ethyl acetate with 0.1 g. of palladium–barium sulfate catalysts (warmed somewhat), absorbed a total of 340 cc. of hydrogen in five hours, 270 cc. having been absorbed in the first two hours (calculated volume for dihydro compound, 325 cc.).

The reaction product after removal of the catalyst and solvent was recrystallized from ether to a constant melting point which was over 10° higher than that reported by Ruzicka and Balas[17] (m. p. 249–250°).

Anal.[18] Calcd.: C, 78.88; H, 10.60. Found: C, 78.87; H, 10.63.

The authors wish to express their appreciation to Mr. R. R. Long, of Atmore, Ala., for his coöperation in furnishing the turpentine gum.

Summary

An investigation of the pimaric acids in *P. palustris*, an improved systematic procedure for their preparation from the "gum," as well as the preparation of catalytic hydrogenation products of these acids are described.

[17] L. Ruzicka and Fr. Balas, *Helv. Chim. Acta*, **6**, 677 (1923).

[18] These analytical data were kindly determined by J. R. Spies, Department of Chemistry, University of Maryland.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Carbon Syntheses with Malonic and Related Acids. I

BY ARTHUR MICHAEL AND JOHN ROSS

In 1879[1] it was shown that mixtures containing benzoic, or cuminic, aldehyde with phenylacetic acid and sodium acetate heated in sealed tubes gave stilbene, or propylstilbene, evidently by loss of carbon dioxide from the first-formed cinnamic acid derivatives. Subsequently,[2] this modification of the Perkin synthesis, using an acid instead of an acid anhydride, was extended to malonic acid, when, with benzoic aldehyde, cinnamic acid was obtained without use of acetate. This synthesis was not extended, as, simultaneously, Claisen and Crismer[3] found that benzalmalonic acid was formed on heating malonic acid with benzoic aldehyde in acetic acid solution, with or without acetic anhydride, and Komenos[4] that replacement of aromatic by fatty aldehydes led to the formation of aliphatic α,β,Δ-dibasic acids, or corresponding monobasic acids through loss of carbon dioxide. A large literature now exists on the use of malonic acid for the preparation of mono- and dibasic α,β,Δ-acids.[5]

Komenos[4] was unable to condense malonic acid with acetone, using acetic anhydride, but Meldrum[6] observed that addition of a little sulfuric acid

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[1] Michael, *Am. Chem. J.*, **1**, 312 (1879).

[2] *Ibid.*, **5**, 14 (1883).

[3] Claisen and Crismer, *Ann.*, **218**, 135 (1883).

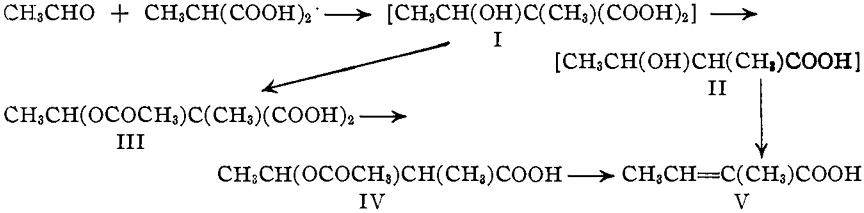
[4] Komenos, *ibid.*, 149 (1883).

[5] Beilstein, Vol. II, p. 245; Suppl., Vol. II, p. 235 (1920). Thirty researches are listed. Knövenagel used pyridine instead of acetic acid and anhydride to induce the reaction.

[6] Meldrum, *J. Chem. Soc.*, **93**, 605 (1908).

to the mixture caused an immediate reaction to form the β-lactone of β-hydroxyisopropylmalonic acid. This interesting synthesis of a β-lactone has been used besides with acetone and methylmalonic acid,[7] and with several homologous ketones and malonic acid.[8] Malonic acid also has been condensed with certain aryl carbinols, yielding arylmalonic acids. Notwithstanding the extensive use of the malonic acid reaction for C-syntheses, its applicability is far from exhausted. We have undertaken a systematic investigation of the chemical behavior of this reagent and derivatives toward mono- and polycarbonyl compounds, including the enol–keto group, to determine the scope of the reaction and the relations of the products formed in the Claisen–Komenos, Meldrum and Knövenagel methods to the structures of the components of the systems.

Tiglic acid has been synthesized by a number of methods, but the preparations are difficult and poor yields are obtained. A mixture of methylmalonic acid with an excess of paraldehyde, acetic anhydride and acetic acid was heated on the water-bath for several hours. There were formed tiglic acid (V) and β-acetoxy-α-methylbutyric acid (IV). The latter distilled unchanged in a vacuum, but at ordinary pressure lost acetic acid to give tiglic acid which, by these simple methods, may be obtained in a 70% yield. In this synthesis the following processes apparently occur



$$CH_3CHO + CH_3CH(COOH)_2 \longrightarrow \underset{\text{I}}{[CH_3CH(OH)C(CH_3)(COOH)_2]} \longrightarrow \underset{\text{II}}{[CH_3CH(OH)CH(CH_3)COOH]}$$

$$\underset{\text{III}}{CH_3CH(OCOCH_3)C(CH_3)(COOH)_2} \longrightarrow \underset{\text{IV}}{CH_3CH(OCOCH_3)CH(CH_3)COOH} \longrightarrow \underset{\text{V}}{CH_3CH{=}C(CH_3)COOH}$$

The stability of I toward elimination of water to form an α,β, Δ-acid is evidently due to the absence of an α-hydrogen. Compound III upon loss of carbon dioxide would form α-methyl-β-acetoxybutyric acid (IV) and tiglic acid (V) may now be formed by loss of acetic acid. This must take place with difficulty under the experimental conditions, since IV remains as a considerable proportion of total products of the reaction. It might be considered, therefore, that tiglic acid is formed solely through II by elimination of water, but this simple interpretation has been shown to be improbable.

