THE CHEMISTRY OF THE MONOCYCLIC α- AND γ-PYRONES

LIEBE F. CAVALIERI[1]

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania

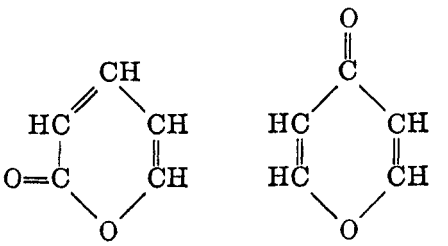
Received April 29, 1947

CONTENTS

[1] Present address: Sloan-Kettering Institute for Cancer Research, New York, New York.

I. Introduction

The pyrones belong to the class of six-membered heterocyclic compounds containing an oxygen atom. An inspection of the formulas of the α- and γ-pyrones



α-Pyrone γ-Pyrone

reveals that a functional similarity exists between these ring systems. α-Pyrone possesses a lactonic structure, while γ-pyrone is the vinylog of a lactone; indeed, many of the chemical properties of these nuclei are similar. It must be emphasized, however, that the γ-pyrone nucleus represents a more complex ring system. The anomalous chemical behavior of this nucleus has obscured its exact nature, and the problem of structure has become one of classical interest.

The present review will be concerned only with the chemistry of the monocyclic

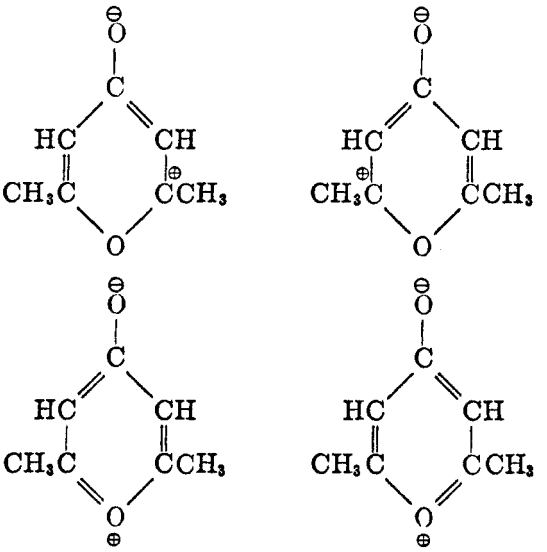
α- and γ-pyrones. Since the chemistry of the γ-pyrones has been of greater general interest, it will be discussed first.

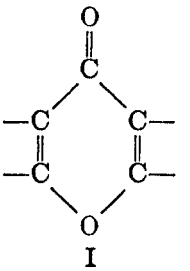
II. γ-Pyrones

A. Structure

The γ-pyrone nucleus contains three types of functional groups joined together in such a manner as to give rise to a ring system which possesses a set of chemical properties quite unlike those of any of its component groups. The carbonyl group does not react with hydroxylamine, phenylhydrazine, or semicarbazide to produce an oxime, a phenylhydrazone, or a semicarbazone, respectively. Addition of halogens or halogen acids does not take place across the carbon–carbon double bond. Stable crystalline oxonium salts are formed on treatment with acids, indicating that γ-pyrones are unusually strong oxygen bases. This anomalous behavior has caused a great deal of uncertainty in assigning a detailed structure to the γ-pyrone ring (15, 28, 29, 38, 41, 50, 54, 58, 81, 117, 143, 144, 203, 260, 261).

Physical data have clarified to some extent the question of structure. Dipole moment measurements (120, 139, 207, 248) require that various resonance forms (3, 5, 6, 7, 115, 147, 217) make major contributions to the actual state of the molecule. These resonance forms are in better agreement with the chemical properties of γ-pyrones than a simple ketonic structure (I). However, parachor deter-

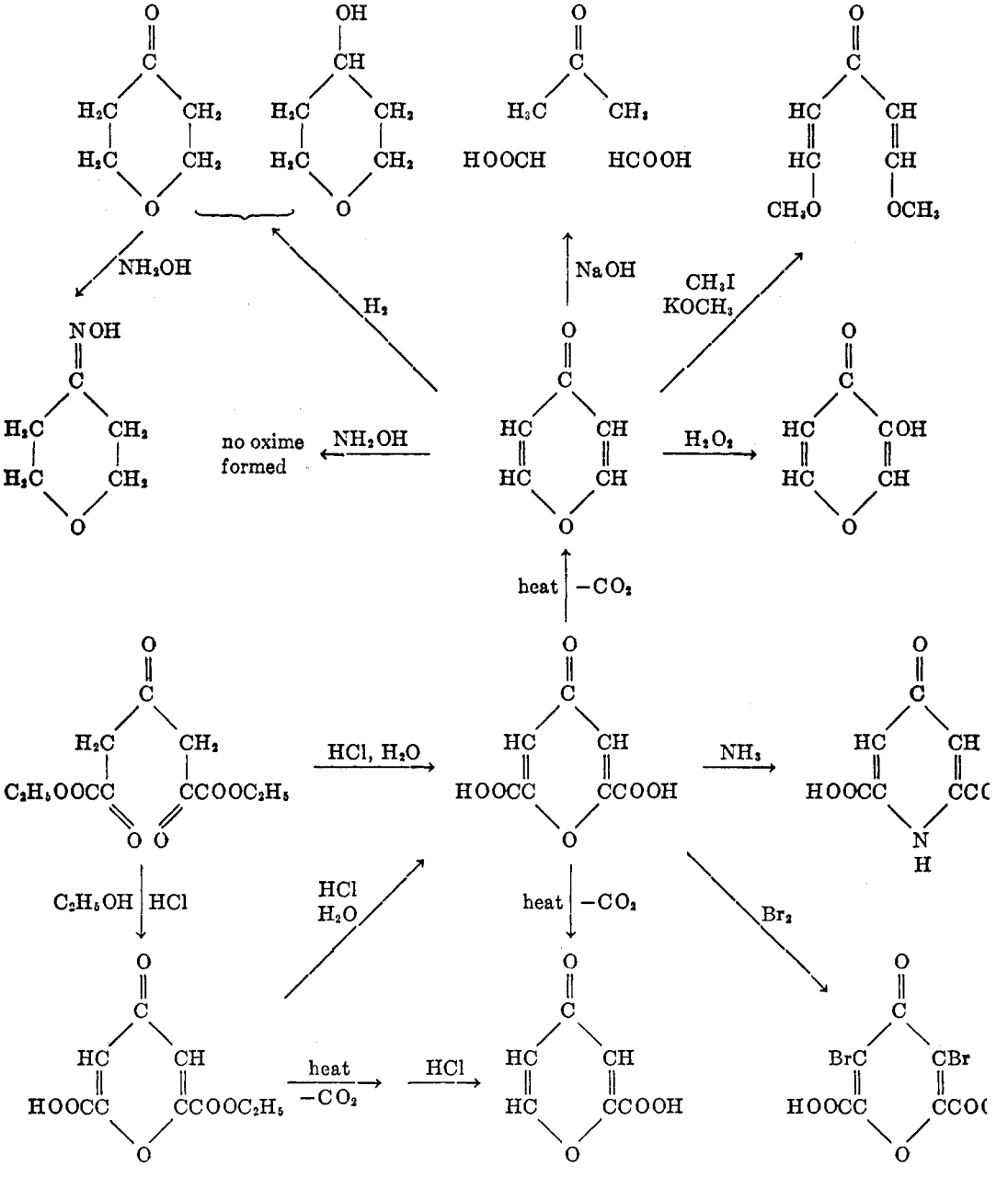




I

TABLE 1

Interconversions in the γ-pyrone series



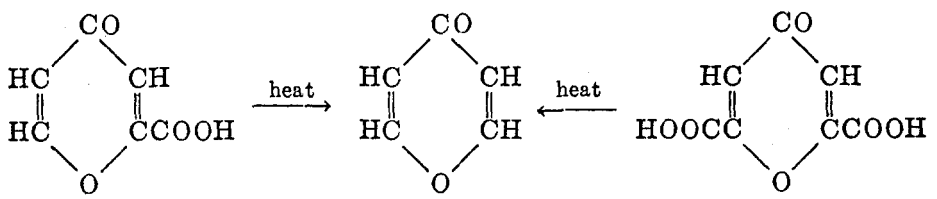
minations (72) and ultraviolet absorption spectra studies (96, 112, 209) indicate that structure I also contributes to the state of the molecule. No single structure, therefore, is adequate to express the true state of the γ-pyrone ring.

B. PREPARATION

Various interconversions which are typical of γ-pyrones are illustrated in table 1.

1. γ-Pyrone

From comanic acid or chelidonic acid: The decarboxylation of either comanic (II) or chelidonic (III) acid leads to the formation of γ-pyrone (106, 169, 259).



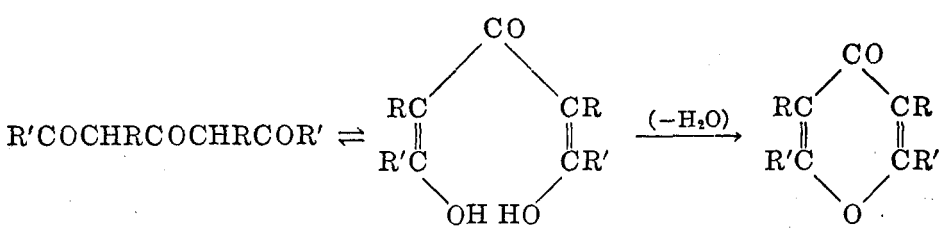
II
Comanic acid

III
Chelidonic acid

The decarboxylation takes place more smoothly in the presence of copper powder (260, 261).

2. Substituted γ-pyrones

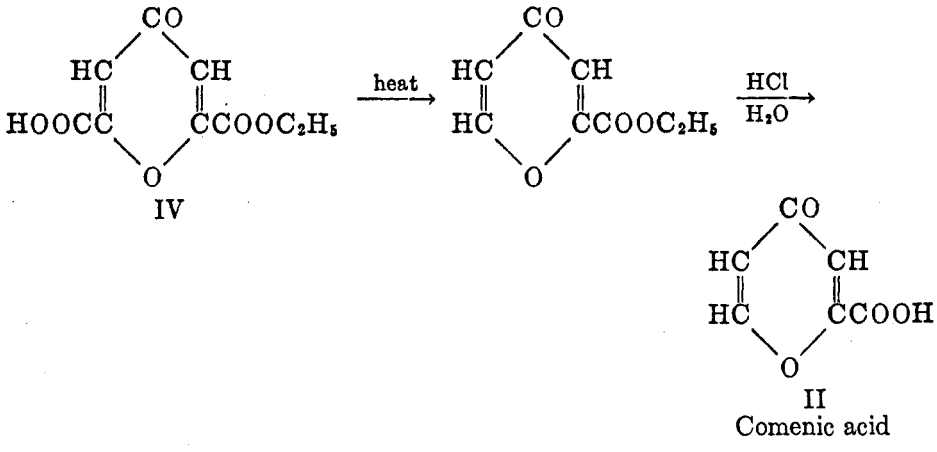
In general, substituted γ-pyrones are prepared by cyclization of the appropriate open-chain keto derivative.



R, R′ = alkyl, aryl, carbethoxyl.

(a) Carboxylic acids

Comanic acid, pyrone-2-carboxylic acid (II): Small quantities of comanic acid are formed by the decarboxylation of chelidonic acid (108). This method has the main disadvantage that the major product of the reaction is γ-pyrone. A more suitable method for the preparation of comanic acid is found in the decarboxylation of monoethyl chelidonate (IV) (42).

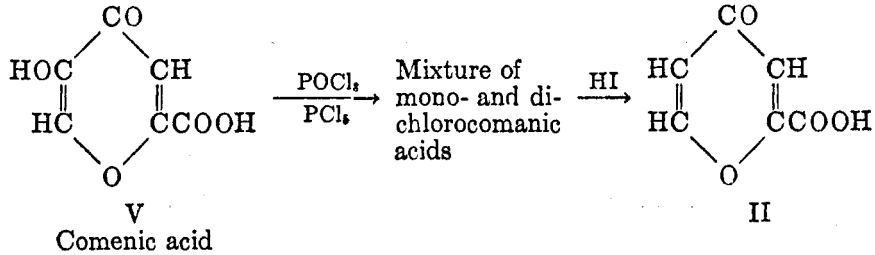


IV

II

Comenic acid

Comanic acid may also be obtained from comenic acid (V) by treatment with a



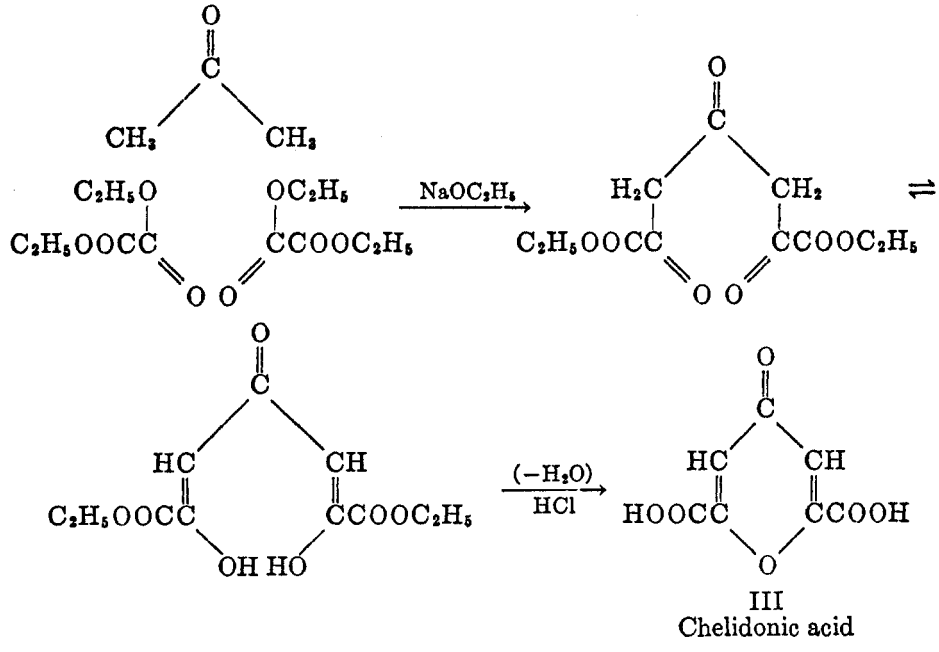
V

Comenic acid

II

mixture of phosphorus pentachloride and phosphorus oxychloride and subsequent reduction of the reaction mixture with hydriodic acid (168).

Chelidonic acid, pyrone-2,6-dicarboxylic acid (III): Chelidonic acid occurs in

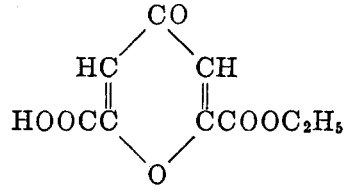


III

Chelidonic acid

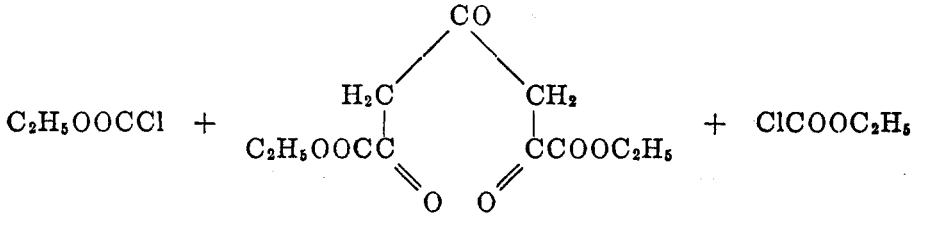
nature in celandine (*Chelidonium majus*) (201, 206), *Polygonatum officinale*, *Polygonatum multiforum* (136), *Asparagus officinalis* (205), and in the alkaloids of white hellebore (*Veratrum grandiflorum* Loes. fil.) (223).

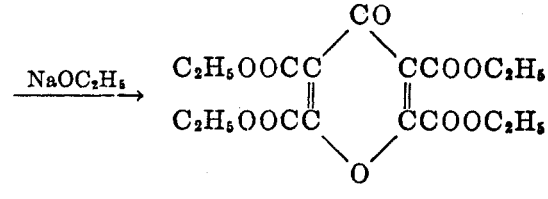
It is prepared by the treatment of acetonedioxalic acid ethyl ester with aqueous hydrochloric acid (42, 50, 106, 140, 141, 201, 259, 260, 261). If this ester is treated with alcoholic hydrogen chloride containing a small quantity of water, monoethyl chelidonate (IV) is produced in good yield (42).



IV

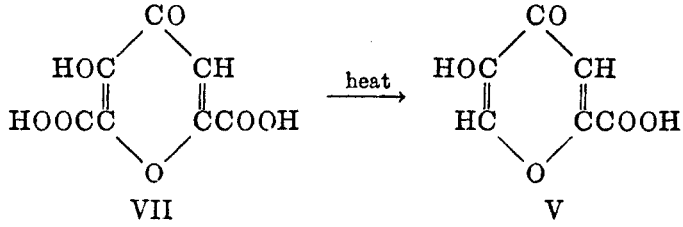
γ-Pyrone-2,3,5,6-tetracarboxylic acid ester (VI): The reaction of ethyl chloroformate with acetonedioxalic ester leads to the formation of the ester VI (189).





VI

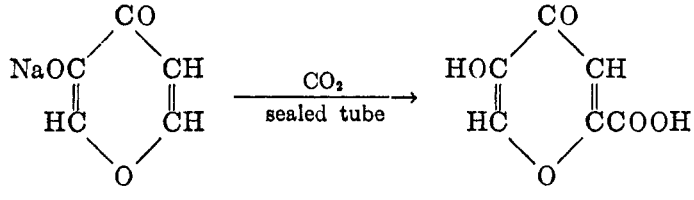
Comenic acid, 5-hydroxypyrone-2-carboxylic acid (V): Comenic acid is produced in nature when acetic acid bacteria (isolated from fruit) act on galactose (237, 238). It may be prepared by the decarboxylation of meconic acid (VII) either



VII Meconic acid V Comenic acid

in the presence of copper powder (31, 118, 119, 153, 165, 187, 212, 214, 215, 234, 245) or in boiling aqueous hydrochloric acid (31, 75, 154). It is formed in low

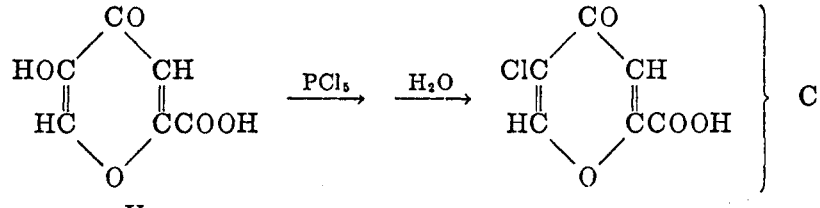
yield by the action of carbon dioxide on the sodium salt of pyromeconic acid (VIII) (186). This reaction calls to mind the Kolbe synthesis of salicylic acid from sodium phenoxide and carbon dioxide.



VIII
Pyromeconic acid

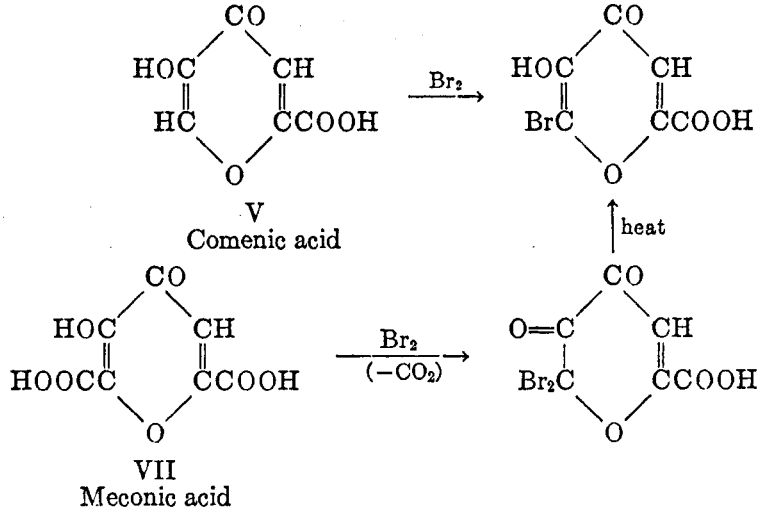
V
Comenic acid

Treatment of comenic acid with phosphorus pentachloride results in the formation of a dichloro compound of unknown structure (167).



