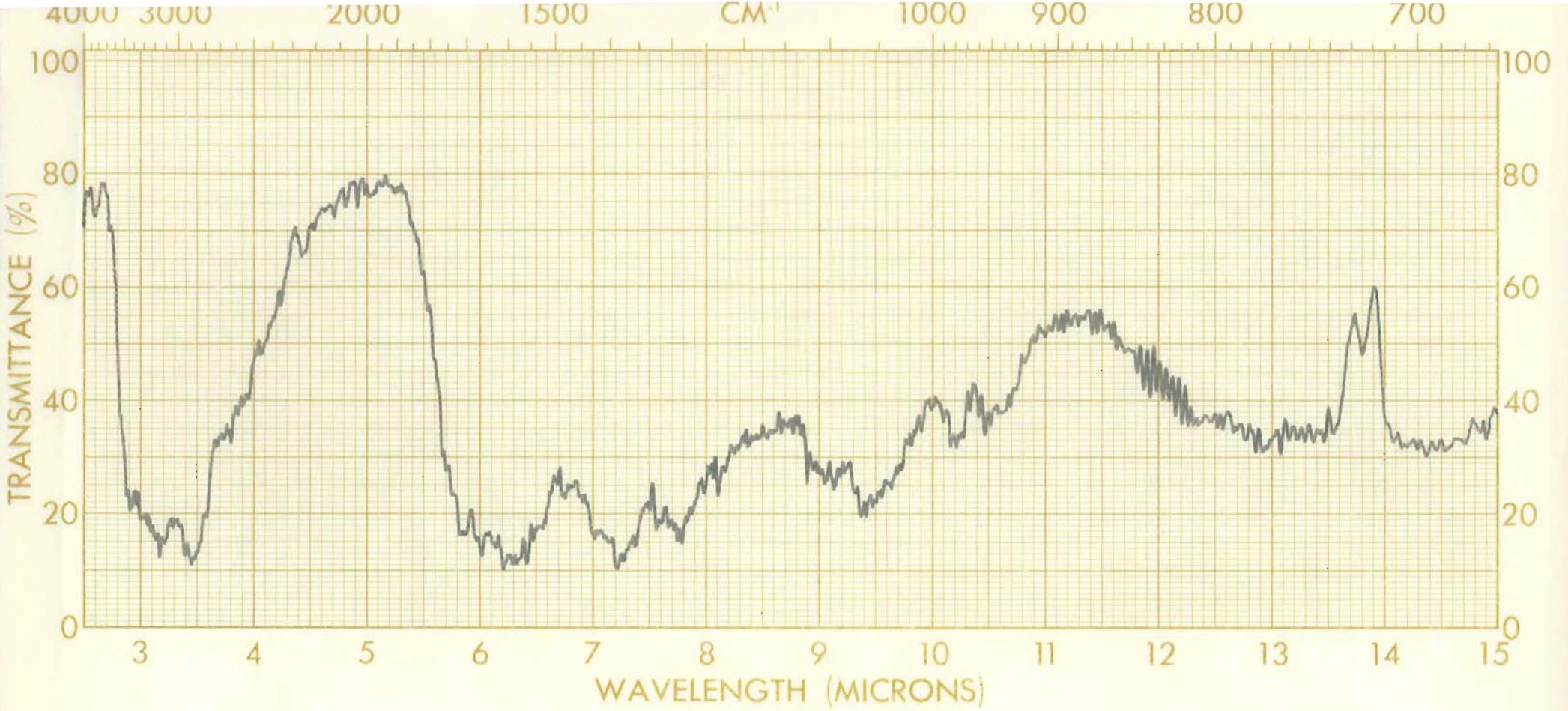


SPECTRUM NO. 2	ORIGIN	LEGEND	REMARKS
SAMPLE	Evaporation of ether extract	1.	Run at fast speed
Unknown product from the	PURITY	2.	
oxidation of d ethyl ketone	PHASE air	DATE May 6, 1966	
acid with Magnesium permanganate	THICKNESS	OPERATOR Peter Donsen	