α-Methyl-α-carboxy-β-hydroxybutyric acid (I) was prepared by a method described later in this paper. On pyrogenic decomposition at 135°, under atmospheric or reduced pressure, it gave acetaldehyde and methylmalonic acid and no appreciable amount of tiglic or α-methyl-β-hydroxybutyric acid. Therefore it seems probable that methylmalonic acid in the

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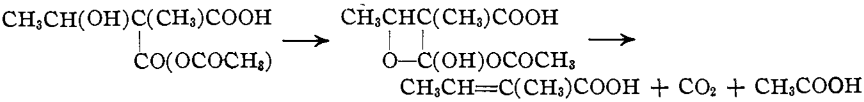
[7] Ott, *Ann.*, **401**, 159 (1913).

[8] Kandhiah, *J. Chem. Soc.*, 1215 (1932).

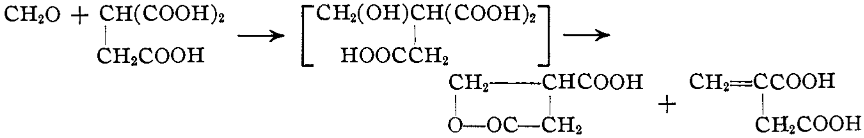
presence of paraldehyde, acetic anhydride and acetic acid follows a different course of reaction. Dimethylmalonic acid warmed with acetic anhydride gives a mixed malonic–acetic anhydride and methylmalonic acid undoubtedly reacts similarly. From this point of view, the formation of tiglic acid, besides through IV, may take place through a β-lactone derivative



$$\begin{array}{l}CH_3CH(OH)C(CH_3)COOH \\ \qquad\qquad\quad | \\ \qquad\qquad CO(OCOCH_3)\end{array} \longrightarrow \begin{array}{l}CH_3CHC(CH_3)COOH \\ \quad | \quad | \\ \quad O{-}C(OH)OCOCH_3\end{array} \longrightarrow$$
$$CH_3CH{=}C(CH_3)COOH + CO_2 + CH_3COOH$$

This very negative β-lactone should undergo facilely such a decomposition and all malonic acid syntheses of α,β, Δ-acids, that require the use of acetic anhydride, may proceed through a mixed acid anhydride.

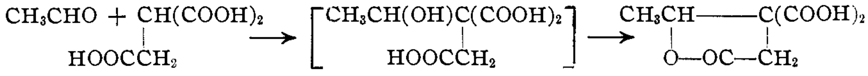
In the above manner, paraformaldehyde and ethinyl tricarboxylic acid gave a good yield of paraconic acid (VI) with itaconic acid (VII) in a small proportion



$$\begin{array}{l}CH_2O + CH(COOH)_2 \\ \qquad\qquad | \\ \qquad\quad CH_2COOH\end{array} \longrightarrow \left[\begin{array}{l}CH_2(OH)CH(COOH)_2 \\ \qquad\qquad | \\ \qquad HOOCCH_2\end{array}\right] \longrightarrow$$
$$\begin{array}{l}CH_2{-\!-\!-}CHCOOH \\ | \qquad\qquad | \\ O{-}OC{-}CH_2\end{array} + \begin{array}{l}CH_2{=}CCOOH \\ \qquad\quad | \\ \qquad CH_2COOH\end{array}$$

VI VII

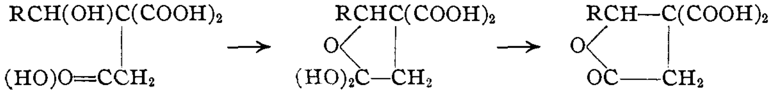
By the same method there was produced from paraldehyde and the tricarboxylic acid in the cold an almost theoretical yield of α-carboxy-β-methylparaconic acid (IX)



$$\begin{array}{l}CH_3CHO + CH(COOH)_2 \\ \qquad\qquad | \\ \qquad HOOCCH_2\end{array} \longrightarrow \left[\begin{array}{l}CH_3CH(OH)C(COOH)_2 \\ \qquad\qquad | \\ \qquad HOOCCH_2\end{array}\right] \longrightarrow \begin{array}{l}CH_3CH{-\!-\!-}C(COOH)_2 \\ \quad | \qquad\qquad | \\ \quad O{-}OC{-}CH_2\end{array}$$

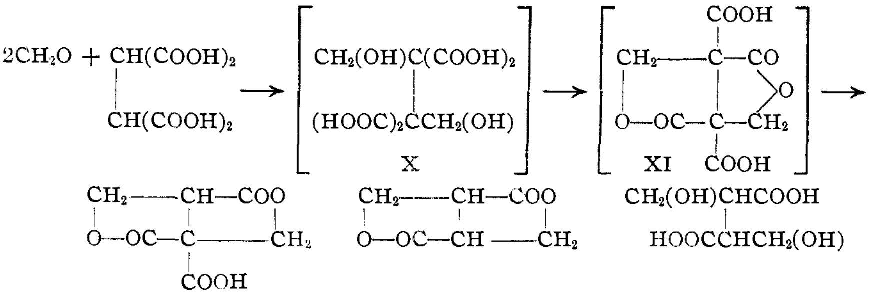
VIII IX

It is evident that when a mono-substituted malonic acid contains a carboxyl in the β-position to the dicarboxylic group, the elimination of water from the first-formed aldol derivative (*e. g.*, VIII), occurs solely, or almost entirely, by way of intramolecular esterification to form a γ-lactone