V

6-Bromocomenic acid: 6-Bromocomenic acid is prepared by the bromination of either comenic acid (V) (166) or meconic acid (VII) (119). In the case of meconic acid the reaction is carried out at elevated temperatures and the di-

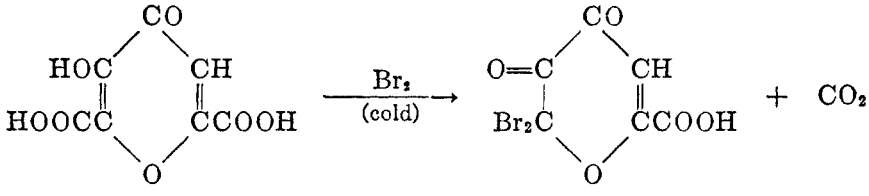


VII
Meconic acid

bromo acid first formed decomposes to produce some of the monobromo acid.

6,6-Dibromocomenic acid: The reaction of bromine and meconic acid (VII)

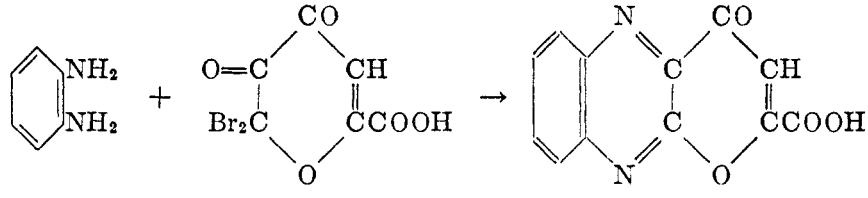
at low temperatures results in the decarboxylation of meconic acid with subsequent formation of 6,6-dibromocomenic acid (153).



VII

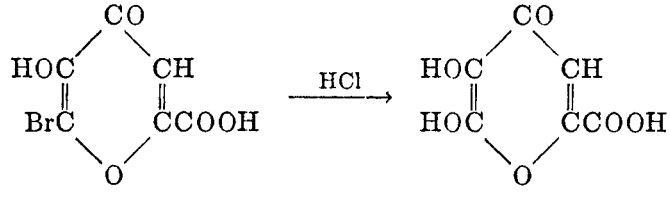
Meconic acid 6,6-Dibromomeconic acid

The interaction of dibromocomenic acid with *o*-phenylenediamine produces the quinoxaline IX (180). Dibromocomenic acid may be reduced to monobromocomenic acid with zinc and mineral acids (152).

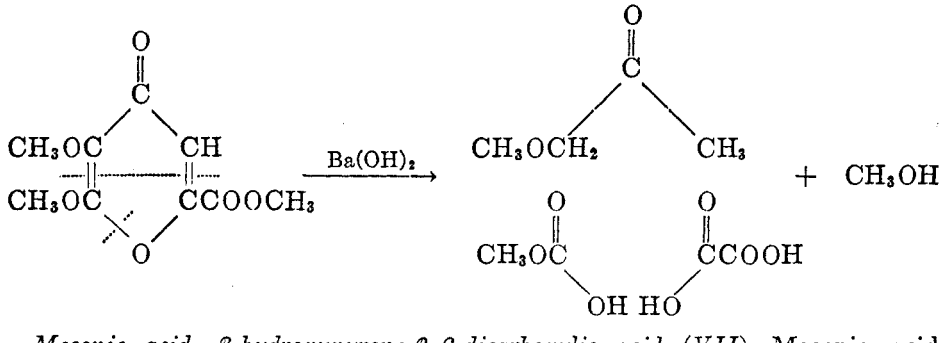


IX

6-Hydroxycomenic acid: 6-Hydroxycomenic acid is prepared by the hydrolysis of 6-bromocomenic acid with either aqueous hydrochloric acid (166) or barium

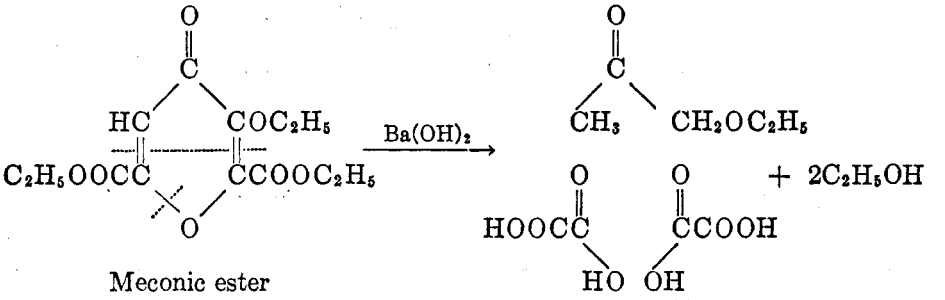


hydroxide (208). The prolonged action of barium hydroxide on the dimethyl ether of 6-hydroxycomenic acid results in complete degradation (183).



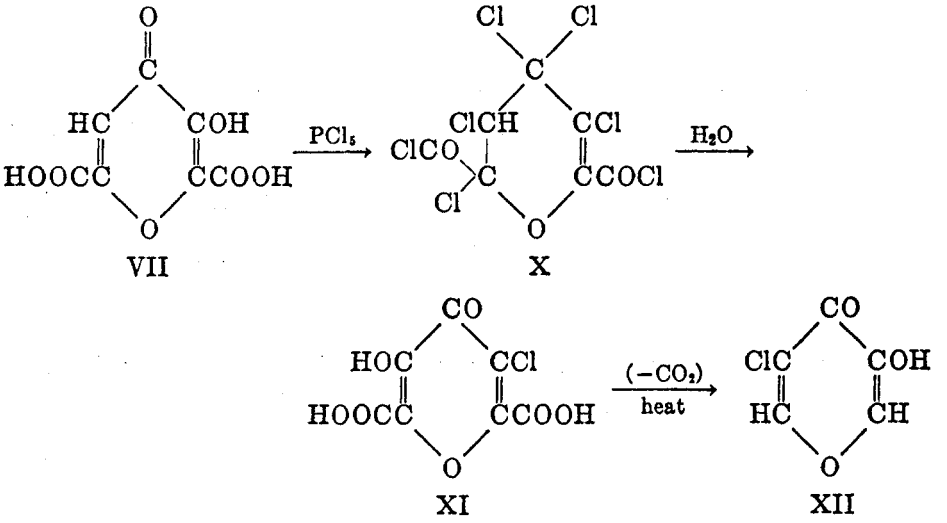
Meconic acid, 3-hydroxypyrone-2,6-dicarboxylic acid (VII): Meconic acid occurs in opium (99, 210, 211, 213, 228), but it does not contribute to the physiological activity of this substance (1, 138).

The structure of meconic acid was demonstrated by the identification of the alkaline degradation products formed with barium hydroxide (22, 142, 145, 146, 184, 191, 241, 249).



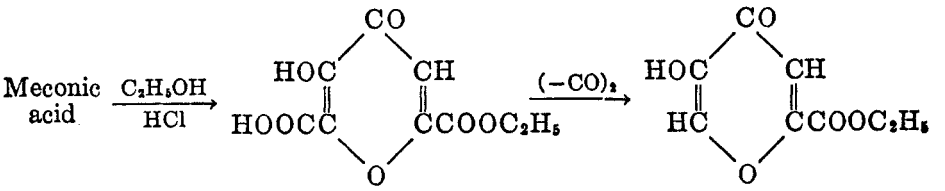
Meconic ester

Treatment of meconic acid (VII) with phosphorus pentachloride yields a dicarboxylic acid chloride containing five atoms of chlorine (X). Digestion of this acid chloride with water produces a dibasic acid (XI) which may be completely decarboxylated to the compound XII (116). Compounds X, XI, and XII have not been characterized, but the following sequence would appear likely.



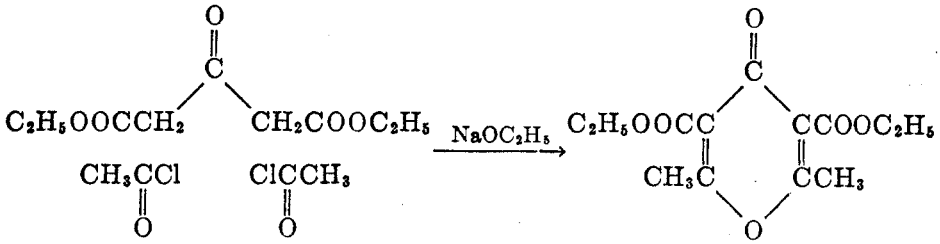
VII X XI XII

Meconic acid may be esterified to the mono acid ester in good yield by means of absolute alcohol and hydrogen chloride (152). Decarboxylation of this ester results in the formation of ethyl comenate.

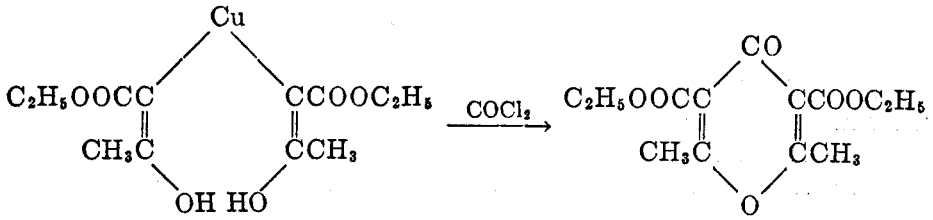


Ethyl comenate

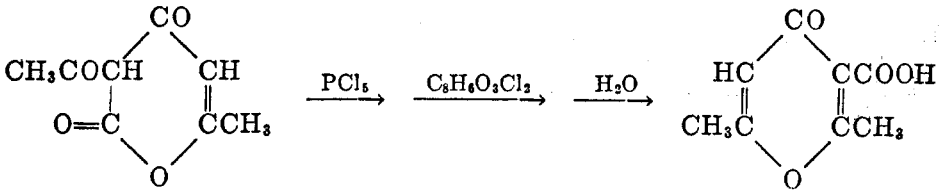
Ethyl 2,6-dimethylpyrone-3,5-dicarboxylate: The preparation of ethyl 2,6-dimethylpyrone-3,5-dicarboxylate may be carried out by treating diethyl acetonedicarboxylate with acetyl chloride (189).



Treatment of the copper salt of acetoacetic ester with phosgene also leads to the formation of ethyl 2,6-dimethylpyrone-3,5-dicarboxylate (64, 246).



2,6-Dimethylpyrone-3-carboxylic acid: Treatment of dehydroacetic acid (XIII) with phosphorus pentachloride results in the formation of 2,6-dimethylpyrone-3-carboxylic acid (55, 57, 81, 164).

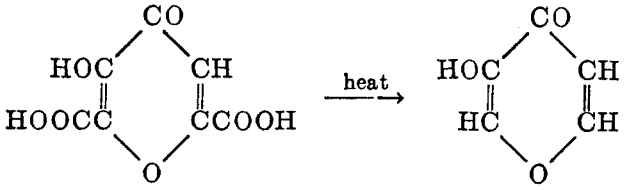


XIII
Dehydroacetic acid

The intermediate chloro derivative has not been characterized.

(b) Hydroxy-γ-pyrones

Pyromeconic acid (VIII): Pyromeconic acid is prepared by the complete decarboxylation of meconic acid (VII) (31, 37, 121, 165, 185, 186, 234). Small

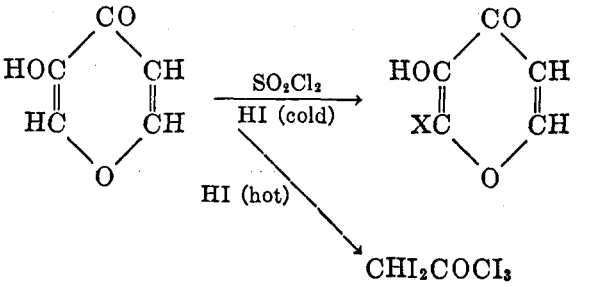


VII
Meconic acid

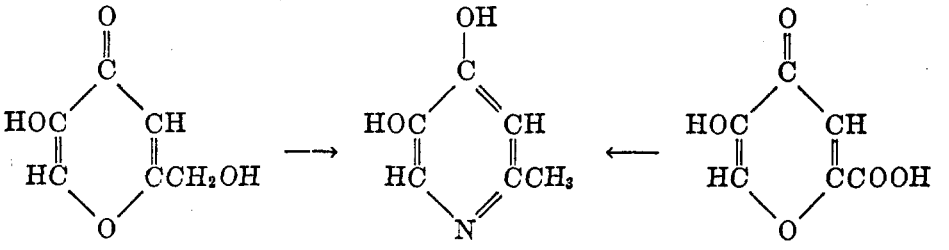
VIII
Pyromeconic acid

quantities (2 per cent) of pyromeconic acid are formed by the oxidation of γ-pyrone with hydrogen peroxide in the presence of sulfuric acid and ferrous sulfate (181).

Halogenating agents react with pyromeconic acid (VIII), resulting in the formation of the 6-halogeno derivative (183, 193, 194). The reaction with hot hydriodic acid leads to the formation of pentaiodoacetone.

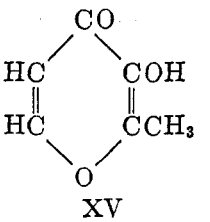


Kojic acid, 5-hydroxy-2-hydroxymethylpyrone (XIV): Kojic acid[2] is formed by the action of the fungus *Aspergillus flavus* on xylose or dextrose (159). The conversion is of interest, since in the case of xylose a five-carbon-atom compound is transformed into a six-carbon-atom compound. Proof of the structure of kojic acid is seen in the following conversions:



XIV
Kojic acid

Maltol, 3-hydroxy-2-methylpyrone (XV): Maltol is found widely distributed



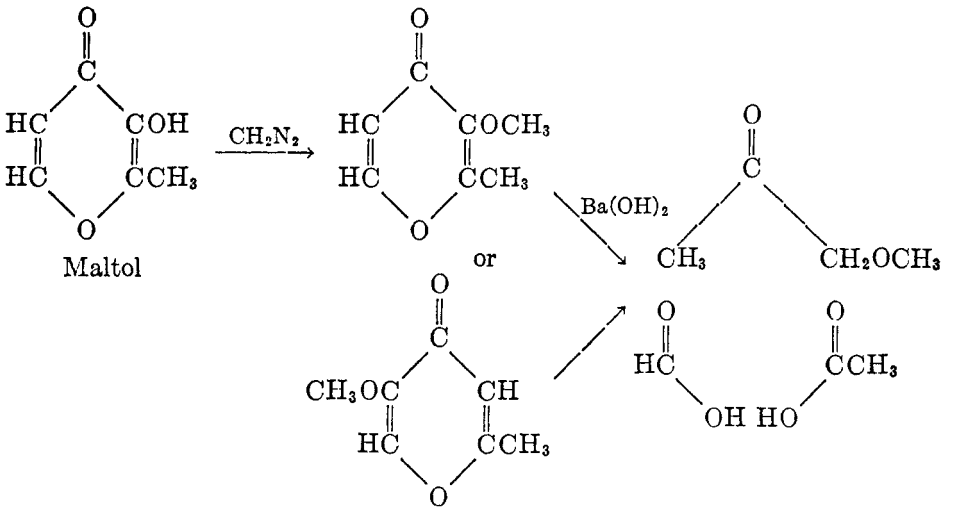
XV
Maltol

in nature. It occurs in the vapors of roasting malt (36), in the branches of the larch tree (190, 235), and in fresh needles of the silver fir (90). It may be ob-

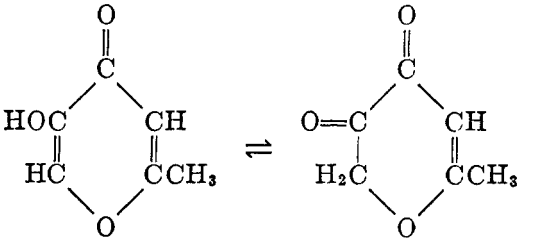
[2] An extended discussion of kojic acid has been omitted, since a review article has already appeared in the literature (18).

tained by the dry distillation of cellulose (79), from the acid hydrolysates of soybeans (129), and as a product of the alkaline hydrolysis of streptomycin (224).

Characterization of maltol was accomplished by means of degradation studies (194).



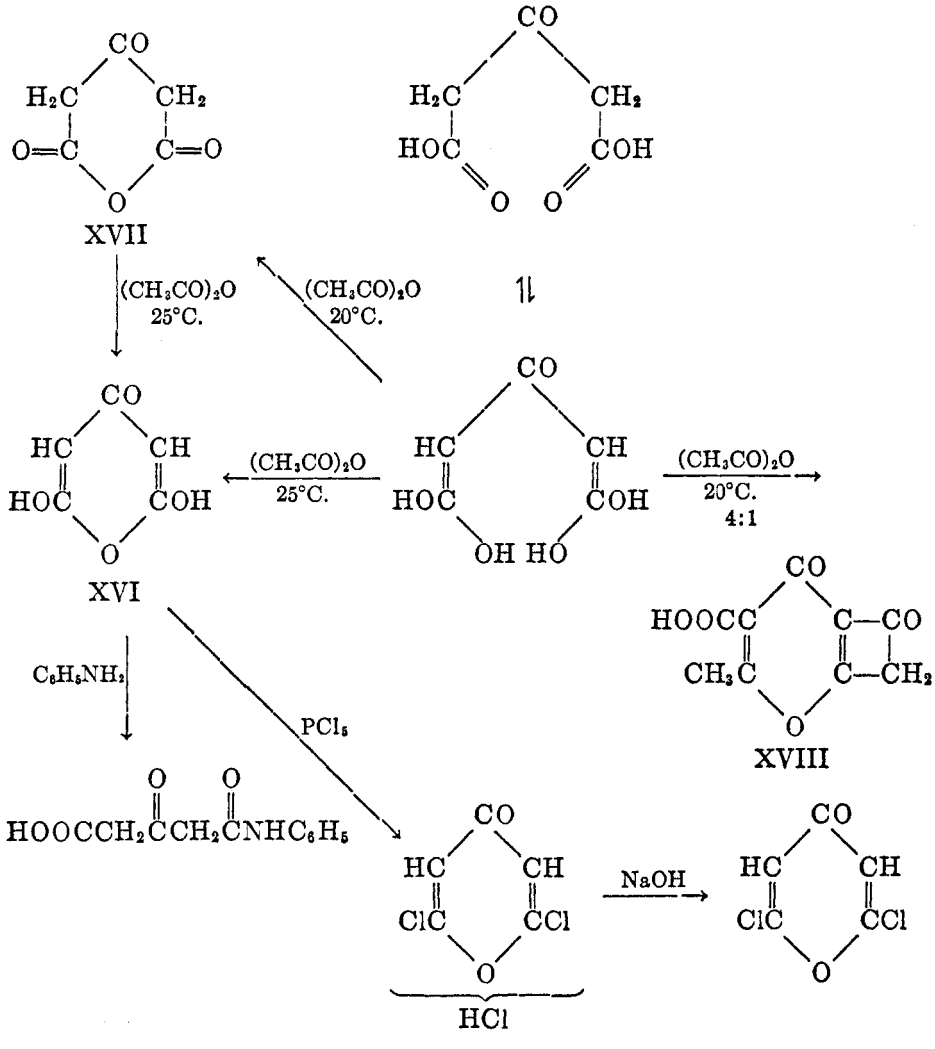
The possibility that maltol is 5-hydroxy-2-methylpyrone rather than 3-hydroxy-2-methylpyrone was ruled out on the basis of the following evidence: Maltol reacts neither with ethyl nitrite to produce an oxime nor with sulfuryl chloride to produce a chloro derivative. These reactions would be expected to take place if maltol possessed the following structure:



The absence of these reaction products, therefore, indicates that the position adjacent to the hydroxyl group is substituted.

2,6-Dihydroxypyrone: When acetic anhydride is caused to react with acetonedicarboxylic acid at 25°C., 2,6-dihydroxypyrone (XVI) (the enol form of acetonedicarboxylic acid anhydride) is produced, m.p. 94°C. At temperatures less than 20°C. the keto form (XVII) is formed, m.p. 136°C. When the ratio of acetic anhydride to acetonedicarboxylic acid is 4:1, compound XVIII is produced (124). The keto form (XVII) may be converted to the enol form (XVI) by treatment with acetic anhydride at 25°C. 2,6-Dichloropyrone may be prepared by the action of phosphorus pentachloride on 2,6-dihydroxypyrone (XVI).