SPECTRUM NO. 2
SAMPLE Unknown oil

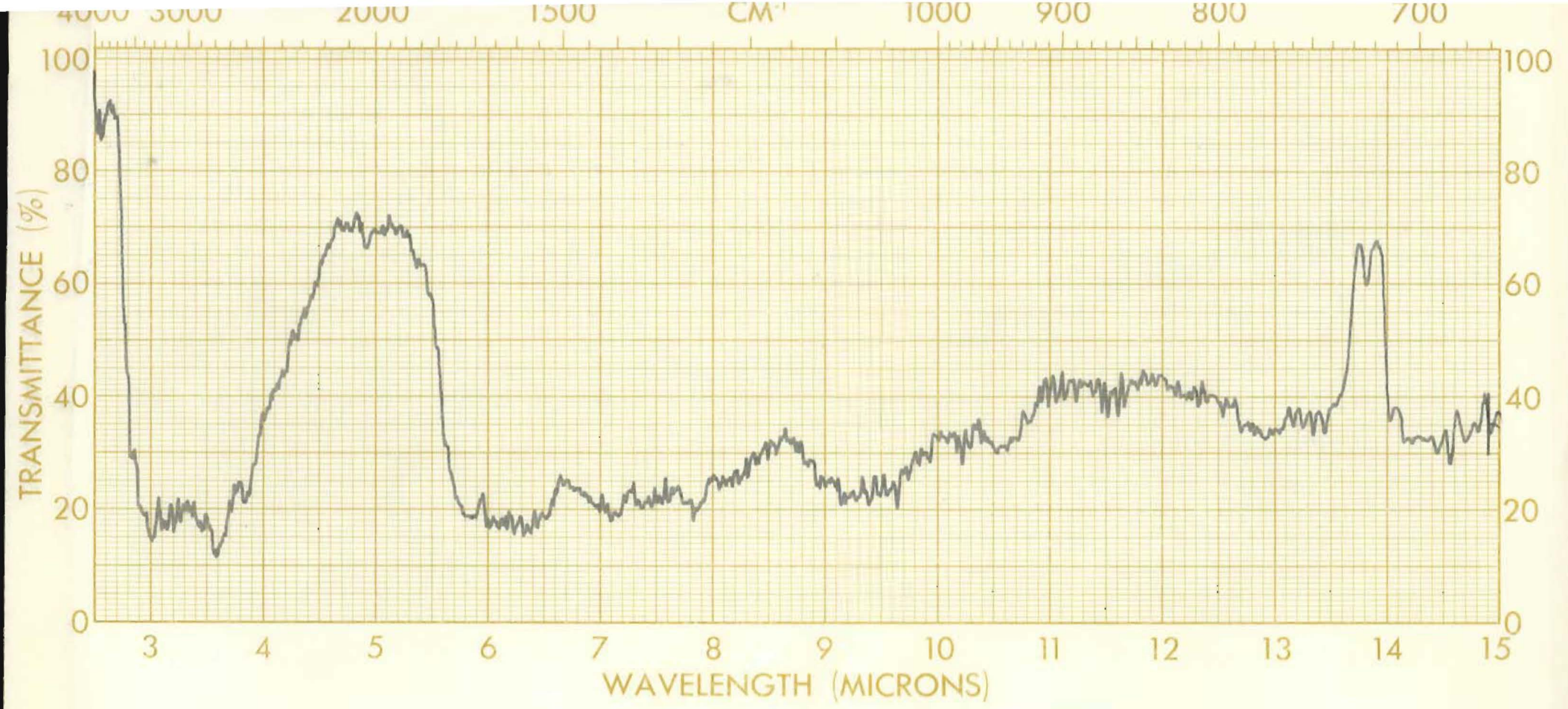


SPECTRUM NO. 3	ORIGIN	LEGEND	REMARKS
SAMPLE An unknown;	Evaporation in air	1.	Run at fast speed
the result of evaporating down	PURITY	2.	
the aqueous permanganate	PHASE Nujol Mull	DATE May 6, 1966	
oxidized solution of 2 ethyl	THICKNESS	OPERATOR Peter Densen	

tetronic acid

SPECTRUM NO. 3
SAMPLE Unknown #old

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO. 4	ORIGIN	LEGEND	REMARKS
SAMPLE	Evaporation in air	1.	Run at fast speed
decarboxylation product of	PURITY	2.	
the unknown oxidation	PHASE Nujol Mull	DATE May 6, 1966	
product	THICKNESS	OPERATOR Peter Densen	