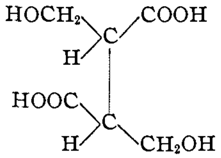
$$\begin{array}{l}RCH(OH)C(COOH)_2 \\ \qquad\quad | \\ (HO)O{=}CCH_2\end{array} \longrightarrow \begin{array}{l}RCHC(COOH)_2 \\ O\langle \quad | \\ (HO)_2C{-}CH_2\end{array} \longrightarrow \begin{array}{l}RCH{-}C(COOH)_2 \\ O\langle \qquad | \\ OC{-\!-\!-}CH_2\end{array}$$

This course of reaction is again illustrated in the case of symmetrical ethane tetracarboxylic acid. That acid and paraformaldehyde, by the Claisen–Komenos method, gave with loss of carbon dioxide the γ-dilactone of dimethylolethinyl tricarboxylic acid (XII) as the main product. Upon fusion acid XII lost carbon dioxide and gave the bicyclic γ-dilactone of dimethylolsuccinic acid (XIII), the simplest possible aliphatic member of this class of dilactones. It dissolved in warm caustic soda to form the neutral sodium salt of *sym*-dimethylolsuccinic acid (XIV)

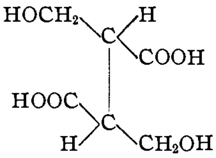


XII XIII XIV

This dihydroxy dicarboxylic acid (XIV) contains two asymmetrical carbon atoms and may exist in the racemic and meso form



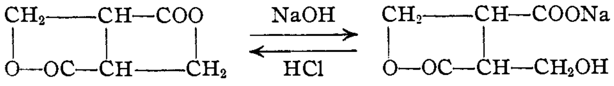
A Racemic



B Meso

From the property of γ-hydroxy acids to condense to γ-lactones, when the involved interacting groups are uniplanar, each of these stereostructures may yield a corresponding racemic and meso form of a mono-lactonic acid and a dilactone. According to Reis,[9] in the meso or "centri" form the hydrogen atoms at the asymmetrical carbon atoms are in *trans* relationship. but no chemical evidence is known to confirm this view. The dissymmetry of the hydrogen atoms should cause a decided increase of free chemical energy in the meso over the racemic stereo form. This does not agree with the relative properties of the members of these groups of compounds and it is not improbable that B would pass over voluntarily into A.

The dilactone (XIII) is soluble in water and in the cold it slowly neutralizes one equivalent of alkali, with fission of one lactone ring, giving the mono-sodium salt (XV). This upon acidifying yields the original dilactone (XIII)



XIII XV

When boiled with two equivalents of caustic soda, both lactone rings are opened and approximately equal amounts of the two stereomeric sodium salts of XIV were obtained. One of the salts appeared as an octahydrate, which separated as a highly crystalline solid from the solution of the other, very soluble compound. The latter upon acidifying gave the original

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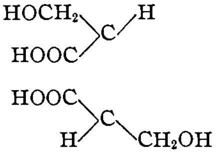
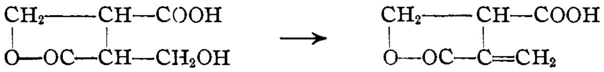
(9) Reis, *Ber.*, **59**, 1551 (1926).

dilactone. On the other hand, the less soluble sodium salt gave a monohydroxy-γ-lactonic acid (XVI).

The formation of the mono-lactonic acid from the less soluble salt can be explained only by racemization of A, when one of its COONa groups undergoes a positional interchange with the hydrogen atom attached to the same asymmetrical carbon atom. The respective methylol and the carboxyl group of the corresponding free acid are no longer in the same plane and therefore cannot undergo lactonization (C Meso). These properties of A and C are of theoretical interest as they offer a rigorous chemical proof that racemization proceeds with rearrangement at one of the asymmetrical carbon atoms. Upon treatment with a dehydrating agent the meso mono-lactonic acid XVI might be reconverted into the racemic acid (A), when it would condense to the dilactone; lose water from the methylol and carboxyl groups in *trans* position to each other, when it would undergo retrogression with elimination of carbon dioxide; or, water might be eliminated from the carbinol hydroxyl and the hydrogen atom at the same asymmetrical carbon atom, when an unsaturated lactonic acid would be formed. As the last process would occur in a β-hydroxy acid group, which always loses water very readily, it is not surprising that treatment of the meso lactonic acid XVI with acetic anhydride proceeded in this direction



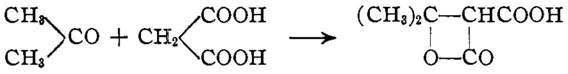
C Meso



$$\begin{array}{l}CH_2\text{——}CH\text{—}COOH\\ |\qquad\quad\ |\\ O\text{—}OC\text{—}CH\text{—}CH_2OH\end{array} \longrightarrow \begin{array}{l}CH_2\text{——}CH\text{—}COOH\\ |\qquad\quad\ |\\ O\text{—}OC\text{—}C{=}CH_2\end{array}$$