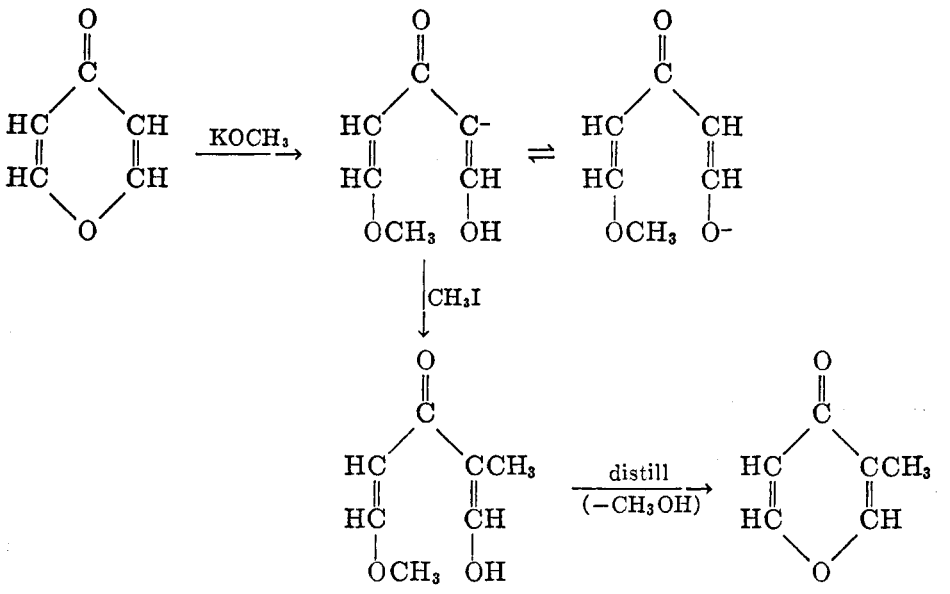
The treatment of XVI with aniline results in the formation of the monoanilide of acetonedicarboxylic acid (125).



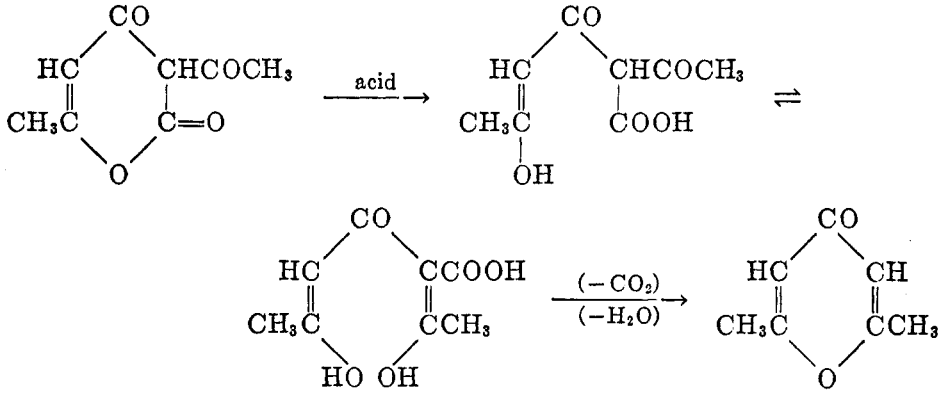
3-Hydroxy-2,6-dimethylpyrone: 2,6-Dimethylpyrone may be oxidized to 3-hydroxy-2,6-dimethylpyrone by the action of hydrogen peroxide in the presence of sulfuric acid and ferrous sulfate (243). This oxidation is analogous to that encountered with γ-pyrone itself.

(c) Alkyl-γ-pyrones

3-Methylpyrone: 3-Methylpyrone is formed when methyl iodide reacts with γ-pyrone in the presence of potassium methoxide (261).

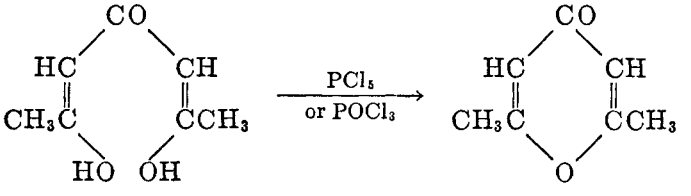


2,6-Dimethylpyrone: 2,6-Dimethylpyrone may be prepared from dehydroacetic acid by the action of either sulfuric, hydrochloric, or hydriodic acid (52, 53, 81, 82). The reaction takes place according to the following equations:

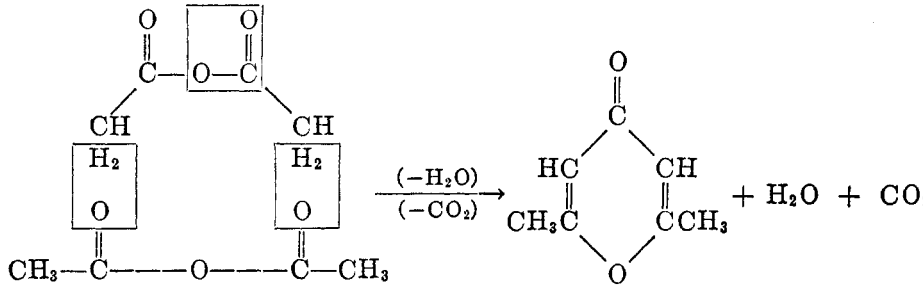


2,6-Dipropylpyrone is similarly prepared from dehydropropionylacetic acid (71).

Diacetylacetone may be cyclized with either phosphorus pentachloride or phosphorus oxychloride to yield 2,6-dimethylpyrone (89).

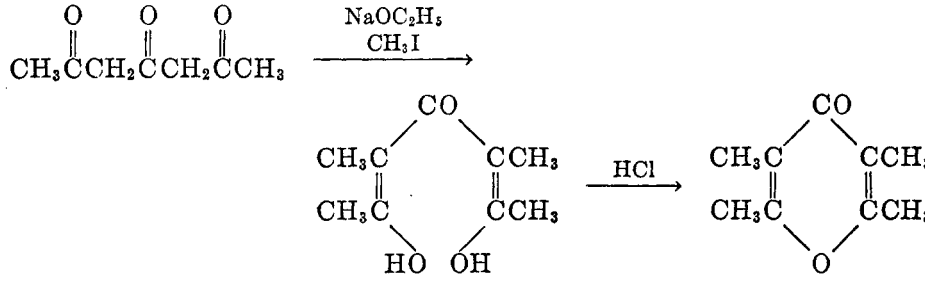


Skraup and Priglinger (232) made the interesting discovery that acetic anhydride is converted to 2,6-dimethylpyrone in low yield (2 per cent) in the presence of either phosphorus pentoxide or concentrated sulfuric acid.



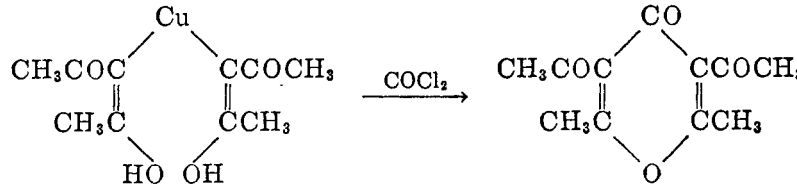
The addition of acetone to the reaction mixture increases the yield of 2,6-dimethylpyrone to 4 per cent (198). In the presence of ethyl methyl ketone, 2,3,6-trimethylpyrone is formed.

2,3,5,6-Tetramethylpyrone: 2,3,5,6-Tetramethylpyrone is prepared by the

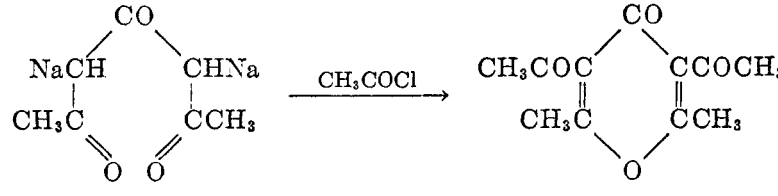


action of hydrochloric acid on dimethyldiacetylacetone (58). If ethyl iodide is substituted for methyl iodide in this reaction, a mixture results which is composed of 2,6-dimethyl-3-ethylpyrone and 2,6-dimethyl-3,5-diethylpyrone (14).

3,5-Diacetyl-2,6-dimethylpyrone: 3,5-Diacetyl-2,6-dimethylpyrone is formed when phosgene reacts with the copper salt of acetylacetone (244).

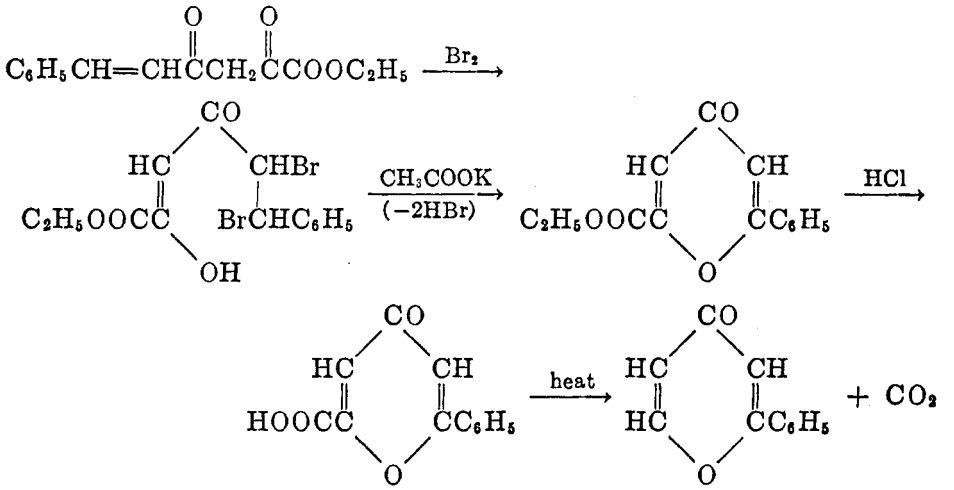


3,5-Diacetyl-2,6-dimethylpyrone may also be prepared by the action of acetyl chloride on the disodium salt of diacetylacetone (54).

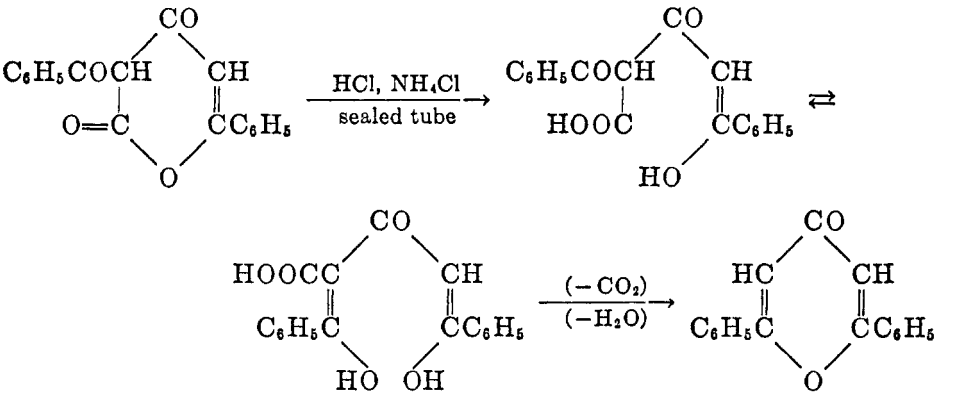


(d) Aryl-γ-pyrones

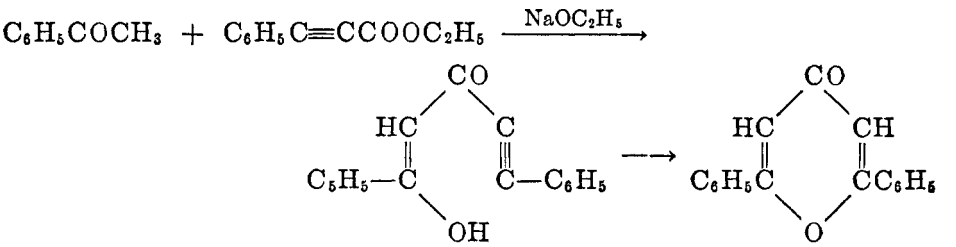
2-Phenylpyrone: 2-Phenylpyrone is prepared by the action of potassium acetate on ethyl cinnamoylacetate dibromide (33).



2,6-Diphenylpyrone: The preparation of 2,6-diphenylpyrone from dehydro-benzoylacetic acid (227) is analogous to that of 2,6-dimethylpyrone from dehydroacetic acid.

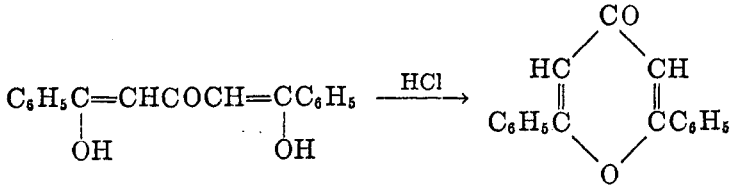


The reaction of acetophenone with ethyl phenylpropiolate yields 2,6-diphenylpyrone (49).



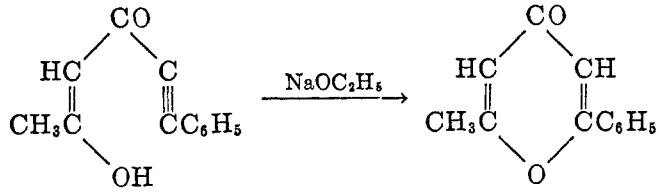
2,6-Diphenylpyrone may also be prepared by the action of alcoholic potassium hydroxide on dibenzalacetone tetrabromide (251).

$$C_6H_5CH{=}CHCOCH{=}CHC_6H_5 \xrightarrow[CHCl_3]{Br_2} C_6H_5CHBrCHBrCOCHBrCHBrC_6H_5 \xrightarrow[(-2HBr)]{\text{alc. KOH}}$$



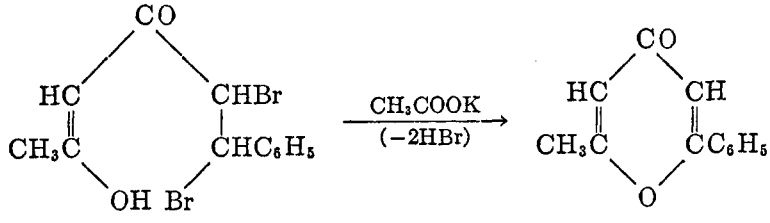
2-Phenyl-6-methylpyrone: 2-Phenyl-6-methylpyrone is prepared by reacting acetone with ethyl phenylpropiolate in the presence of sodium ethylate (17, 219).

$$CH_3COCH_3 + C_2H_5OOCC{\equiv}CC_6H_5 \xrightarrow{NaOC_2H_5} CH_3COCH_2COC{\equiv}CC_6H_5 \rightleftharpoons$$



2-Phenyl-6-methylpyrone may also be prepared by the action of potassium acetate on cinnamoylacetone dibromide.

$$C_6H_5CH{=}CHCOCH_2COCH_3 \xrightarrow{Br_2} C_6H_5CHBrCHBrCOCH_2COCH_3 \rightleftharpoons$$



(e) Halogenated γ-pyrones

Halogenated γ-pyrones may be produced by direct halogenation of either the γ-pyrone ring or the appropriate open-chain compound. The former method is discussed on page 563.

The action of bromine on acetonedioxalic ester results in the formation of diethyl 3,5-dibromochelidonate (88). If chlorine is used in place of bromine, decomposition occurs and a considerable quantity of oxalic acid and chloroacetones is formed together with a small quantity of the desired diethyl 2,6-di-

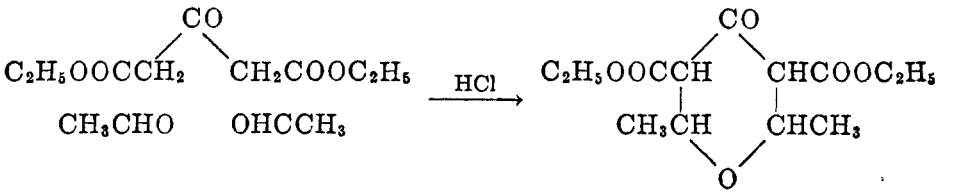
chlorochelidonate. A higher yield of diethyl 2,6-dichlorochelidonate may be obtained by the use of sulfuryl chloride; in this case, however, the product is contaminated with the monochloro derivative (86). Iodination of acetonedioxalic ester does not produce an iodopyrone.

Treatment of the barium salt of diacetylacetone with selenium tetrachloride results in the formation of 3,5-dichloro-2,6-dimethylpyrone (158).

3. Hydropyrones

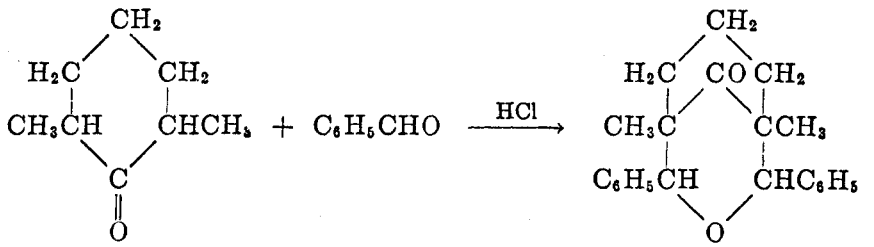
Hydropyrones resulting from either the catalytic hydrogenation or the chemical reduction of the γ-pyrone nucleus will be discussed on page 551. We shall be concerned here only with the hydropyrones which are formed directly.

Hydropyrones may be prepared by an aldol reaction in either acid or alkaline solution. For example, the reaction of acetaldehyde with diethyl acetonedicarboxylate in the presence of aqueous hydrochloric acid leads to the formation of ethyl 2,6-dimethyltetrahydropyrone-3,5-dicarboxylate (196, 222). Diethyl ketone condenses with benzaldehyde in aqueous sodium hydroxide to yield 2,6-



diphenyl-3,5-dimethyltetrahydropyrone (196). The action of 40 per cent formaldehyde on acetone in alkaline solution produces small quantities of 3-(or 5-)-hydroxymethyltetrahydropyrone (156).

The reaction is not limited to open-chain carbonyl compounds. Cornubert (66, 67) obtained tetrahydropyrones from cyclic ketones.

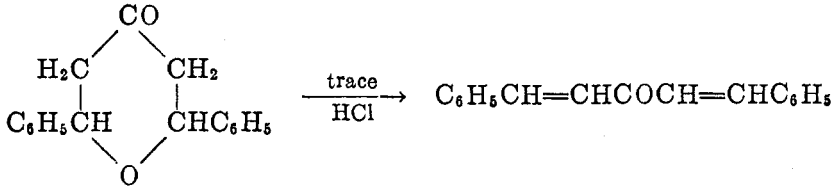


XVIII

Compound XVIII would be expected to have four optically active forms existing as two *d,l* racemic modifications, together with four *meso* forms. Cornubert isolated three forms: A, m.p., 175°C.; B, m.p., 216°C.; C, m.p., 206°C. A and B are obtained from *cis*-2,6-dimethylcyclohexanone, while C results from the action of hydrochloric acid on A.