SPECTRUM NO. 4
SAMPLE Decarboxylation Product

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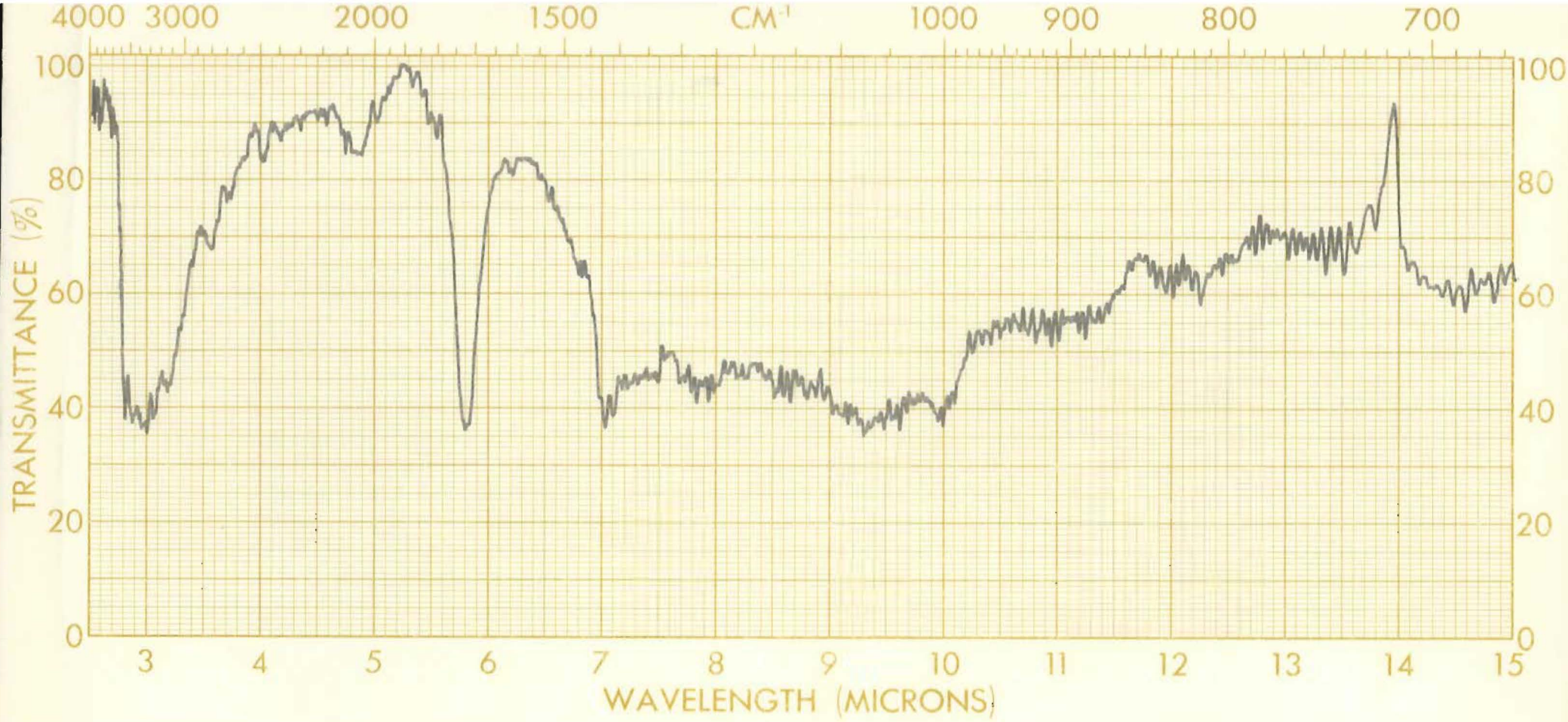

SPECTRUM NO. 5	ORIGIN	LEGEND	REMARKS
SAMPLE	Chemical Procurement Laboratories	1.	Run at fast speed
Dihydroxy Acetone	PURITY m.pt. 81-83°	2.	
	PHASE Nujol Mull	DATE May 6, 1966	
	THICKNESS	OPERATOR Peter Densen	

SPECTRUM NO. 5
SAMPLE Dihydroxy Acetone

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.