XVI XVII[10]

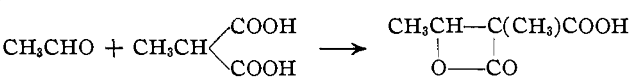
Related to the γ-lactone reaction is the Meldrum[6] synthesis of the β-lactone of β-hydroxyisopropylmalonic acid (XVIII) from a mixture of malonic acid, acetone and acetic anhydride with a small amount of concentrated sulfuric acid



$$\begin{array}{l}CH_3\\ \quad\ \ >CO\\ CH_3\end{array} + CH_2\!\begin{array}{l}COOH\\ COOH\end{array} \longrightarrow \begin{array}{l}(CH_3)_2C\text{—}CHCOOH\\ \qquad\ \ |\quad\ |\\ \qquad\ O\text{—}CO\end{array}$$

XVIII

Similarly, Ott[7] obtained from methylmalonic acid the α-methylated derivative (XIX) of XVIII. We have found that aldehydes may be used in place of ketones in the Meldrum β-lactonic acid synthesis. Thus, aldehyde reacts with methylmalonic acid to give β-lactonic acid XX



$$CH_3CHO + CH_3CH\!\begin{array}{l}COOH\\ COOH\end{array} \longrightarrow \begin{array}{l}CH_3CH\text{—}C(CH_3)COOH\\ \quad\ |\qquad |\\ \quad\ O\text{——}CO\end{array}$$

XX

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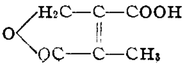
(10) The structure of XVII is uncertain. Itaconic acid, and its anhydride, give citraconic anhydride on distillation, which points to the isomeric



$$O\!\begin{array}{l}H_2C\text{—}C\text{—}COOH\\ \qquad\ \ \ \|\\ OC\text{—}C\text{—}CH_3\end{array}$$

as a possible formula.

Until recently, the interpretation of Erlenmeyer[11] has been accepted that alkene formation from salts of β-halogen acids proceeded through a β-lactone. However, Einhorn[12] obtained the β-lactone of the three nitrophenyllactic acids, which decomposed in this manner only at the melting points, and Baeyer and Villiger[13] the β-lactone of β,β-dimethylmalic acid from the corresponding β-halogen acid, which on distillation did not undergo the olefin decomposition. Johansson and Hagman[14] attributed the isolation of these β-lactones that their insolubility in the surrounding media resisted conversion into hydroxy derivatives. By dissolving liberated β-lactones in chloroform as they are formed, they showed that aliphatic β-halogen salts on decomposing in aqueous solution yield mixtures of β-lactones and alkenes. These fatty β-lactones boiled in a vacuum without decomposition and, in some of the reactions, were formed in much larger proportion than the corresponding alkenes. They concluded from these results that such β-bromo salts yield simultaneously a mixture of β-lactone and olefin, but gave no reason for this double mode of decomposition. This is to be sought in the stereostructures of the β-bromo salts. There are good grounds to accept favored, comparatively stable, stereostructures, which represent the maximum degradation of energy, for all saturated aliphatic compounds[15] from the second carbon series on, but, according to the partition principle, the other possible configurations may occur in more or less minor proportions. From this point of view, the β-lactone formation proceeds from the stereostructure in which the halogen and the metallic atom of the salt are in *cis* position to each other. In configurations where these atoms are *trans* to one another, the lactone rings would be formed under such strain that rupture to alkenes and carbon dioxide would occur.

The pyrogenic decomposition of the alkylated β-propiolactonic acids is complicated. Ott[7] showed that β,β-dimethylpropiolactonic acid (XVIII) gave acetone with dimethylketene; its α-methyl derivative (XIX) gave acetone with high boiling products. Although that β-lactonic acid decomposes above its melting point, we found that it can be distilled unchanged in a vacuum. The introduction of an α-methyl into XVIII has increased decidedly the stability of the β-lactone ring toward heat. In striking contrast to the ketonic mode of decomposition, is that of β-lactonic acid XX, whose structure may be derived from that of XVIII by replacing one of the β-methyls by hydrogen. The thermal decomposition of this β-lactonic acid involves merely the elimination of carbon dioxide from the carboxyl, leaving α,β-dimethylpropio-β-lactone (XXI); a fairly stable compound toward heat, since it boils without decomposition

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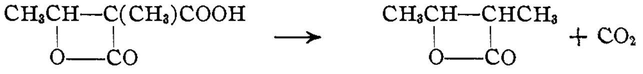
(11) Erlenmeyer, Sr., *Ber.*, **13**, 305 (1880); **14**, 320 (1881).

(12) Einhorn, *ibid.*, **16**, 2208 (1883).

(13) Baeyer and Villiger, *ibid.*, **30**, 1955 (1897).

(14) Johansson and Hagman, *ibid.*, **55**, 647 (1922).

(15) Michael, THIS JOURNAL, **40**, 707 (1918).