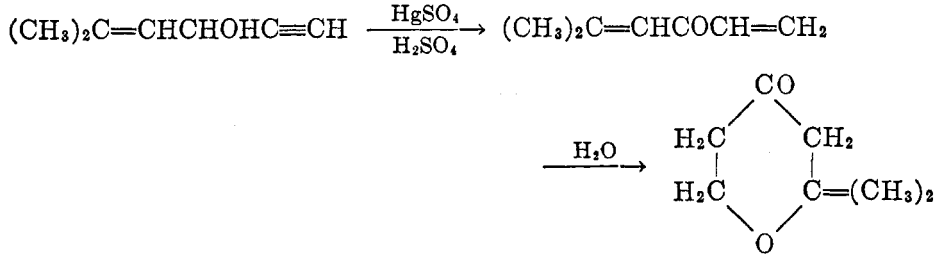
Treatment of diphenyltetrahydropyrones with aqueous hydrochloric acid at high temperatures (125–150°C.) results in the formation of a variety of hydrolysis

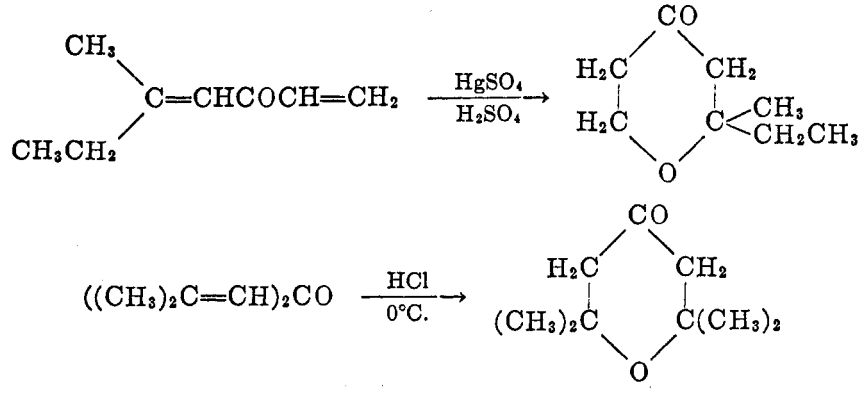
products, from which only benzaldehyde has been isolated (66). In the presence of traces of hydrochloric acid the degradation is incomplete. Thus, dibenzalacetone is produced when hydrochloric acid acts on 2,6-diphenyltetrahydropyrone (68).



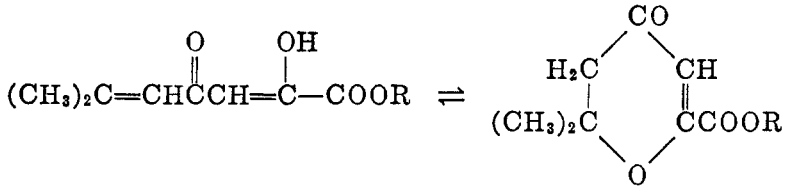
Attempts to reduce the carbonyl group in tetrahydropyrones with sodium and alcohol have been unsuccessful (79). The oxidation of 2,6-diphenyltetrahydropyrone with potassium permanganate results in the formation of formic, benzoic, oxalic, and carbonic acids.

Hydropyrones may also be prepared by the isomerization and subsequent hydration of the appropriate unsaturated carbinols (77, 78). For example, (dimethylvinyl)ethynylcarbinol is isomerized to dimethylvinyl vinyl ketone by the action of mercuric sulfate and sulfuric acid. The divinyl ketone is hydrated and then undergoes cyclization to 2,2-dimethyltetrahydropyrone. The intermediate unsaturated ketone need not be isolated; in fact, unsaturated ketones may be used as the starting materials (161).



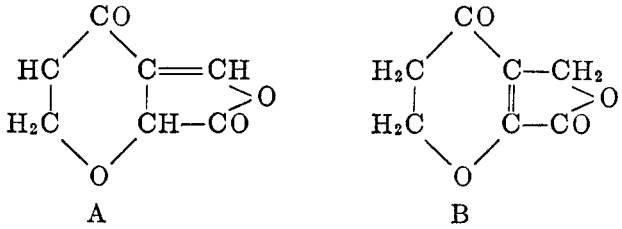


The formation of dihydropyrones by the isomerization of the appropriate monovinyl ketone presents an interesting case (9, 34, 73, 92, 130). The enol form of XIX exists in equilibrium with the cyclic dihydro derivative XX. The equilibrium lies far to the right.

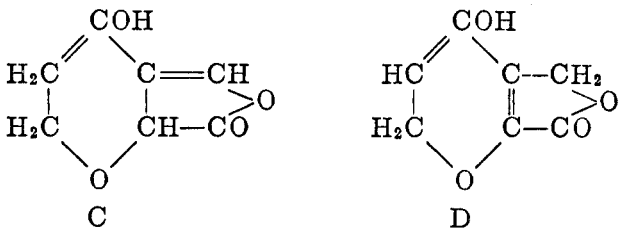


XIX (3 per cent) ⇌ XX (97 per cent)

Clavacin: Clavacin (patulin) is a tetrahydropyrone derivative which has been isolated from culture media of *Aspergillus clavatus* (253) and *Penicillium claviforme* (20). According to Raistrick (204), clavacin may be considered to be the lactone of 3-hydroxymethylenetetrahydrocomanic acid (structure A). However, Bergel and coworkers (21) have presented evidence that clavacin exists in solution as a mixture of isomers, and suggested the forms A, B, C, and D.

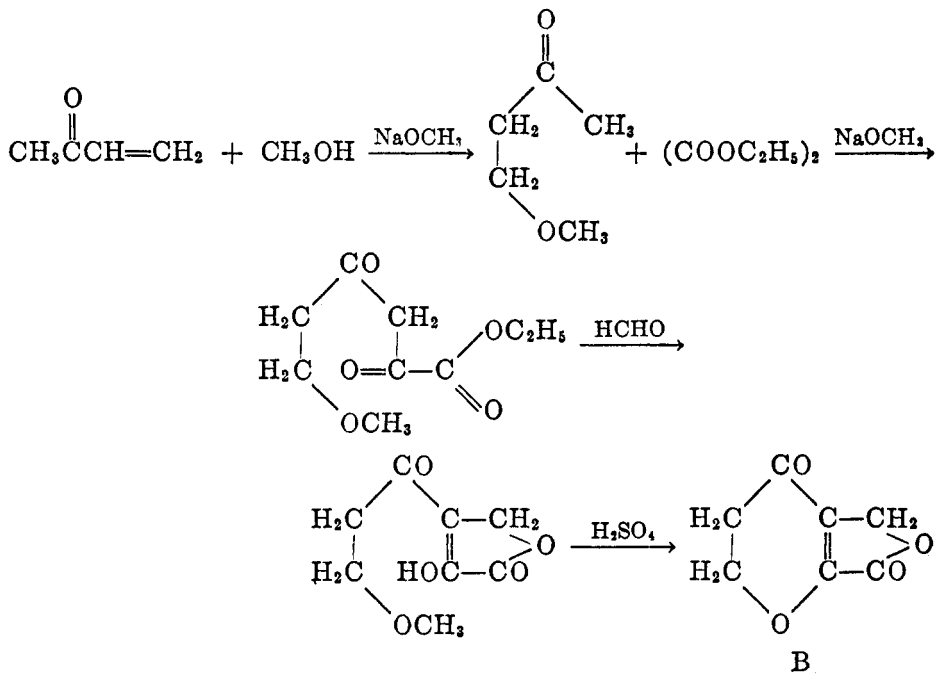


A B



C D

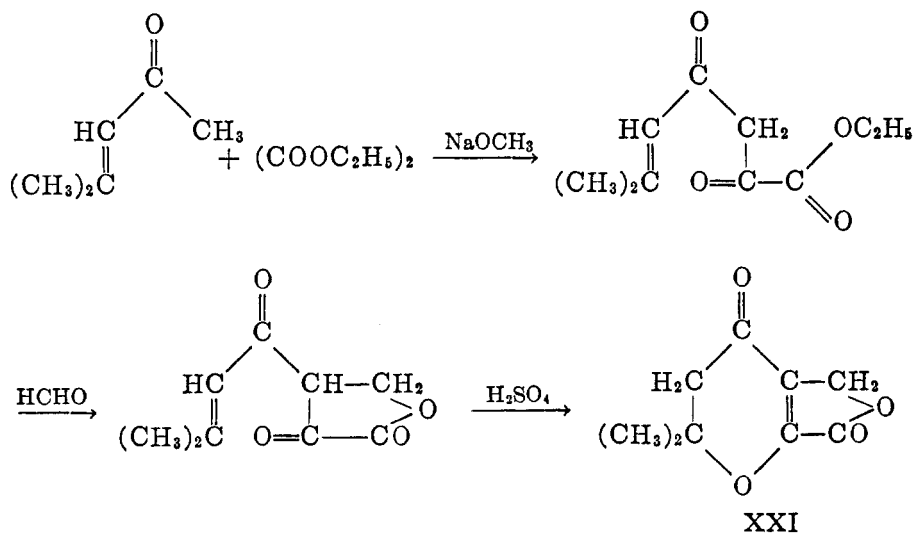
The isomer B has been synthesized by Puetzer, Nield, and Barry (202) by the reactions shown. It does not exhibit the characteristics of clavacin and may be eliminated from the list of possibilities.



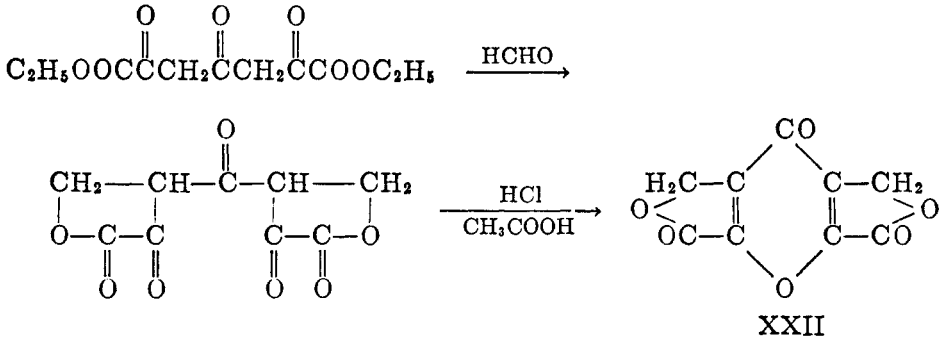
B

Clavacin and the isomer B are not mutually interconvertible by the action of either acids or heat.

Compounds related to clavacin: Various compounds related to clavacin have been synthesized (202), among them XXI and XXII. The reaction sequence is similar to that employed in the synthesis of compound B.



XXI



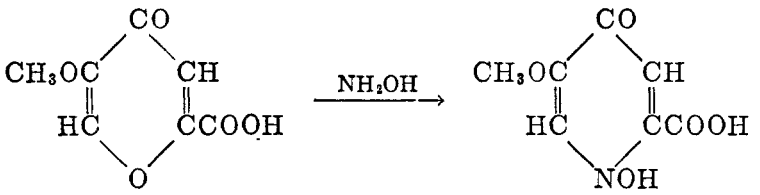
XXII

C. CHEMICAL PROPERTIES

1. Reactivity of the carbonyl group

The carbonyl group in the γ-pyrone nucleus exhibits an anomalous behavior. The reaction of γ-pyrones with reagents such as hydroxylamine and phenylhydrazine does not lead to the formation of the oxime or phenylhydrazone. This may be explained on the basis that γ-pyrones are not simple unsaturated ketones but are instead ester vinylogs (—C(=O)—C=C—O—) in which the carbonyl group has lost its activity as such and has taken on the characteristics of a carbonyl group present in an ester. The action of phenylhydrazine on 2,6-dimethylpyrone does not result in the formation of 2,6-dimethylpyrone phenylhydrazone (81). No known products have been isolated from this reaction.

The action of hydroxylamine on comenic (163), 6-hydroxycomenic, chelidonic, meconic (245), or pyromeconic (163) acids or their esters or on maltol (36) does not yield the oxime. In all cases the γ-pyrone nucleus remains intact. In the case of meconic acid the hydroxylamine salt is formed (192). The methyl ether of comenic acid yields an *N*-hydroxypyridone (XXIII) with hydroxylamine (195).

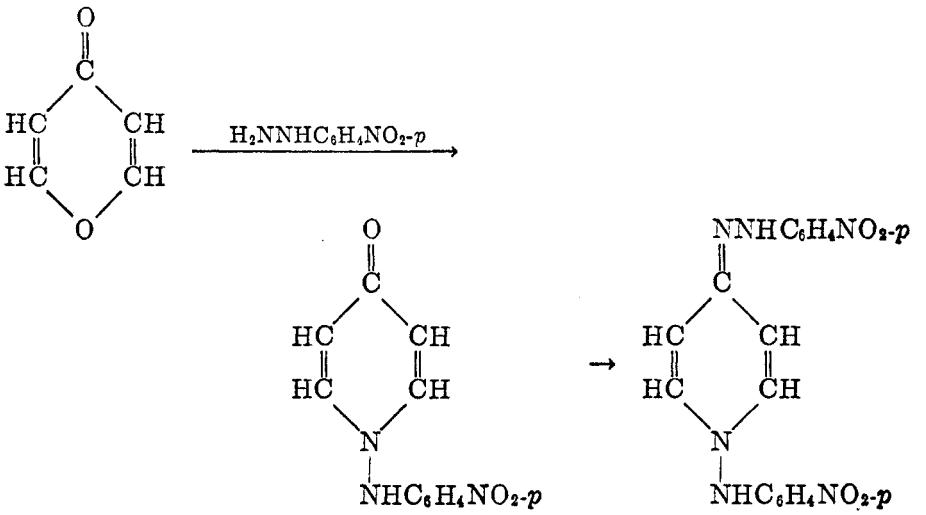


XXIII

This reaction is analogous to that encountered with ammonia.

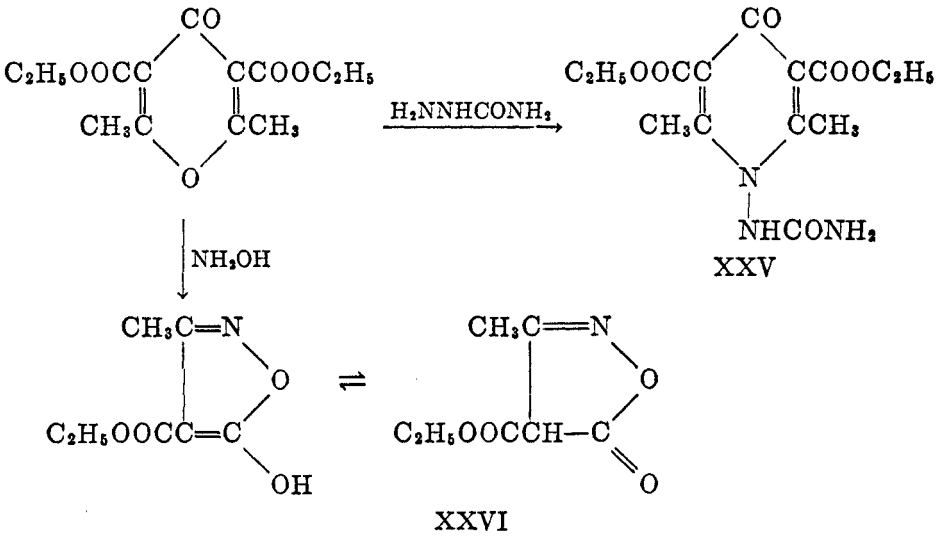
With the more reactive *p*-nitrophenylhydrazine, diethyl chelidonate and diethyl 3,5-dibromochelidonate react to give the *p*-nitrophenylhydrazones.

Under these conditions, γ-pyrone, chelidonic acid, and ethyl comanate produce the *p*-nitrophenylhydrazones of the *N*-*p*-nitrophenylamino-γ-pyridone.



XXIV

The action of semicarbazide on ethyl 2,6-dimethylpyrone-3,5-dicarboxylate produces an *N*-substituted γ-pyridone (XXV) (246). The reaction of hydroxyl-



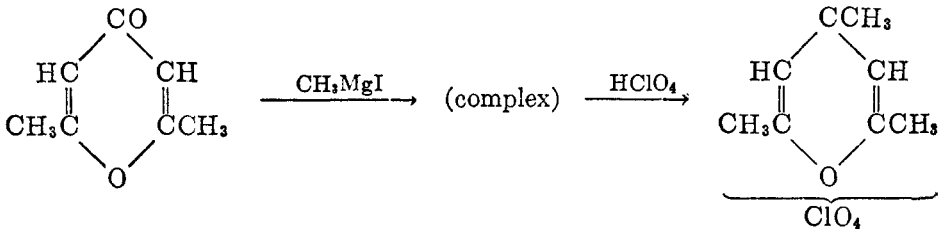
XXV

XXVI

amine with ethyl 2,6-dimethylpyrone-3,5-dicarboxylate results in the formation of an isoxazalone (XXVI). The mechanism of this reaction is not clearly understood (170, 171).

The reaction between 2,6-dimethylpyrone and hydrazine produces a colorless liquid of unknown structure (131).

Grignard reagent: The action of methylmagnesium iodide on 2,6-dimethylpyrone produces a Grignard complex which yields 2,4,6-trimethylpyroxonium perchlorate when it is decomposed with perchloric acid (11). Phenylmagnesium



bromide behaves in an analogous manner. Ammonia converts 2,4,6-trimethylpyroxonium perchlorate into 2,4,6-trimethylpyridine (collidine) (11).

2. *Behavior as α,β-unsaturated carbonyl compounds*

Reactions typical of α,β-unsaturated ketones do not occur with γ-pyrones. Thus, 2,6-dimethylpyrone does not react with malonic ester in the manner of the Michael condensation. The product of the reaction contains a molecule of 2,6-dimethylpyrone and a molecule of sodium malonic ester:

$$C_7H_8O_2 \cdot CHNa(COOC_2H_5)_2$$

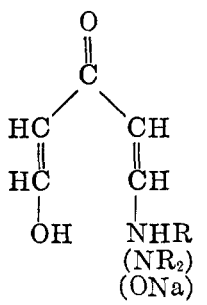
This salt-like addition compound is decomposed by water to yield a solution containing 2,6-dimethylpyrone and malonic ester (250).

The reaction of ammonia or amines to produce β-amino ketones does not occur in the pyrone series.

3. *Stability in alkaline and acid media*

(a) In alkaline solution

The action of bases on γ-pyrones causes cleavage of the ring. The ultimate product of this cleavage depends upon the nature of the base and the temperature



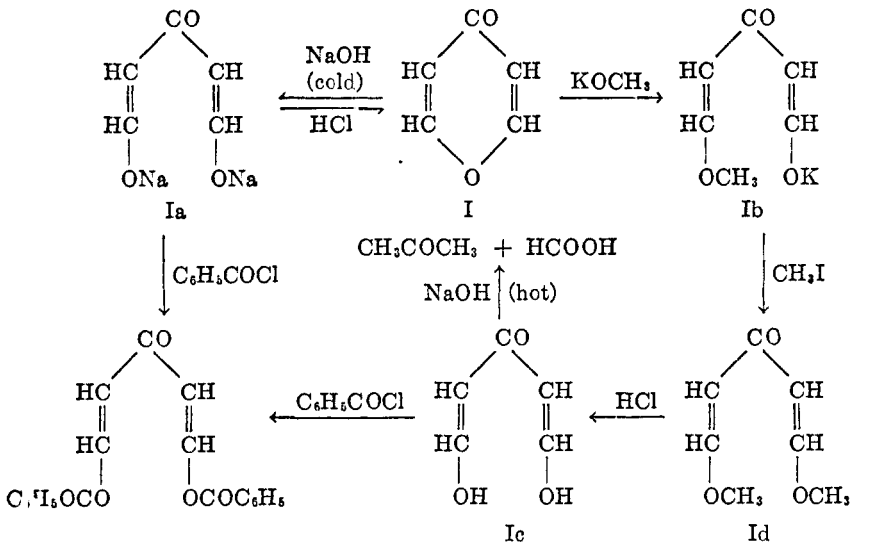
of the reaction.

Alkali: The various reaction products obtained in alkaline media are shown in table 2 (261). γ-Pyrone is converted to the sodium salt of diformylacetone (Ia) by the action of cold sodium hydroxide. Diformylacetone dibenzoate may be formed by treating Ia with benzoyl chloride. Potassium methoxide cleaves

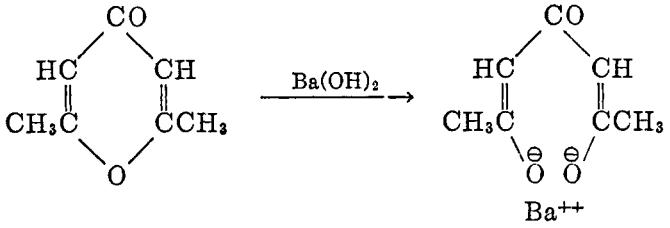
γ-pyrone, producing the monomethyl ether of diformylacetone (Ib). The action of methyl iodide on Ib produces the dimethyl ether. The latter compound is hydrolyzed in acid solution with great ease. At elevated temperatures, the action of sodium hydroxide on γ-pyrone results in complete degradation, producing acetone and formic acid.

TABLE 2

Reactions of γ-pyrone under alkaline conditions



Barium hydroxide converts 2,6-dimethylpyrone into the barium salt of diacetylacetone (61).