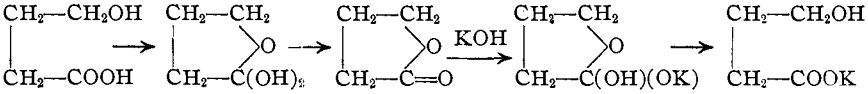
$$\begin{array}{l}CH_3CH{-}C(CH_3)COOH\\ |\qquad\quad |\\ O{-}{-}{-}CO\end{array} \longrightarrow \begin{array}{l}CH_3CH{-}CHCH_3\\ |\qquad\quad |\\ O{-}{-}{-}CO\end{array} + CO_2$$

XX XXI

This shows that the unusual fission at the saturated linkages between the α- and β-carbons of XVIII and XIX cannot be ascribed wholly to the lessening of their affinity to each other by the negative influence of the COOH- and COO-groups, since then this influence should be somewhat greater in these lactones than in XX. These reactions further illustrate that if strain in the sense of the Baeyer hypothesis[16] functions it can be only one of the energy factors which enter into the thermal stability of rings.

Upon treatment of β,β-dimethylpropiolactonic acid (XVIII) with cold, aqueous alkali, Meldrum[6] found that it functioned monobasic and when heated with baryta water it decomposed into acetone and malonate. Kandiah[8] stated that β,β-dipropylpropiolactonic acid titrated monobasic with cold alkali and dibasic with the reagent at 100°. We examined the α,β,β-trimethyl derivative XIX toward aqueous caustic soda and observed a still greater stability of the β-lactone ring. With two equivalents at 100° only the mono-sodium salt was produced and from the evaporated dry residue the original monobasic lactonic acid could be recovered. The existing observations on the relative stability of β-lactone rings toward heat and toward alkali with reference to chemical structures show that they run parallel to each other and that they are developed constitutive properties.[16a]

The γ-butyrolactone formation from γ-hydroxybutyric acids,[17] and rupture of the lactone ring by alkali, should be represented as follows



$$\begin{array}{l}CH_2{-}CH_2OH\\ |\\ CH_2{-}COOH\end{array} \longrightarrow \begin{array}{l}CH_2{-}CH_2\\ |\qquad\ \ \rangle O\\ CH_2{-}C(OH)_2\end{array} \longrightarrow \begin{array}{l}CH_2{-}CH_2\\ |\qquad\ \ \rangle O\\ CH_2{-}C{=}O\end{array} \xrightarrow{KOH} \begin{array}{l}CH_2{-}CH_2\\ |\qquad\ \ \rangle O\\ CH_2{-}C(OH)(OK)\end{array} \longrightarrow \begin{array}{l}CH_2{-}CH_2OH\\ |\\ CH_2{-}COOK\end{array}$$

The primary phase of the internal esterification proceeds at the energetic Δ-CO of the acidic group. This carbonyl possesses the chemical potential at the Δ-C and Δ-O atoms for the carbinol O and H atoms to overcome the slight hindrance to the formation of the hydrated pentacyclic lactone

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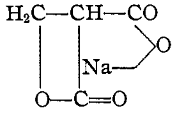
[16] Baeyer, *Ber.*, **18**, 2277 (1885). This chemist [*ibid.*, **23**, 1275 (1890)] made a curious error in endeavoring to interpret the "Strain Theory" in terms of mechanical energy. The tension in a cyclic chain was compared to that in a bent elastic spring, it increasing in each case with the magnitude of the pressure. Baeyer overlooked that the strain in the spring is due to energy exerted externally, while spontaneous ring-formation is caused by internal, intramolecular energy, in a large measure to the free chemical energy and the chemical affinity, *i. e.*, the chemical potential, between the two groups that react directly to form the cyclic system. It can occur only with a decrease of the free chemical energy of the corresponding compound with the open-chain form. The more of the free chemical energy used to complete the closure, the less must be available to hold the terminal groups that unite to form the ring together by bound chemical energy and, therefore, the less will be chemical hindrance to ring-fission. Evidently, this interpretation is the reverse of that implied in the bent spring explanation, where the free energy increases with closure. The magnitude of this chemical hindrance to ring-fission must be one of the major energy factors that determine the stability of rings.—A. M.

[16a] In opposition to the "Strain Theory" the tetracyclic ring of XIX shows greater stability toward alkaline reagents than the pentacyclic ring of any lactone that has been examined.

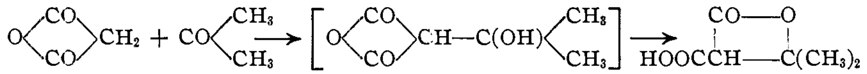
[17] Michael, *J. prakt. Chem.*, **60**, 338 (1899); THIS JOURNAL, **40**, 1694 (1918).

ring. The alkali hydrolysis of the lactone ring proceeds through the intermediate addition of alkali at the Δ-CO[18] to pass over into the γ-hydroxy salt. In these reactions the formation of the neutral lactone and hydroxycarboxylate evidently determine the maximum degradation of chemical energy of the systems.

These theoretical standpoints permit an insight into several of the above β-lactone reactions. If the primary phase of the action of caustic alkali upon a β-lactone consists in its addition to the ring carbonyl, then the introduction of any chemical influence into the lactone molecule, acting directly or through space, that increases or decreases this additive capacity, must result in a greater lability or stability, respectively, of the lactone ring. The replacement of an α-hydrogen of a lactone by carboxyl should augment the chemical potential of the ring carbonyl for water and alkali, and, accordingly, should lessen the stability of the lactone ring toward aqueous mineral acid and alkali. Toward acid this conclusion holds for β-lactones, but not toward alkali. However, in this case the primary product is the corresponding carboxylate and the not wholly neutralized positive chemical energy of the alkali atom must decrease the facility of addition, depending more or less upon the extent of the free positive energy remaining in the alkali atom. In all cases, the retardation should be noticeable, for the natroxyl group is in the *cis* position to the lactone carbonyl and the metal in the spatially near 5–6 places to the carbon and oxygen of that group. The configuration of the β-propiolactonate may be represented by the formula shown.