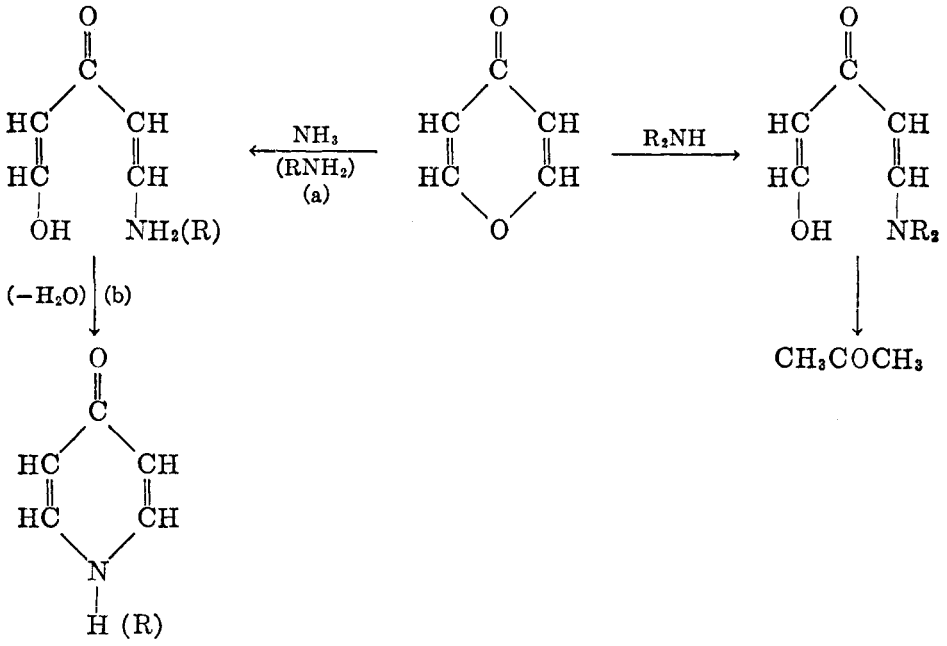


Ammonia and amines: The γ-pyrone ring is transformed into a γ-pyridone ring by the action of ammonia (140, 168) and of primary amines (32, 65, 108, 171, 233).

Secondary amines cause the same type of cleavage; however, in this case cyclization (step b) cannot occur and the open-chain intermediate is hydrolyzed under the alkaline action of the dialkylamine.

The reaction to produce γ-pyridones is general with only a few exceptions. For example, the γ-pyrone nucleus in pyromeconic acid and maltol remains intact

under the action of ammonia. In these cases an ammonium salt is formed. However, the methyl ethers of these compounds do react to yield the corresponding γ-pyridones (193, 194).



Potassium amide: The action of potassium amide (226) or 4-phenylbenzophenone potassium (225) on 2,6-dimethylpyrone produces a monopotassium salt.

(b) In acid solution

The γ-pyrone ring is stable in acid media. The only change which occurs involves the formation of pyroxonium salts (page 559).

4. Reduction

(a) Chemical reduction

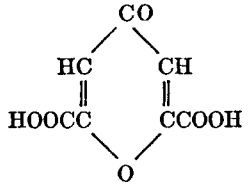
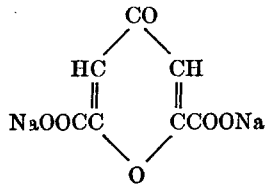
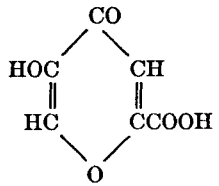
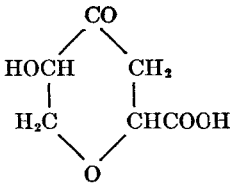
Reduction of the γ-pyrone ring by chemical means generally produces a complex reaction mixture. In some cases the ring is cleaved and aliphatic fragments result. This method is therefore not recommended for the preparation of tetrahydropyrones. Table 3 contains the known cases of chemical reduction.

(b) Catalytic hydrogenation

Catalytic hydrogenation affords a more successful method for the preparation of tetrahydropyrones than does chemical reduction. An outline of all the γ-pyrones that have been hydrogenated is contained in table 4.

TABLE 3

Chemical reduction of γ-pyrones

COMPOUND	REDUCING AGENT	PRODUCT	REFERENCE
 Chelidonic acid	Zn, CH_3COOH HI	$HOOCCHCH_2CHCH_2CH_2COOH$	(81, 107, 141)
	Na(Hg)	$HOOCCHOHCH_2CHOHCH_2CHOHCOOH$	(107)
 Comenic acid	Na(Hg)		(135)

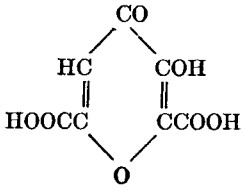
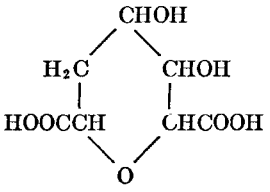
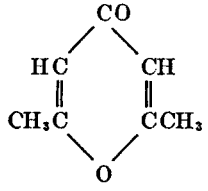
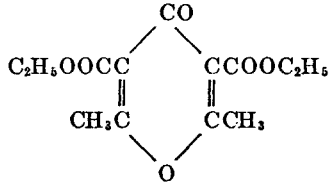
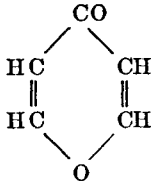
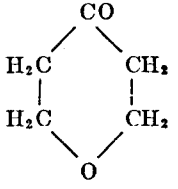
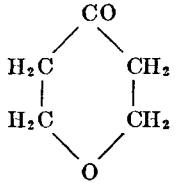
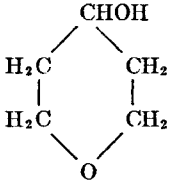
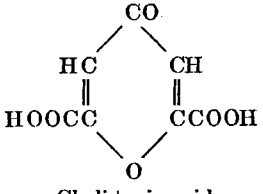
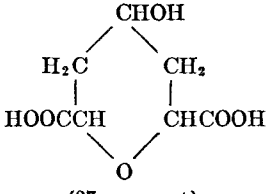
 Meconic acid	Na(Hg)		(135)
	Mg, CH_3COOH	Unidentified products	(12)
	Al(Hg)	No reduction	(246)
	Na(Hg), CH_3COOH	Unidentified product	

TABLE 4

*Catalytic hydrogenation of γ-pyrones**

COMPOUND	PRODUCT (PER CENT YIELD)	CATALYST	REFERENCE
 γ-Pyrone		$PdCl_2$	(30)
	 (23 per cent)  (50 per cent)	CuCrO	(160)†
 Chelidonic acid	No reduction	PtO_2	(156)
	 (97 per cent)	$Pd/BaSO_4$	(8)

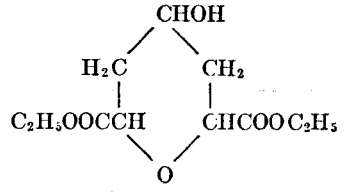
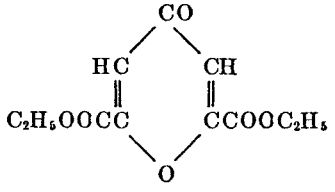
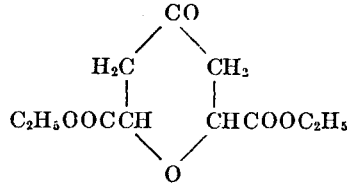
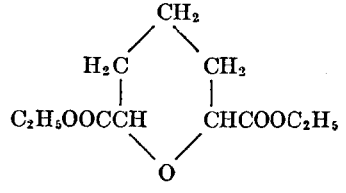
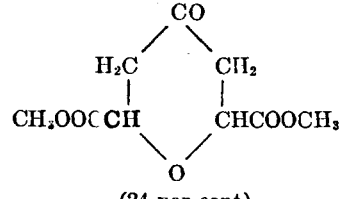
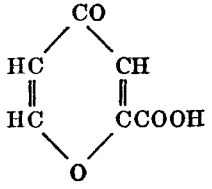
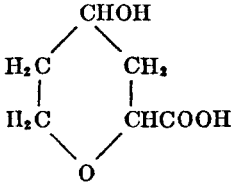
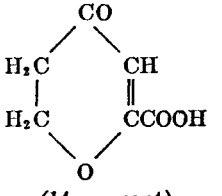
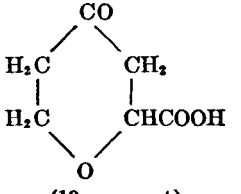
	 (25 per cent)	$Pd/BaSO_4$	(8)
 Diethyl chelidonate	 (9 per cent)	Raney nickel PtO_2 (alcohol) $PdCl_2$ (alcohol) $Pd/BaSO_4$	(8) (70) (30) (8)
		PtO_2 (CH_3COOH)	(69)
Dimethyl chelidonate	 (24 per cent)	Raney nickel	(8)

TABLE 4—*Continued*

COMPOUND	PRODUCT (PER CENT YIELD)	CATALYST	REFERENCE
 Comanic acid	  (14 per cent)	$Pd/BaSO_4$	(8)
	 (10 per cent)	$Pd/BaSO_4$ Pd/charcoal	(8)

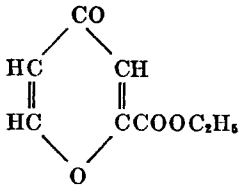
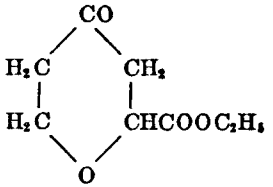
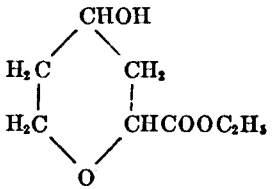
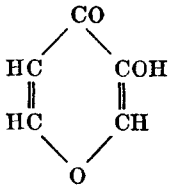
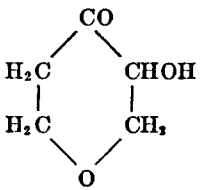
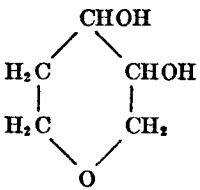
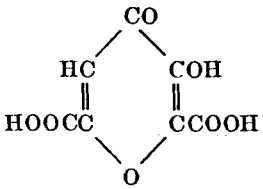
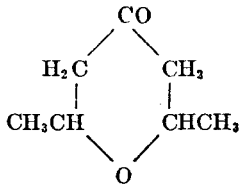
 Ethyl comanate	 (20 per cent)	Pd (colloidal)	(8)
	 (23 per cent)		
 Pyromeconic acid	 	$PdCl_2$	(31)
 Meconic acid	$HOOCCHOHCHOHCHOHCH_2CHOHCOOH$	$PdCl_2$	

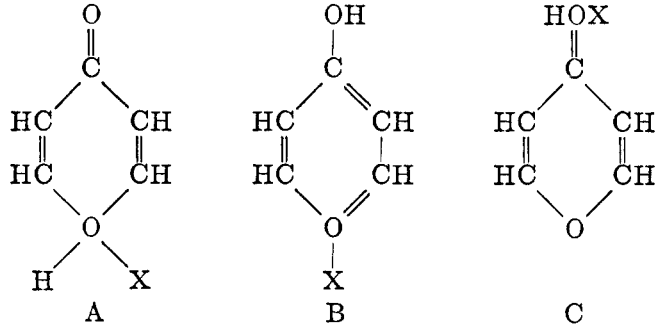
TABLE 4—*Continued*

COMPOUND	PRODUCT (PER CENT YIELD)	CATALYST	REFERENCE
2,6-Dimethylpyrone		PtO_2	(70)
		$PdCl_2$	(30)

* All hydrogenations were carried out at room temperature and atmospheric pressure unless otherwise noted.
† High pressure; 125°C.

D. PYROXONIUM SALTS

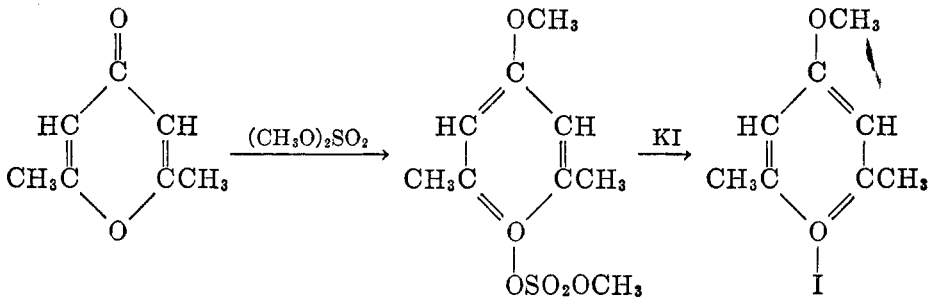
The treatment of γ-pyrones with either organic or inorganic acids results in the formation of stable salt-like compounds which are known as pyroxonium salts. The structure of the pyroxonium salts has been the subject of wide discussion and at present no definite structure can be assigned to them. The major difficulty arises from the fact that there are two oxygen atoms present in the nucleus, each of which could theoretically participate in the salt formation.



In the nitrogen system, structure A (a vinylogous tautomer of B) may be considered to be analogous to the acid salt of an amine (12, 13, 15, 51, 53, 54, 117), while structure C is equivalent to a ketimine hydrochloride. This analogy has served as the basis for the structure of the pyroxonium salts. Thus Hantzsch (111) has shown that freezing-point and conductivity measurements taken on a solution of 2,6-dimethylpyrone in concentrated sulfuric acid give rise to data similar to those observed on a system containing an amine and sulfuric acid. Further, the intense band in the ultraviolet region of the spectrum exhibited by 2,6-dimethylpyrone in alcohol is no longer evident when concentrated sulfuric acid is used as the solvent. This evidence has been interpreted as indicating the existence of structure B (256, 257). Gibbs, Johnson, and Hughes (96) reported that the ultraviolet absorption spectrum of 2,6-dimethylpyrone in alcohol is similar to that observed in alcohol containing an equivalent of hydrogen chloride. These workers suggested that the formation of pyroxonium salts does not involve any change in the structure of the γ-pyrone ring and proposed structure C. It is quite doubtful, however, that this solution is similar to that employing concentrated sulfuric acid as the solvent. At least part of the discrepancy may be due to the fact that 2,6-dimethylpyrone is a very weak base and the presence of only one equivalent of hydrogen chloride might not be sufficient to allow appreciable formation of pyroxonium salts.

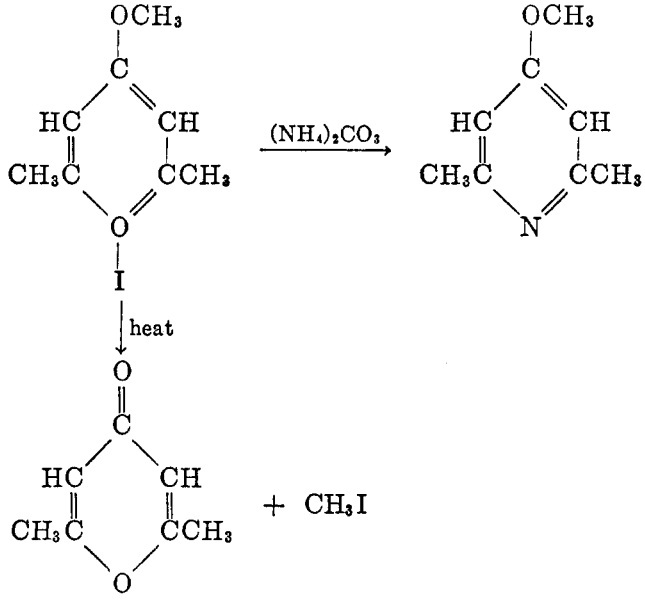
A more complex type of pyroxonium salt is one in which the ratio of acid to pyrone is not 1:1 (150). For example, Kendall (98, 127) isolated the following types of compounds from systems containing 2,6-dimethylpyrone and an organic acid: $C_7H_8O_2 \cdot HX$, $2C_7H_8O_2 \cdot 3HX$, $C_7H_8O_2 \cdot 2HX$. The salts containing one molecule of pyrone for each molecule of acid were assigned structure C (173, 260), while the more complex salts were believed to involve the heterocyclic oxygen atom (148).

A second type of pyroxonium salt corresponds to the structure $(R_3O^+)\ X^-$. Kehrmann and Duttenhöfer (126) prepared this type by reacting 2,6-dimethylpyrone with methyl sulfate, followed by treatment with potassium iodide (97, 247).

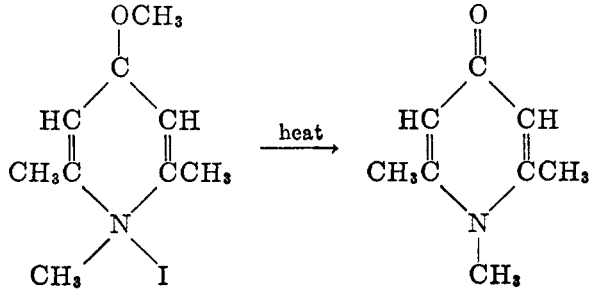


XXVII

Direct proof (10) of structure XXVII lies in the fact that it is converted to 2,6-dimethyl-4-methoxypyridine on treatment with ammonium carbonate. On heating, compound XXVII reverts to 2,6-dimethylpyrone and methyl iodide.



The latter reaction has a counterpart in the nitrogen system (63).



E. BASIC STRENGTH

Walker (255) and Wood (264) studied the rate of hydrolysis of methyl acetate in hydrochloric acid solution containing an equivalent of 2,6-dimethylpyrone. The velocity constant thus obtained was compared to that obtained from a solution of hydrochloric acid containing no 2,6-dimethylpyrone. The rate of hydrolysis was lower in the mixture containing 2,6-dimethylpyrone. They calculated 2,6-dimethylpyrone to be a stronger base than urea, and 2,3,5,6-tetramethylpyrone to be a weaker base than urea.

Using a similar point of attack, Johnson and Partington (122) and Mitchell and Partington (155) noted the decrease in the extent of esterification of phenylacetic acid in the presence of various γ-pyrones, using hydrochloric acid as the catalyst. It was concluded that this decrease was due to a combination between the γ-pyrone and the hydrochloric acid catalyst, an effect which would decrease the effective concentration of the hydrochloric acid. The retarding effect was found to be in the following decreasing order: 2,6-dimethylpyrone > 2-phenyl-6-methylpyrone > 2,6-diphenylpyrone > γ-pyrone. This interpretation overlooks the possibility that the pyroxonium ion may also contribute to the acid catalysis.

Rordam (216) approached the problem of the basicity of 2,6-dimethylpyrone from a different viewpoint. In an aqueous solution of 2,6-dimethylpyroxonium chloride the chloride-ion concentration is greater than the hydrogen-ion concentration if it is assumed that the unhydrolyzed pyroxonium salt dissociates into (2,6-dimethylpyrone)$H^+ + Cl^-$ (13).

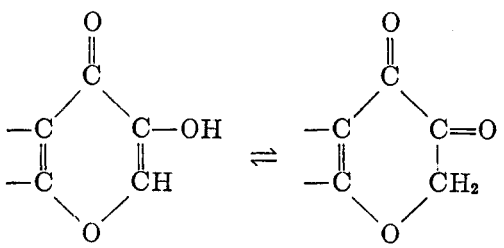
$$\text{2,6-Dimethylpyrone}\cdot HCl \xrightarrow{\text{hydrolysis}} \text{2,6-dimethylpyrone} + H^+ + Cl^-$$

$$\text{2,6-Dimethylpyrone}\cdot HCl \xrightarrow{\text{dissociation}} \text{2,6-dimethylpyrone}\cdot H^+ + Cl^-$$

Experimentally the chloride-ion concentration was found to be greater than the hydrogen-ion concentration. From his data, Rordam calculated the K_B for 2,6-dimethylpyrone to be 1.9×10^{-14} (254) (K_B for urea = 1.5×10^{-14}).

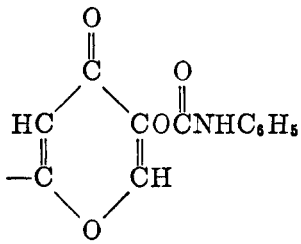
F. THE TAUTOMERISM OF HYDROXYPYRONES

The hydroxyl group in 3-hydroxypyrones is a component of a keto–enol tautomeric system. Evidence for the existence of this equilibrium is as follows:

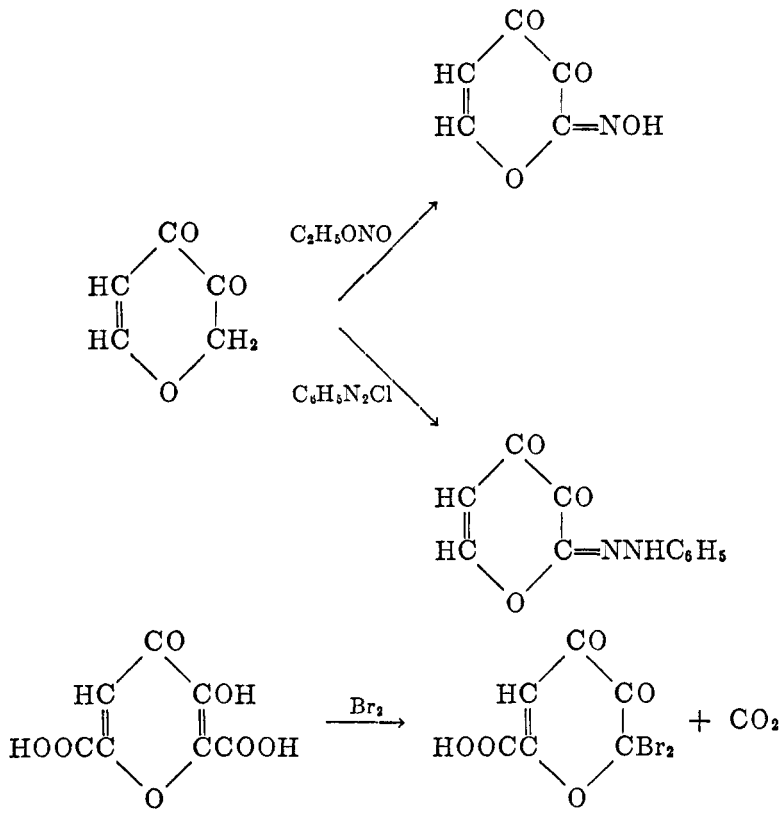


The reaction of hydroxypyrones with diazomethane yields the methyl ethers (188, 239, 245). Under the conditions of the Schotten–Baumann reaction a benzoate is formed (193). With acetic anhydride an acetate is produced (208).

The action of phenyl isocyanate results in the formation of a urethan (56). Hydroxypyrones develop a red coloration with ferric chloride.



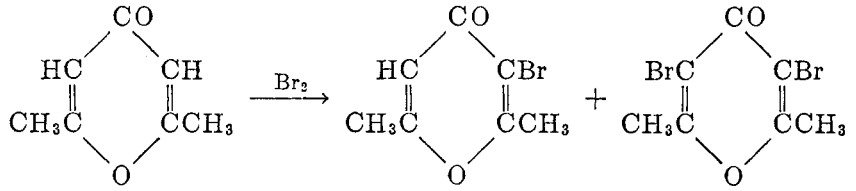
Evidence for the keto form is seen in the following reactions (182):



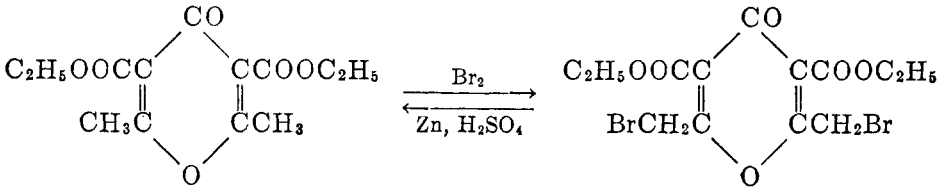
G. THE AROMATIC CHARACTER OF γ-PYRONES

γ-Pyrones undergo several reactions which are typical of aromatic compounds. The reactions which will be considered are halogenation, mercuration, and nitration.

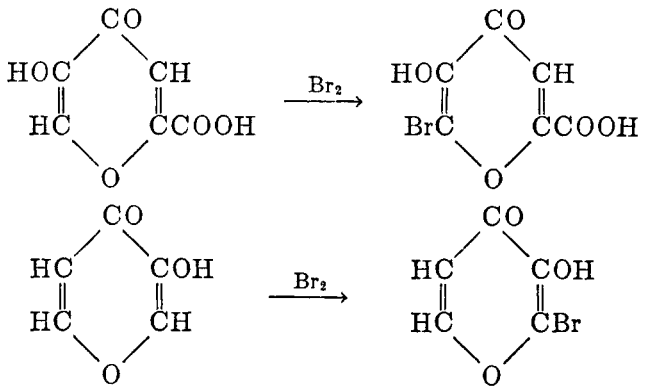
The pyrone nucleus exhibits a low degree of unsaturation toward halogens; substitution rather than addition occurs. For example, the action of bromine on 2,6-dimethylpyrone produces 3-bromo- and 3,5-dibromo-2,6-dimethylpyrones (56, 59, 86, 87, 88, 113). The bromination (or chlorination) of chelidonic acid



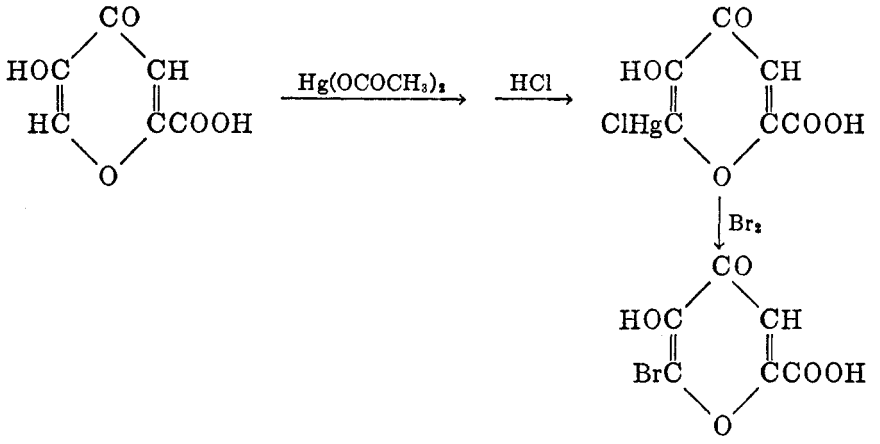
yields 3,5-dibromochelidonic acid. Iodination of chelidonic acid under alkaline conditions results in the formation of 3,5-diiodochelidonic acid (140). When four groups are present in the pyrone nucleus, halogenation occurs in the side chain (172). Reduction of the bromo derivatives with zinc and sulfuric acid



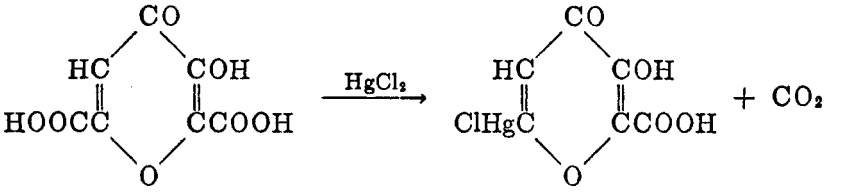
produces the starting compound. With hydroxypyrones bromination occurs on the carbon atom adjacent to the hydroxyl group (62, 183).



γ-Pyrones are mercurated in the same manner as aromatic compounds. For example, the action of mercuric acetate on comenic acid results in the formation of anhydro-6-mercuricomenic acid. Treatment of this compound with hydrochloric acid produces 6-chloromercuricomenic acid. The chloromercuri group is replaced by bromine (91).



6-Bromopyromeconic acid is prepared in a similar manner. Mercuration may also be accomplished by the use of mercuric chloride.

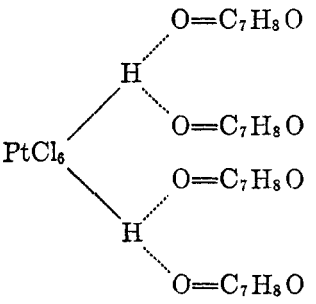


Nitration of the pyrone nucleus is carried out by employing fuming nitric acid as the nitrating agent (165, 208). Both comenic and pyromeconic acids yield a mononitro derivative in which the substituent is believed to be in position 6. Reduction with zinc and sulfuric acid produces the amino-γ-pyrone.

H. COMPLEX SALTS

A large number of complex salts have been prepared from 2,6-dimethylpyrone and heavy metal salts. Thus the reaction of zinc chloride and 2,6-dimethylpyrone results in the formation of a salt which contains one molecule of each component ($C_7H_8O_2 \cdot ZnCl_2$). In the presence of hydrochloric acid a zinc chloride hydrochloride ($C_7H_8O_2HCl \cdot ZnCl_2$) results (98). Mercuric chloride (257) or antimony chloride (151) yields similar compounds. A mixture of benzoyl chloride and antimony chloride produces $C_7H_8O_2 \cdot C_6H_5COCl \cdot SbCl_5$ (151).

Treatment of 2,6-dimethylpyrone with chloroplatinic acid produces a salt which contains two γ-pyrone ring residues (60). The structure of these complex salts has been discussed by Werner (257) and Morgan and Micklethwait (157). Werner proposed that the secondary valence forces of the carbonyl oxygen in the γ-pyrone ring are satisfied by the secondary valence forces of the hydrogen atoms in chloroplatinic acid.



III. α-PYRONES

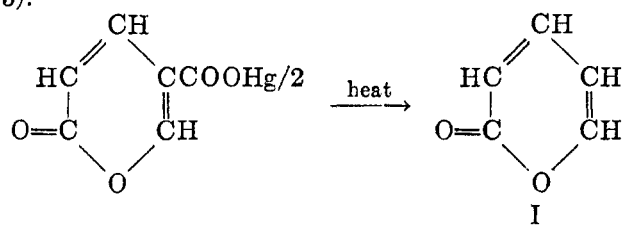
A. STRUCTURE

The α-pyrone ring possesses an unsaturated lactonic structure. The chemistry of the α-pyrones is not as complex as that of the γ-pyrones. Perhaps the most striking difference is that α-pyrones do not form pyroxonium salts with acids; however, the behavior toward alkaline reagents and halogens is similar.

B. PREPARATION

1. α-Pyrone (coumalin) (I)

Coumalin (I) may be prepared by the pyrolysis of the mercuric salt of coumalic acid (174, 175).

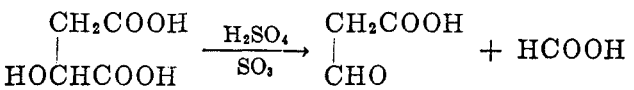


2. Substituted α-pyrones

Substituted α-pyrones may be prepared by either condensation, cyclization, or rearrangement reactions or from pyrazolines. These reactions are briefly illustrated in table 5.

(a) By condensation

Coumalic acid: Coumalic acid (II) is formed by the action of fuming sulfuric acid on malic acid (174, 175). The intermediate in this reaction is formylacetic acid, which condenses as its enol form.



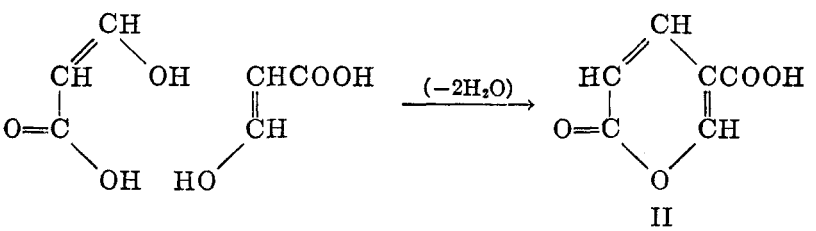
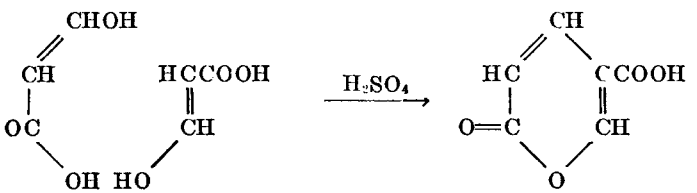
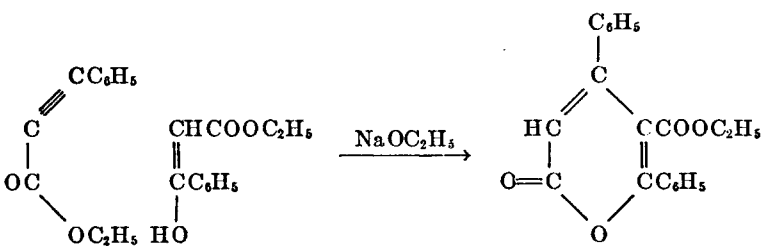
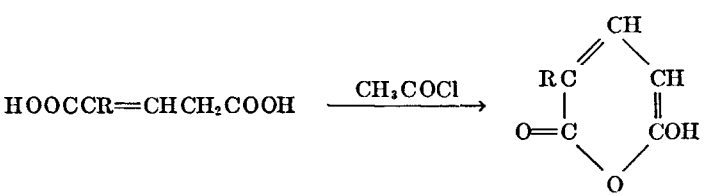


TABLE 5

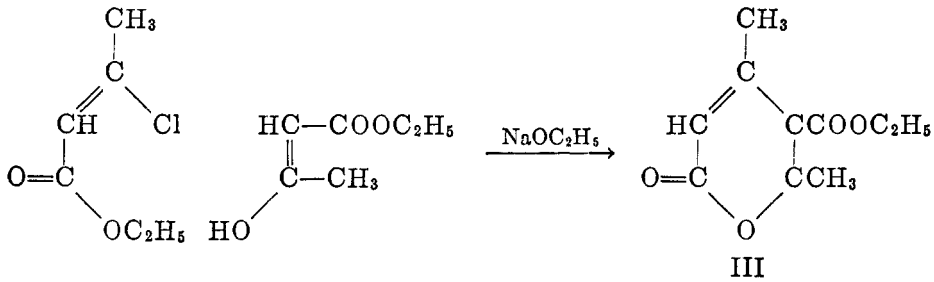
Preparation of substituted α-pyrones

(*a*) Condensation.....	
	
(*b*) Cyclization.....	

(c) Rearrangement.....

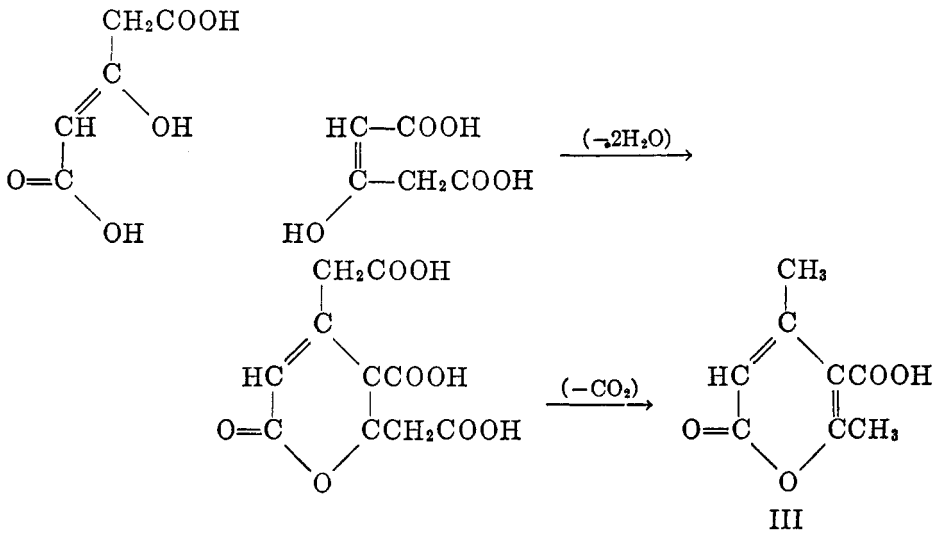
(d) From pyrazolines.....

Isodehydroacetic acid: Isodehydroacetic acid (III) may be prepared either from ethyl acetoacetate and ethyl β-chlorocrotonate (2)



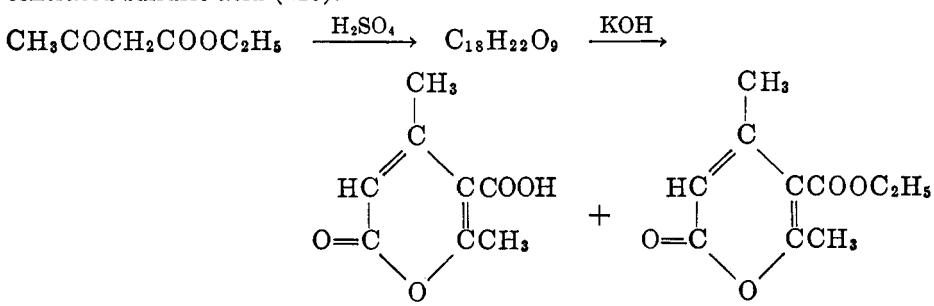
III

or by the action of fuming sulfuric acid on acetonedicarboxylic acid (162). De-



III

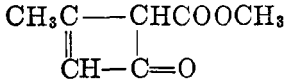
carboxylation of isodehydroacetic acid produces 4,6-dimethylcoumalin (2, 110). Isodehydroacetic acid is also obtained when acetoacetic ester is treated with concentrated sulfuric acid (110).



The structure of compound $C_{18}H_{22}O_9$ is unknown and the mechanism of the reaction is not understood.

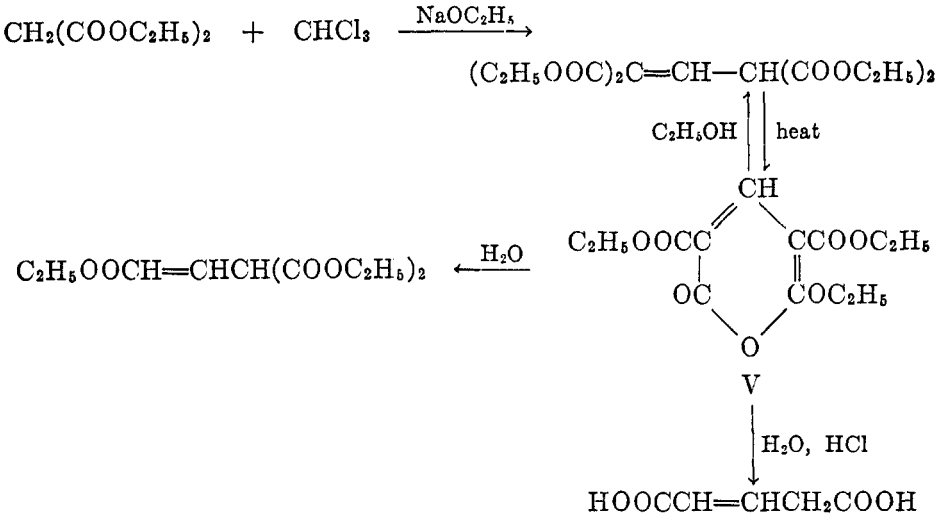
The action of dry hydrogen chloride on acetoacetic ester produces a compound which is believed to be isodehydroacetic acid (76, 85, 199). However, evidence

has been presented which indicates that the compound may have structure IV (95).



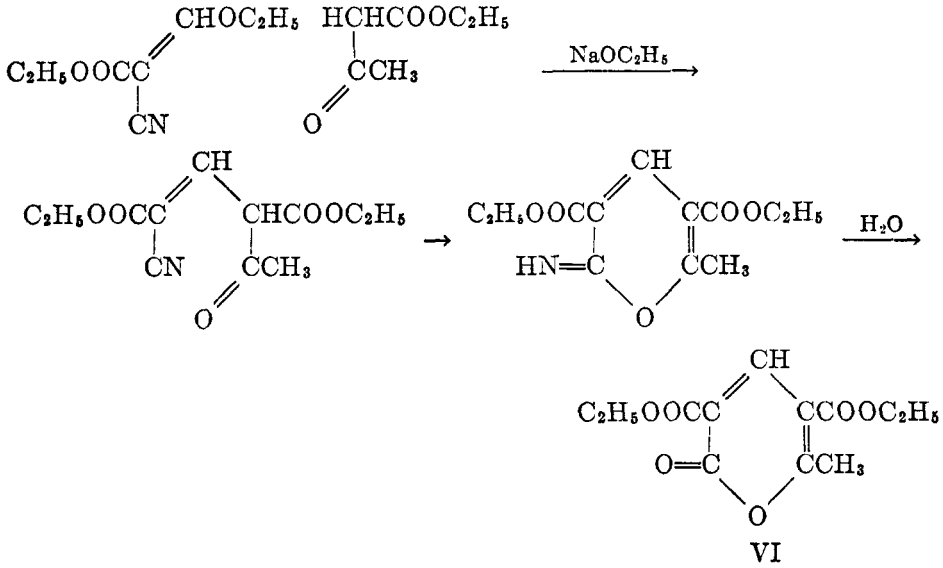
IV

Diethyl 6-ethoxycoumalin-3,5-dicarboxylate (V): The condensation of malonic ester with chloroform in the presence of sodium ethoxide results in the formation of compound V (102, 103). V undergoes both alcoholysis and hydrolysis with



great ease. In the absence of hydrochloric acid V is partially saponified with subsequent decarboxylation; in the presence of acid, glutaconic acid is formed.