According to Ott,[7] malonic acid with acetic anhydride and a little sulfuric acid may give the mixed malonic–monoacetic anhydride. He assumed that malonic anhydride, formed from it by loss of acetic acid, may react with aldolization upon acetone with subsequent rearrangement



It should be stated that the "malonic anhydride" here assumed contained acetyl and that it was also considered a mixed anhydride. Since there is no evidence that sulfuric acid had been entirely removed from the preparation, and the composition of the latter as malonic anhydride is not established, it is evident that the interpretation has no experimental basis. The comparison with the malic β-lactonic acid change is not applicable; if they rearranged similarly the anhydride of isopropylmalonic acid should be formed and not a β-lactone derivative. A simpler and more probable interpretation is that the synthesis of the β-lactone proceeds through a mixed anhydride

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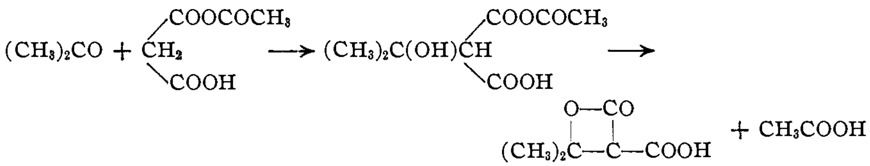
[18] Analogous alkali addition derivatives have been isolated [Michael, *Am. Chem. J.*, **5**, 93 (1883); Michael and Lamb, *ibid.*, **31**, 552 (1906)].



The probable function of sulfuric acid is to facilitate the formation of the mixed anhydride[19] and to catalyze intramolecular esterification as it does the intermolecular process. In the mixed anhydride the hydrogen attached to the α-carbon becomes more reactive, through replacement of COOH by the more negative radical $COOCOCH_3$, and that replacement of hydroxyl hydrogen by acetyl favors cyclization has been long known.[20]

Experimental

Preparation of Tiglic Acid.—A mixture of 50 g. of methylmalonic acid, 37 g. of paraldehyde, 43 g. of acetic anhydride and 25 g. of acetic acid was heated under a condenser for forty-eight hours, then gently boiled on a sand-bath for four hours. The liquid was distilled with a 15-cm. column until the thermometer read 140°. The residual liquid was then fractionated under reduced pressure, two main fractions being collected; tiglic acid (19 g.), distilling at 90–115° (15 mm.), solidified in the receiver, and a second fraction (13 g.), distilling at 147–150° (10 mm.), which was β-acetoxy-α-methylbutyric acid.

β-Acetoxy-α-methylbutyric acid is a colorless liquid of not unpleasant odor.[21] It readily decomposed into acetic and tiglic acids on distillation at ordinary pressure.

Anal. Calcd. for $C_7H_{12}O_4$: C, 52.5; H, 7.5. Found: C, 52.4; H, 7.3.

This method will give a total yield of tiglic acid of approximately 70% of the theoretical. The tiglic acid upon recrystallization melted at 65° and was identical in all other respects with tiglic acid.

Preparation of α-Ethylcrotonic Acid.—A mixture of ethylmalonic acid (38 g.), paraldehyde (22 g.), acetic anhydride (26 g.), and acetic acid (15 g.) was heated as in the preparation of tiglic acid. Upon fractionation there was obtained 20 g. of liquid which distilled at 100–120° (20 mm.), and upon cooling almost completely solidified to large crystals of α-ethylcrotonic acid melting at 42°. There was also obtained a small amount (3.0 g.) of liquid boiling at 156–160° (10 mm.), presumably β-acetoxy-α-ethylbutyric acid.

Action of Aldehydes on Carboxysuccinic Acid. Formaldehyde.—A mixture of 4.0 g. of paraformaldehyde, 8.0 g. of the tricarboxylic acid, 7.0 g. of acetic anhydride and 7.0 g. of acetic acid stood at room temperature for two weeks. The mixture was heated

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[19] Fittig and Stuart [*Ber.*, **16**, 1436 (1883); *J. Chem. Soc.*, **43**, 403 (1883)] obtained cinnamic and α-methylcinnamic acids from the products of the action of benzaldehyde on sodium malonate, sodium methylmalonate, respectively, and acetic anhydride at room temperature. Under these conditions the aldehyde does not act on the anhydride and sodium acetate mixture and they therefore contended that the syntheses must proceed through the aldehyde and malonate, a view which was practically universally accepted. The writer [*Am. Chem. J.*, **5**, 14 (1883)] gave reasons to show that this interpretation was not tenable and that the reaction proceeded through the primarily formed, mixed malonic–acetic anhydride. Later [*J. prakt. Chem.*, **60**, 366 (1899); *Ber.*, **34**, 918 (1901)], it was proved experimentally that the synthesis with monobasic derivatives takes place through the aldehyde and acid anhydride. The recent preparation and properties of mixed malonic–acetic anhydrides now show unmistakably that the synthesis with malonic derivatives proceeds by action of the aldehyde on mixed anhydrides, not on malonates.—A. M.

[20] Michael, *J. prakt. Chem.*, **44**, 113 (1891).