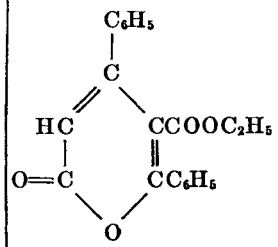
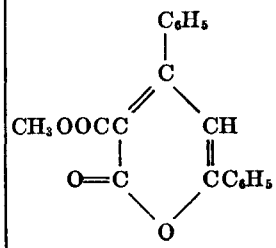
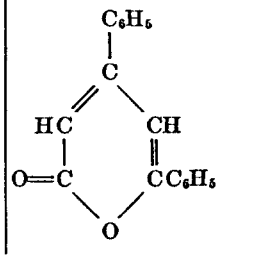
Diethyl 6-methylcoumalin-3,5-dicarboxylate (VI): VI is prepared in quantitative yield from ethyl ethoxymethylenecyanoacetate and ethyl acetoacetate.



VI

TABLE 6

Preparation of substituted α-pyrones by condensation

REACTANTS	CONDENSING AGENT	PRODUCT	REFERENCE
$C_6H_5C{\equiv}CCOOC_2H_5$ $C_6H_5COCH_2COOC_2H_5$	$NaOC_2H_5$		(218)
$CH_3OOCCH_2COOCH_3$ $C_6H_5C{\equiv}CCOC_6H_5$	$NaOC_2H_5$, then CH_3COOH		(132)
$C_6H_5COCH_2COOC_2H_5$	H_2SO_4 (concentrated)		(4)

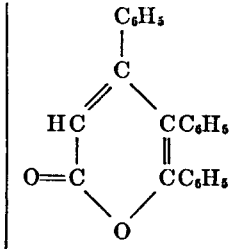
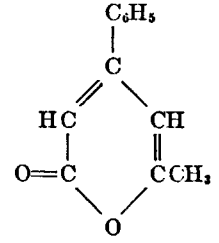
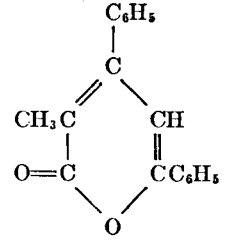
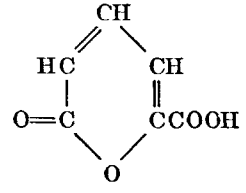
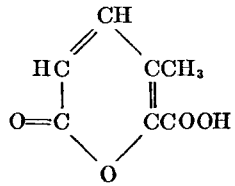
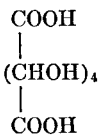
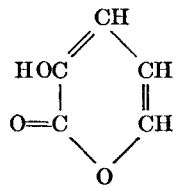
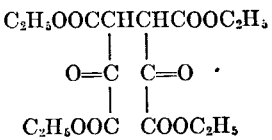
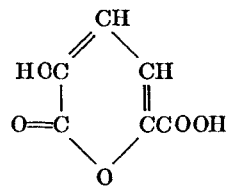
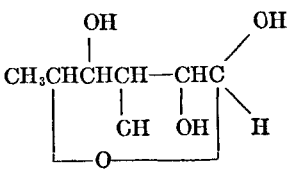
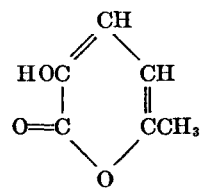
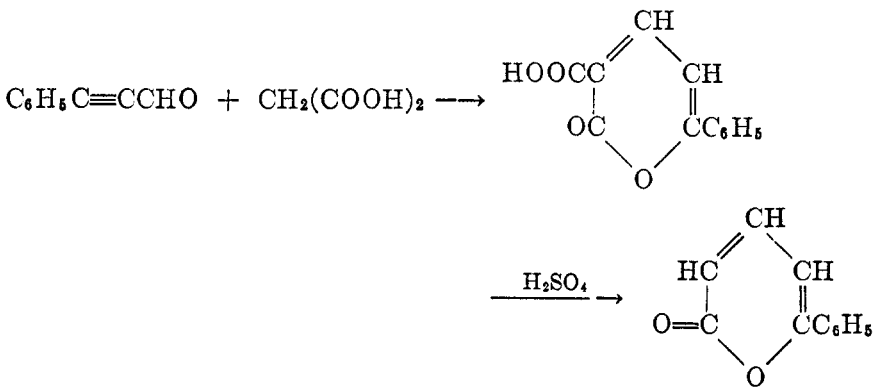
$C_6H_5C{\equiv}CCOOC_2H_5$ $C_6H_5COCH_2C_6H_5$	$NaOC_2H_5$		(220)
$C_6H_5{\equiv}CCOOC_2H_5$ $CH_3COCH_2COCH_3$	$NaOC_2H_5$		(221)
CH_2 | $CNCHCOOCH_3$ $C_6H_5C{\equiv}CCOC_6H_5$	$NaOCH_3$		(133)
$CH_2CH{=}CHCOOC_2H_5$ $(COOC_2H_5)_2$	$NaOC_2H_5$		(137, 200)

TABLE 6—*Continued*

REACTANTS	CONDENSING AGENT	PRODUCT	REFERENCE
$CH_3CH_2CH{=}CHCOOC_2H_5$ $(COOC_2H_5)_2$	$KOCH_3$		(93, 236, 258)
	K_2SO_4, heat		(43, 43a, 44, 46, 230)
	HCl		(25, 26)
	$KHSO_4$, heat		(230a, 252)

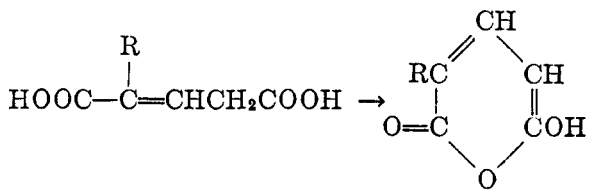
6-Phenylcoumalin: 6-Phenylcoumalin may be synthesized from phenylpropiolaldehyde and malonic acid (123). The mechanism of this reaction is not understood.



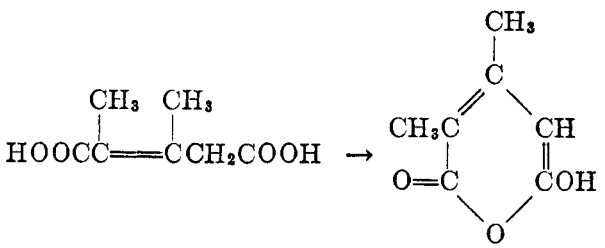
Other pyrones: In table 6 are listed other α-pyrones which may be prepared by condensation reactions.

(b) By cyclization

A large number of substituted α-pyrones have been prepared by cyclizing the the corresponding glutaconic acid derivatives (197, 240, 242). The following examples will serve to illustrate the generality of the method:



R = CH_3, C_6H_5, $C_6H_5CH_2$



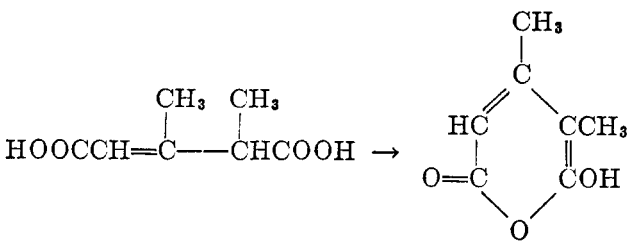
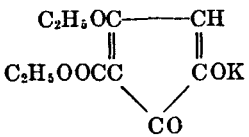
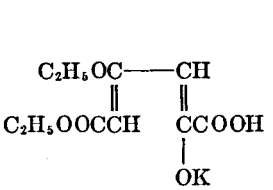
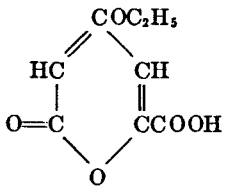
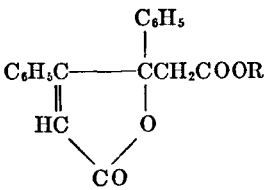
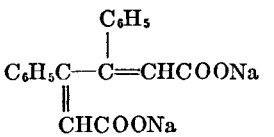
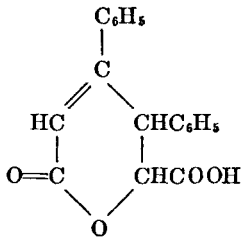
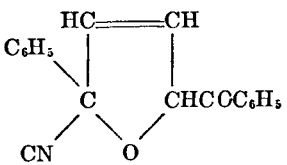
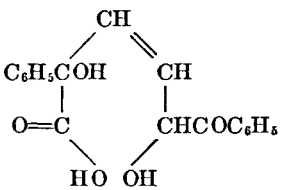
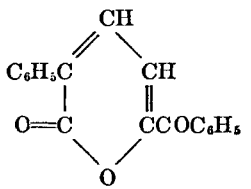
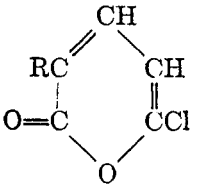


TABLE 7

Preparation of α-pyrones by rearrangement

STARTING COMPOUND	REAGENT	INTERMEDIATE	PRODUCT	REFERENCE
	H_2O			(262)
	Alcoholic NaOH			(23, 24)
	HCl, CH_3COOH			(94)

These cyclizations are effected by means of acetyl chloride at 100°C. In all cases the product is contaminated with the corresponding 6-chloro derivative.

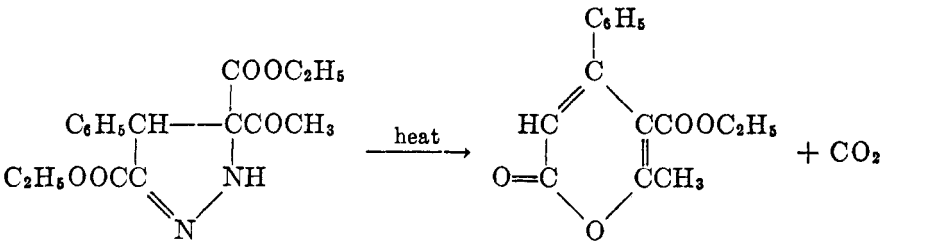


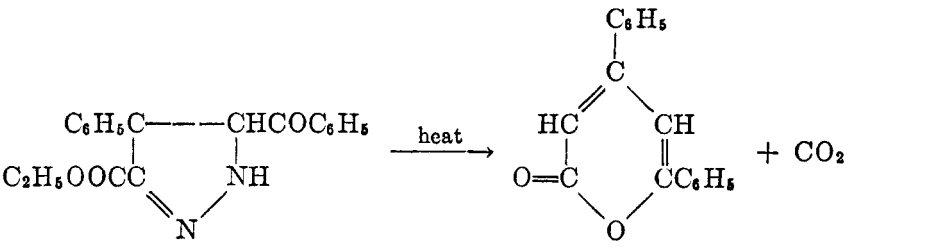
(c) By rearrangement

Rearrangements leading to the formation of substituted α-pyrones are listed in table 7.

(d) Coumalins from pyrazolines

Certain substituted pyrazolines may be converted to α-pyrones by heating (39, 134).



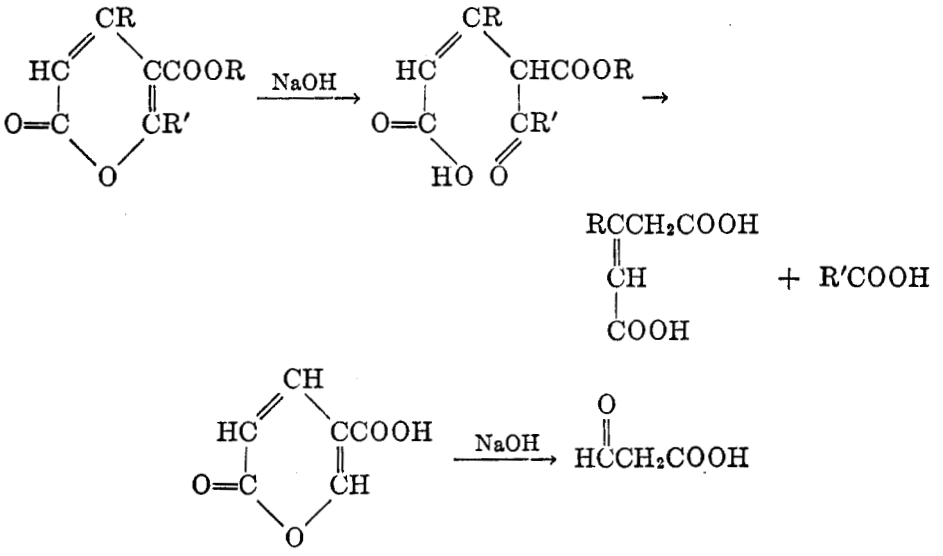


C. CHEMICAL PROPERTIES

1. Action of bases

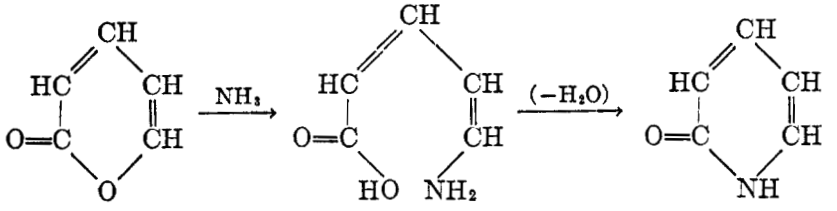
(a) Alkali

Alkali causes cleavage of the ring with subsequent hydrolysis of the cleavage product (27, 48, 49, 84, 102, 103, 132, 176, 229).

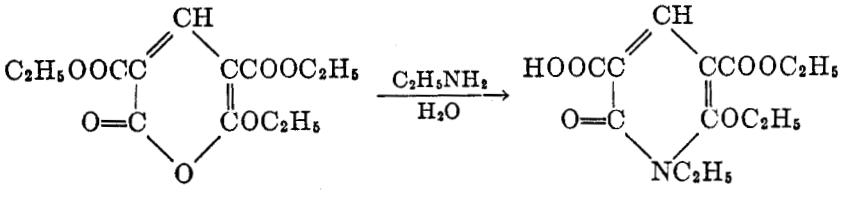


(b) Ammonia and amines

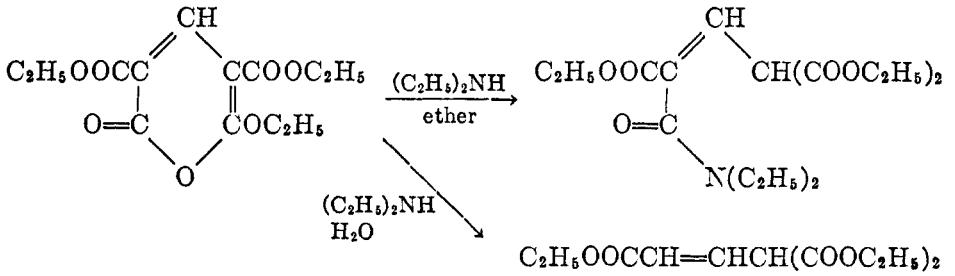
In general, the action of ammonia on α-pyrones produces α-pyridones (35, 80, 100, 128, 132, 149, 174, 175, 229). A similar type of reaction was observed in the γ-pyrone series. The mechanism for the formation of α-pyridones as proposed by Pechmann (179) is as follows:



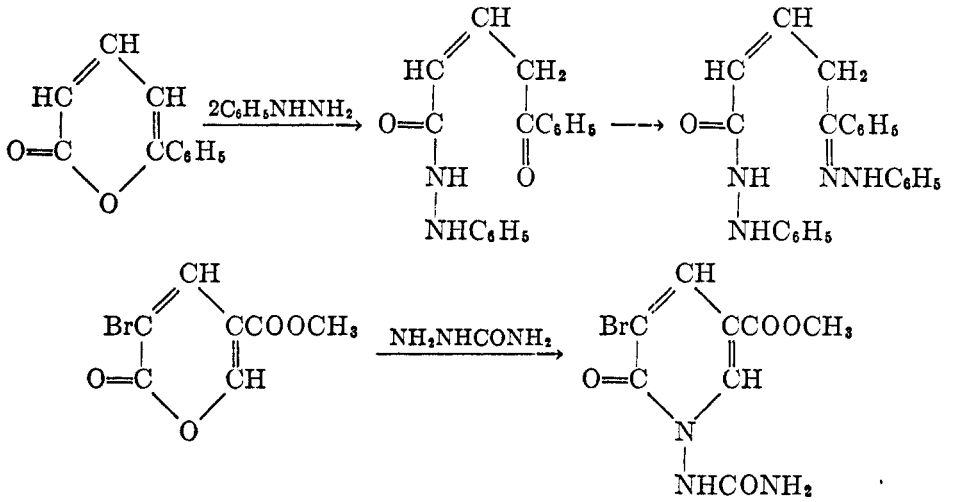
The action of primary amines results in the formation of *N*-substituted α-pyridones. Secondary amines cause cleavage of the ring, but cyclization of the



cleavage product does not occur (16, 101, 104, 105, 114).

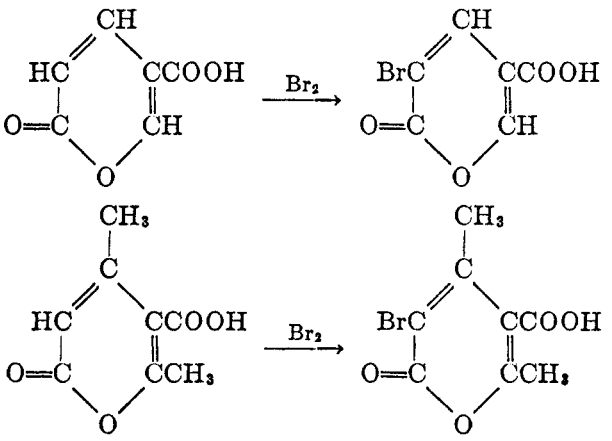


The action of phenylhydrazine or semicarbazide also causes cleavage of the α-pyrone ring (40, 43, 229). In the case of phenylhydrazine a phenylhydrazide is produced. With semicarbazide an *N*-substituted α-pyridone is formed.



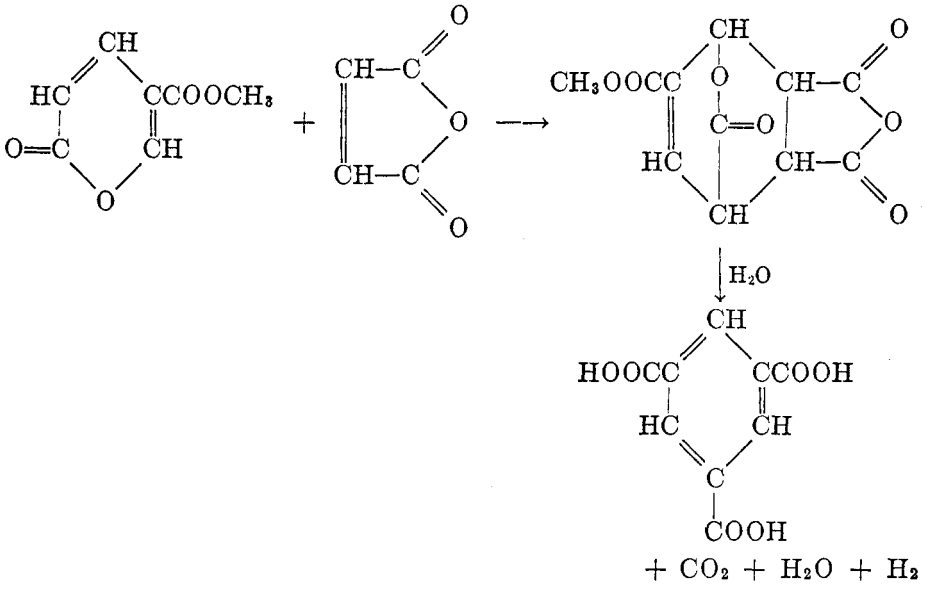
2. Halogenation

The action of bromine or chlorine on α-pyrones results in the formation of substitution rather than addition products (39, 45, 47, 83, 109, 175, 177, 178, 263).