[21] Blaise and Herman, *Compt. rend.*, **146**, 1327 (1908); *Ann. chim.*, [8] **20**, 189 (1910).

on a water-bath for six hours and boiled under a condenser for an hour. The excess acetic anhydride and acetic acid was removed by distillation under reduced pressure, the flask being placed in a water-bath. There remained a thick sirup containing some unchanged paraformaldehyde, which was removed by warming with excess caustic soda and the acid extracted with ether upon acidifying. On removal of the solvent the sirupy residue deposited crystals (1.0 g.) of an acid (m. p. 161°), which was proved by analysis and a direct comparison to be itaconic acid.

Anal. Calcd. for $C_5H_6O_4$: C, 46.16; H, 4.6. Found: C, 46.26; H, 4.8.

The residual sirup in a desiccator gradually crystallized and was found to be paraconic acid (m. p. 57°); yield 5.0 g.

Anal. Calcd. for $C_5H_6O_4$: C, 46.16; H, 4.6. Found: C, 46.05; H, 4.7.

Acetaldehyde.—A mixture of 3.0 g. of paraldehyde, 5.4 g. of ethinyl tricarboxylic acid, 4.0 g. of acetic anhydride and 5.0 g. of acetic acid stood at room temperature for two weeks. After heating gently on a water-bath for six hours, the excess paraldehyde, acetic anhydride and acetic acid was distilled off under reduced pressure. On cooling, the residue crystallized almost completely and the solid was filtered from the adhering liquid. Recrystallization from a mixture of ether and ligroin gave large prisms of β-carboxy-γ-methylparaconic acid, melting at 165°.

Anal. Calcd. for $C_7H_8O_6$: C, 44.68; H, 4.75. Found: C, 44.52; H, 4.43.

This acid on melting lost carbon dioxide to give γ-methylparaconic acid,[22] melting at 84° after recrystallization from ether–ligroin mixture.

Anal. Calcd. for $C_6H_8O_4$: C, 50.0; H, 5.5. Found: C, 49.81; H, 5.61.

An excellent yield of β-carboxy-γ-methylparaconic acid (approximately 80%) was also obtained from the above mixture by adding a drop of concentrated sulfuric acid and allowing to stand at room temperature for one week. The acid crystallized from the reaction mixture.

Sym-ethane tetracarboxylic acid was prepared by saponifying the ethyl ester with caustic potash and acidifying the dry potassium salt suspended in ether with concentrated hydrochloric acid while cooling well in an ice–salt freezing mixture. The aqueous solution was extracted in the cold with ether in a continuous extractor. The solid acid was obtained from the concentrated ether extract by evaporation in a vacuum desiccator. The crude acid melted at 181° and crystallized from acetone–chloroform solution as fine needles, melting at 183°. By this method a very pure acid can be obtained in excellent yield.

Action of Formaldehyde on Sym-Ethane Tetracarboxylic Acid.—A mixture of 20 g. of the tetracarboxylic acid with 20 g. of acetic anhydride was added to a solution of 7.0 g. of paraformaldehyde in 20 g. of acetic acid and left at room temperature for two weeks. Some evolution of carbon dioxide occurred and after a few days nearly all the solid acid dissolved. The mixture was then warmed on the steam-bath for six hours when evolution of gas almost ceased. The excess acetic acid and acetic anhydride were distilled off under reduced pressure and the residual sirup was taken up in ether and ligroin added. On standing there was deposited 4.5 g. of a mixture of crystalline compounds. Upon fractional crystallization from acetone–ether it gave a compound which melted at 178° with decomposition, to give a second compound melting at 138°. The analysis and properties of the first substance correspond to the dilactone of dimethylol ethinyl tricarboxylic acid (XII).

Anal. Calcd. for $C_7H_6O_6$: C, 45.16; H, 3.28. Found: C, 45.34; H, 3.28.

The compound, melting at 138°, crystallized in large prisms, was soluble in water and analyzed for the γ-dilactone of dimethylol succinic acid (XIII).

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[22] Fittig, *Ann.*, **255**, 1 (1889).

Anal. Calcd. for $C_6H_6O_4$: C, 50.7; H, 4.72. Found: C, 50.72; H, 4.43. *Neutral equivalent.* Calcd. for $C_6H_6O_4$: 142. Found: 140.5.

On treatment with $N/20$ baryta water slow neutralization occurred; 0.06 g. of dilactone was neutralized, added dropwise, in approximately thirty minutes.

After separation of the above acid considerable sirupy material remained. When this was heated under 20 mm. pressure about 5.0 g. distilled over at 210°; the residual resin in the distilling flask decomposed upon further heating. The distillate solidified upon cooling and was separated by fractional crystallization into the dilactone, m. p. 138° (2.5 g.), and an isomeric compound melting at 165°. The latter, an unsaturated acid, crystallized from chloroform in fine needles and gave the following analysis.

Anal. Calcd. for $C_6H_6O_4$: C, 50.7; H, 4.22. Found: C, 50.48; H, 4.34. *Neutral equivalent.* Calcd. for $C_6H_6O_4$: 142. Found: 145.2.

It dissolved immediately in bicarbonate solution with evolution of carbon dioxide and the solution decolorized permanganate solution instantaneously. However, in chloroform solution, it did not readily take up bromine. In analysis and properties it corresponds to the γ-lactone of β-methylol-itaconic (XVII), or -citraconic acid.

Racemization of Dimethylolsuccinic Acid.—The dilactone melting at 138° was dissolved in the calculated amount of 2 N caustic soda and the solution boiled for fifteen minutes. Upon cooling there separated large prisms of an hydrated sodium salt. These crystals were filtered off and, after drying on a porous plate, were analyzed.

Anal. 0.5130 g. of the salt lost 0.2042 g. on drying at 110°, and the dry salt gave 0.1990 g. of anhydrous Na_2SO_4. Calcd. for $C_6H_8O_6Na_2 \cdot 8H_2O$: H_2O, 39.35; Na, 12.57. Found: H_2O, 39.8; Na, 12.51.

This octahydrate was not formed on standing of the alkaline solution of dilactone for two days in the cold. The mother liquor from the octahydrate was evaporated to dryness and acidified, when the original dilactone (m. p. 138°) was obtained.

γ-Monolactone of Meso Dimethylolsuccinic Acid (XVI).—The disodium salt octahydrate was dried at 110°, the anhydrous salt suspended in ether and acidified with the theoretical amount of hydrogen chloride. Upon evaporation of the ether extract, there was obtained large crystals of the meso hydroxy-lactonic acid, m. p. 122°.

Anal. Calcd. for $C_6H_{10}O_5$: C, 44.44; H, 6.17. Found: C, 44.18; H, 5.95. *Neutral equivalent.* Calcd. for $C_6H_{10}O_5$: 160. Found: 159.3.

Upon boiling with acetic anhydride and distilling under reduced pressure this acid gave the unsaturated γ-lactonic acid (XVII) (m. p. 165°).

α-Methyl-α-carboxybutyrolactone.—To a mixture of 20 g. of methylmalonic acid, 20 g. of acetic anhydride, 10 g. of acetic acid and 10 g. of paraldehyde was added one drop of concentrated sulfuric acid. There was an immediate evolution of heat and all the solid acid dissolved. After standing overnight, 0.2 g. of anhydrous sodium acetate was added, in order to convert the sulfuric acid to sodium sulfate, and the excess paraldehyde and acetic acid was removed by heating under reduced pressure, the flask being kept in water at about 80°. The sirupy residue was taken up in ether and ligroin added. Upon standing large crystals of α-methyl-β-hydroxy-α-carboxybutyric acid separated; yield 4 g.

This acid melted at 135° with decomposition. It crystallized in large prisms from chloroform–ligroin.

Anal. Calcd. for $C_6H_{10}O_6$: C, 44.44; H, 6.17. Found: C, 44.67; H, 6.44.

When heated at its melting point, under reduced or at atmospheric pressure, it decomposed into acetaldehyde and methylmalonic acid, both of which were identified. There was no identifiable amount of tiglic acid or the β-lactone of β-hydroxy-α-methylbutyric acid obtained in this pyrogenic decomposition.

The β-lactone of α-methyl-α-carboxy-β-hydroxybutyric acid remained as a sirup after removal of crystalline acid.

α-Methylbutyro-β-lactone.—When the sirupy residue was heated above 100° under reduced pressure, decomposition occurred with elimination of carbon dioxide and the above β-lactone distilled over. The original reaction mixture distilled directly gave 70% of this lactone. It is a colorless liquid boiling at 80° (15 mm.)[23] and has a pleasant odor. It is insoluble in cold sodium carbonate but dissolves on warming; it is also soluble in warm caustic soda.

Anal. Calcd. for $C_5H_8O_2$: C, 60.0; H, 8.0. Found: C, 59.84; H, 8.15.

Preparation of Tiglic Acid from α-Methylbutyro-β-lactone.—Seven and one-half grams of the lactone was mixed with 38 cc. of 2 *N* caustic soda and the mixture warmed on a steam-bath. The major part of the lactone rapidly dissolved but there was formed a small amount of deep, yellowish brown resinous material, which had an unpleasant odor, and which was filtered off. The clear, colorless filtrate was evaporated to dryness and the cold sodium salt, suspended in ether, acidified with concentrated hydrochloric acid. The ether extract, which contained β-hydroxy-α-methylbutyric acid, was concentrated and the hydroxy acid distilled under reduced pressures, when it lost water to give almost the theoretical yield of tiglic acid.

Summary

1. The preparation of α-alkyl-α,β-olefinic acids, by the action of aliphatic aldehydes upon mono-alkylmalonic acids, has been described.

2. The method with ethinyl tricarboxylic acid gave γ-lactonic acids; from paraformaldehyde and *sym*-ethane tetracarboxylic acid a γ-dilactonic acid was obtained, which upon heating gave the simplest aliphatic γ-dilactone.

3. The racemic dimethylolsuccinate, obtained from this γ-dilactone upon warming with alkali, reformed the γ-dilactone with mineral acid. On longer heating it racemized partially to the meso salt, which yielded a mono-γ-lactonic acid upon acidifying. These relations offer a rigorous chemical proof that the racemization took place by a rearrangement between a methylol group and a hydrogen atom at one of the asymmetrical carbon centers.

4. It has been shown that aldehyde may replace acetone in the Meldrum malonic synthesis of β-lactonic acids.

5. The thermal and chemical properties of β-lactonic acids in relation to structure have been examined. It has been shown that an intramolecular strain in β-lactone rings can be only one of the energy factors that determine their physical and chemical stability. The relations deduced solely from Baeyer's "Strain Theory" are therefore erroneous.

6. The β-lactone of α-methyl-β-hydroxy-α-carboxybutyric acid has been examined and the preparation of tiglic acid from this acid described.

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[23] Johannson and Hagman, *Ber.*, **55**, 647 (1922), gave b. p. 67° (21 mm.).