3. The Diels–Alder reaction with α-pyrones

Diels and Alder (74) demonstrated that methyl coumalate undergoes the typical Diels–Alder reaction with maleic anhydride. It is interesting to note that



$+ CO_2 + H_2O + H_2$

hydrolysis of the addition product results in the formation of a benzene derivative.

The author is indebted to Dr. Marvin Carmack for many helpful criticisms and suggestions.

IV. References

(1) Aloy, J., and Valdiguie, A.: J. pharm. chim. [8] **1**, 369 (1925); Chem. Abstracts **19**, 2389 (1925).
(2) Anschutz, R., Bendix, P., and Kerp, W.: Ann. **259**, 151, 181 (1890).
(3) Arndt, F.: Ber. **63**, 2963 (1930).
(4) Arndt, F., and Eistert, B.: Ber. **58**, 2318 (1925).
(5) Arndt, F., and Kalischek, A.: Ber. **63**, 587 (1930).
(6) Arndt, F., and Lorenz, L.: Ber. **63**, 3125 (1930).
(7) Arndt, F., Scholz, E., and Nachtwey, P.: Ber. **57**, 1905 (1924).
(8) Attenburrow, J., Elks, J., Elliott, D., Hems, B., Harris, J., and Brodrick, C.: J. Chem. Soc. **1945**, 571.
(9) Auwers, K. von, and Diekmann, W.: Ber. **56**, 1527 (1923).
(10) Baeyer, A.: Ber. **43**, 2337 (1910).
(11) Baeyer, A., and Piccard, J.: Ann. **384**, 215 (1911).
(12) Baeyer, A., and Piccard, J.: Ann. **407**, 332 (1915).
(13) Baeyer, A., and Villiger, V.: Ber. **34**, 3612 (1901).
(14) Bain, A.: J. Chem. Soc. **89**, 1230 (1906).
(15) Baly, E. C., Collie, J. N., and Watson, H. E.: J. Chem. Soc. **95**, 144 (1909).
(16) Band, J.: Ann. **285**, 108 (1895).

(17) BARGER, G., AND STARLING, W. J.: J. Chem. Soc. **107**, 418 (1915).
(18) BARHAM, H., AND SMITS, B.: Trans. Kansas Acad. Sci. **37**, 91 (1934); Chem. Abstracts **29**, 2544 (1935).
(19) BEDEKAR, D., KAUSHAL, R., AND DESHAPANDE, S. J.: J. Indian Chem. Soc. **12**, 465 (1935); Chem. Abstracts **30**, 459 (1936).
(20) BERGEL, F., MORRISON, A. L., MOSS, A. R., KLEIN, R., RINDERKNECHT, H., AND WARD, J. L.: Nature **152**, 750 (1943).
(21) BERGEL, F., MORRISON, A. L., MOSS, A. R., AND RINDERKNECHT, H.: J. Chem. Soc. **1944**, 415.
(22) BERTHELOT, M. P.: Ann. chim. phys. [6] **7**, 199 (1886).
(23) BESCHKE, E.: Ann. **384**, 163 (1911).
(24) BESCHKE, E.: Ann. **391**, 117 (1912).
(25) BLAISE, E., AND GAULT, H.: Compt. rend. **147**, 198 (1908).
(26) BLAISE, E., AND GAULT, H.: Compt. rend. **148**, 177 (1909).
(27) BLAND, N., AND THORPE, J.: J. Chem. Soc. **101**, 1557 (1912).
(28) BOON, A. A., MCKENZIE, K. J., AND TROTTER, J.: Proc. Chem. Soc. (London) **30**, 206 (1914); Chem. Abstracts **9**, 2893 (1915).
(29) BOON, A. A., WILSON, F. J., AND HEILBRON, I. M.: J. Chem. Soc. **105**, 2177 (1914).
(30) BORSCHE, W.: Ber. **48**, 686 (1915).
(31) BORSCHE, W.: Ber. **49**, 2544 (1916).
(32) BORSCHE, W., AND BONACKER, I.: Ber. **54**, 2678 (1921).
(33) BORSCHE, W., AND PETER, W.: Ann. **453**, 148 (1927).
(34) BORSCHE, W., AND THEILE, K.: Ber. **56**, 2132 (1923).
(35) BOSSI, U.: Gazz. chim. ital. **29**, I, 6 (1899).
(36) BRAND, J.: Ber. **27**, 806 (1894).
(37) BROWN, J.: Ann. **84**, 33 (1852).
(38) BRUHL, J. W.: Ber. **24**, 2450 (1891).
(39) BUCHNER, E., AND SCHRÖDER, H.: Ber. **35**, 790 (1902).
(40) BULOW, C., AND FILCHNER, H.: Ber. **41**, 3283 (1908).
(41) BURAWOY, A.: Ber. **64**, 476 (1931).
(42) CAVALIERI, L., AND CARMACK, M.: Unpublished work.
(43) CHAVANNE, G.: Compt. rend. **133**, 167 (1901).
(43a) CHAVANNE, G.: Compt. rend. **134**, 1511 (1902).
(44) CHAVANNE, G.: Bull. soc. chim. [3] **29**, 400 (1903).
(45) CHAVANNE, G.: Ann. chim. phys. [8] **3**, 532 (1904).
(46) CHAVANNE, G.: Compt. rend. **137**, 992 (1903).
(47) CHAVANNE, G.: Compt. rend. **136**, 50 (1903).
(48) CIAMICIAN, G., AND SILBER, P.: Ber. **27**, 849 (1894).
(49) CIAMICIAN, G., AND SILBER, P.: Gazz. chim. ital. **24**, 533 (1894).
(50) CLAISEN, L.: Ber. **24**, 111 (1891).
(51) COEHN, A.: Ber. **35**, 2673 (1902).
(52) COLLIE, J. N.: J. Chem. Soc. **59**, 617 (1891).
(53) COLLIE, J. N.: J. Chem. Soc. **75**, 710 (1899).
(54) COLLIE, J. N.: J. Chem. Soc. **85**, 973 (1904).
(55) COLLIE, J. N., AND HILDITCH, T.: J. Chem. Soc. **91**, 787 (1907).
(56) COLLIE, J. N., AND KLEIN, L.: J. Chem. Soc. **1927**, 2162.
(57) COLLIE, J. N., AND MEYERS, W.: J. Chem. Soc. **63**, 124 (1893).
(58) COLLIE, J. N., AND STEELE, B. D.: J. Chem. Soc. **77**, 962 (1900).
(59) COLLIE, J. N., AND STEELE, B. D.: J. Chem. Soc. **77**, 1116 (1900).
(60) COLLIE, J. N., AND TICKLE, T.: J. Chem. Soc. **75**, 710 (1899).
(61) COLLIE, J. N., AND WILSMORE, N. T.: J. Chem. Soc. **69**, 293 (1896).
(62) COMPANGO, L.: Gazz. chim. ital. **38**, II, 126 (1908).
(63) CONRAD, M., AND ECKHARDT, F.: Ber. **22**, 81 (1889).
(64) CONRAD, M., AND GUTHZEIT, M.: Ber. **20**, 151 (1887).

(65) CONRAD, M., AND GUTHZEIT, M.: Ber. **20**, 154 (1887).
(66) CORNUBERT, R., AND ROBINET, P.: Compt. rend. **194**, 107, 1081 (1932).
(67) CORNUBERT, R., AND ROBINET, P.: Bull. soc. chim. [4] **53**, 619 (1933).
(68) CORNUBERT, R., AND ROBINET, P.: Bull. soc. chim. [5] **1**, 90 (1934).
(69) DAVILLA, J. P.: Anales soc. españ. fis. quím. **27**, 637 (1929); Chem. Abstracts **24**, 368 (1930).
(70) DAVILLA, J. P.: Rev. acad. cienc. **28**, 343 (1932); Chem. Abstracts **26**, 4815 (1932).
(71) DESHAPANDE, S.: J. Indian Chem. Soc. **9**, 303 (1932); Chem. Abstracts **27**, 294 (1933).
(72) DESHAPANDE, S. S., KAWEESHWAR, S., AND BHAGWAT, W.: J. Indian Chem. Soc. **19**, 153 (1942); Chem. Abstracts **38**, 3176 (1944).
(73) DIEKMANN, W.: Ber. **53**, 1772 (1920).
(74) DIELS, O., AND ALDER, K.: Ann. **490**, 257 (1931).
(75) DOTT, D.: Pharm. J. **106**, 232 (1921); Chem. Abstracts **15**, 1600 (1921).
(76) DUISBERG, C.: Ann. **213**, 178 (1882).
(77) ELIZAROVA, A. N., AND NAZAROV, I. N.: Bull. acad. sci. U.R.S.S., Classe sci. chim. **1940**, 223; Chem. Abstracts **36**, 747 (1942).
(78) ELIZAROVA, A. N., AND NAZAROV, I. N.: Bull. acad. sci. U.R.S.S., Classe sci. chim. **1941**, 423; Chem. Abstracts **36**, 1295 (1942).
(79) ERDMAN, E., AND SCHAEFER, C.: Ber. **43**, 2398 (1910).
(80) ERRERA, G.: Ber. **34**, 3703 (1901).
(81) FEIST, F.: Ann. **257**, 253 (1890).
(82) FEIST, F.: Ber. **25**, 1067 (1892).
(83) FEIST, F.: Ber. **26**, 754 (1893).
(84) FEIST, F.: Ber. **34**, 1994 (1901).
(85) FEIST, F.: Ann. **345**, 69 (1906).
(86) FEIST, F.: Ber. **39**, 3662 (1907).
(87) FEIST, F.: Ber. **40**, 3649 (1907).
(88) FEIST, F., AND BAUM, E.: Ber. **38**, 3574 (1905).
(89) FEIST, F., AND BELART, H.: Ber. **28**, 1823 (1895).
(90) FEUERSTEIN, W.: Ber. **34**, 1804 (1901).
(91) FILES, J. R., AND CHALLENGER, F.: J. Chem. Soc. **1940**, 663.
(92) FORD: U. S. patent 2,138,450 (1938).
(93) FRIED, J., AND ELDERFIELD, R: J. Org. Chem. **6**, 566, 567 (1941).
(94) FUSON, R. C., LITTLE, J. R., AND MILLER, G.: J. Am. Chem. Soc. **60**, 2404 (1938).
(95) GENVRESSE, P.: Ann. chim. phys. [6] **24**, 122 (1891).
(96) GIBBS, R. C., JOHNSON, J. R., AND HUGHES, E. C.: J. Am. Chem. Soc. **52**, 4900 (1930).
(97) GIBSON, C. S., AND SIMONSEN, J. L.: J. Chem. Soc. **1928**, 2308.
(98) GOMBERG, M., AND CONE, L. H.: Ann. **376**, 226 (1910).
(99) GREGORY: Ann. **24**, 43 (1837).
(100) GUTHZEIT, M.: Ber. **26**, 2796 (1893).
(101) GUTHZEIT, M.: Ann. **285**, 35 (1895).
(102) GUTHZEIT, M., AND DRESSEL, O.: Ber. **22**, 1415 (1889).
(103) GUTHZEIT, M., AND DRESSEL, O.: Ann. **262**, 105 (1891).
(104) GUTHZEIT, M., AND EYSSEN, H.: J. prakt. chem. [2] **80**, 38 (1909).
(105) GUTHZEIT, M., WEISS, A., AND SCHAEFER, W.: J. prakt. chem. [2] **80**, 447 (1909).
(106) HAITINGER, L., AND LIEBEN, A.: Monatsh. **5**, 363 (1884).
(107) HAITINGER, L., AND LIEBEN, A.: Monatsh. **5**, 341 (1884).
(108) HAITINGER, L., AND LIEBEN, A.: Monatsh. **6**, 279 (1885).
(109) HANTZSCH, A.: Ann. **222**, 18 (1883).
(110) HANTZSCH, A.: Ann. **222**, 9 (1883).
(111) HANTZSCH, A.: Z. physik. Chem. **61**, 282 (1908); Chem. Abstracts **2**, 930 (1908).
(112) HANTZSCH, A.: Ber. **52**, 1535 (1919).
(113) HANTZSCH, A., AND DENSTORFF, O.: Ann. **349**, 39 (1906).

(114) HAUSMANN, E.: Ann. **285**, 61 (1895).
(115) HEILBRON, I. M., BARNES, H., AND MORTON, R. A.: J. Chem. Soc. **123**, 2559 (1923).
(116) HILSEBEIN, E.: J. prakt. Chem. [2] **32**, 132 (1885).
(117) HOMFRAY, I. F.: J. Chem. Soc. **87**, 1447 (1905).
(118) HOW, H.: Ann. **80**, 67 (1851).
(119) HOW, H.: Ann. **83**, 354 (1852).
(120) HUNTER, E. C., AND PARTINGTON, J. R.: J. Chem. Soc. **1933**, 87.
(121) IHLEE, E.: Ann. **188**, 32 (1877).
(122) JOHNSON, E., AND PARTINGTON, J.: J. Chem. Soc. **1931**, 86.
(123) KALFF, J.: Rec. trav. chim. **46**, 594 (1927).
(124) KAUSHAL, R.: J. Indian Chem. Soc. **17**, 138 (1940); Chem. Abstracts **34**, 5449 (1940).
(125) KAUSHAL, R., BHISSE, P., AND DESHAPANDE, S.: J. Indian Chem. Soc. **20**, 51, 127 (1943); Chem. Abstracts **37**, 6663 (1943).
(126) KEHRMANN, F., AND DUTTENHÖFER, A.: Ber. **39**, 1299 (1906).
(127) KENDALL, J.: J. Am. Chem. Soc. **36**, 1223 (1914).
(128) KERP, W.: Ann. **274**, 280 (1893).
(129) KIHARA, K.: J. Soc. Chem. Ind. Japan **43**, 132 (1940).
(130) KILGORE: U. S. patent 2,149,917 (1939).
(131) KISHNER, N.: J. Russ. Phys. Chem. Soc. **55**, 539 (1924); Chem. Abstracts **19**, 2822 (1925).
(132) KOHLER, E. P.: J. Am. Chem. Soc. **44**, 379 (1922).
(133) KOHLER, E. P., AND BARRETT, G.: J. Am. Chem. Soc. **46**, 747 (1924).
(134) KOHLER, E. P., AND STEELE, L.: J. Am. Chem. Soc. **41**, 1100 (1919).
(135) KORFF, J.: Ann. **138**, 195 (1866).
(136) LANGECKER, H.: Lotos **77**, No. 5–12, 147 (1930); Chem. Abstracts **24**, 5377 (1930).
(137) LAPWORTH, A.: J. Chem. Soc. **79**, 1265 (1901).
(138) LAUTENSCHLÄGER, L.: Biochem. Z. **96**, 73 (1919); Chem. Abstracts **14**, 932 (1920).
(139) LE FEVRE, C. G., AND LE FEVRE, R. J.: J. Chem. Soc. **1937**, 1088.
(140) LERCH, J.: Monatsh. **5**, 367 (1884).
(141) LERCH, J.: Ann. **57**, 310 (1846).
(142) LEROY, E.: Ann. chim. phys. [7] **21**, 138 (1900).
(143) LIEBEN, A. AND HAITINGER, L.: Ber. **16**, 1259 (1883).
(144) LIEBEN, A., AND HAITINGER, L.: Monatsh. **4**, 273, 339 (1883).
(145) LIEBIG, J.: Ann. **5**, 287 (1833).
(146) LIEBIG, J.: Ann. **26**, 147 (1838).
(147) LORENZ, L., AND STERNITZKE, H.: Z. Elektrochem. **40**, 501 (1934); Chem. Abstracts **28**, 6439 (1934).
(148) MAAS, O., AND MCINTOSH, D.: J. Am. Chem. Soc. **34**, 1273 (1912).
(149) MARCKWALD, W.: Ber. **27**, 1319 (1894).
(150) MCINTOSH, D.: J. Am. Chem. Soc. **32**, 543 (1910).
(151) MEERWEIN, H., AND MAIER-HUSER, H.: J. prakt. Chem. **134**, 51 (1932).
(152) MENNEL, E.: J. prakt. Chem. [2] **26**, 449 (1882).
(153) MENNEL, E.: J. prakt. Chem. [2] **26**, 458 (1882).
(154) MEYER, H.: Monatsh. **26**, 1328 (1905).
(155) MITCHELL, V., AND PARTINGTON, J.: J. Chem. Soc. **1929**, 1562.
(156) MORGAN, G., AND HOLMES, E.: J. Chem. Soc. **1932**, 2667.
(157) MORGAN, G. T., AND MICKLETHWAIT, F. M.: J. Chem. Soc. **89**, 868 (1906).
(158) MORGAN, G., AND PORTER, C.: J. Chem. Soc. **125**, 1269 (1924).
(159) MOYER, A. J., MAY, O. E., WELLS, P. A., AND HERRICK, H. T.: J. Am. Chem. Soc. **53**, 774 (1931).
(160) MOZINGO, A., AND ADKINS, H.: J. Am. Chem. Soc. **60**, 669 (1938).
(161) NAZAROV, I., TORGOV, I., AND TEREKHOVA, L.: Bull. acad. sci. U.R.S.S., Classe sci. chim. **1943**, 50; Chem. Abstracts **38**, 1729 (1944).

(162) NEIME, A., AND PECHMANN, H. VON: Ann. **261**, 199 (1891).
(163) ODERNHEIMER, E.: Ber. **17**, 2087 (1884).
(164) OPPENHEIM, A., AND PRECHT, H.: Ber. **9**, 1101 (1876).
(165) OST, H.: J. prakt. Chem. [2] **19**, 178 (1879).
(166) OST, H.: J. prakt. Chem. [2] **23**, 440 (1881).
(167) OST, H.: J. prakt. Chem. [2] **27**, 293 (1883).
(168) OST, H.: J. prakt. Chem. [2] **29**, 62 (1884).
(169) OST, H.: J. prakt. Chem. [2] **29**, 63 (1884).
(170) PALAZZO, F.: Gazz. chim. ital. **34, I**, 458 (1904).
(171) PALAZZO, F.: Gazz. chim. ital. **36, I**, 596 (1906).
(172) PALAZZO, F.: Gazz. chim. ital. **35, II**, 468 (1905).
(173) PALAZZO, F. AND ONORATO, P.: Gazz. chim. ital. **35, II**, 490 (1905).
(174) PECHMANN, H. VON: Ber. **17**, 937 (1884).
(175) PECHMANN, H. VON: Ann. **264**, 261 (1891).
(176) PECHMANN, H. VON: Ber. **34**, 1406 (1901).
(177) PECHMANN, H. VON: Ber. **17**, 2396 (1884).
(178) PECHMANN, H. VON, AND MITTS, W.: Ber. **37**, 3830 (1904).
(179) PECHMANN, H. VON, AND WELSH, W.: Ber. **17**, 2391 (1884).
(180) PERATONER, A.: Gazz. chim. ital. **41, II**, 646 (1911).
(181) PERATONER, A.: Gazz. chim. ital. **41, II**, 694 (1911).
(182) PERATONER, A.: Atti accad. Lincei [5] **11, I**, 246; Beilstein, Vol. XVII, p. 436.
(183) PERATONER, A., AND CASTELLANA, V.: Gazz. chim. ital. **36, I**, 21 (1906).
(184) PERATONER, A., AND LEONARDI, G.: Gazz. chim. ital. **30, I**, 560 (1900).
(185) PERATONER, A., AND LEONARDI, G.: Gazz. chim. ital. **30, I**, 562 (1900).
(186) PERATONER, A., AND LEONE, R.: Gazz. chim. ital. **24, II**, 83 (1894).
(187) PERATONER, A., AND PALAZZO, F.: Gazz. chim. ital. **36, I**, 4, 7 (1906).
(188) PERATONER, A., AND SPALLINO, R.: Gazz. chim. ital. **36, I**, 19 (1906).
(189) PERATONER, A., AND STRAZZERI, B.: Gazz. chim. ital. **21, I**, 293, 310 (1891).
(190) PERATONER, A., AND TAMBURELLO, A.: Ber. **36**, 3407 (1903).
(191) PERATONER, A., AND TAMBURELLO, A.: Gazz. chim. ital. **33, II**, 233 (1903).
(192) PERATONER, A., AND TAMBURELLO, A.: Gazz. chim. ital. **33, II**, 236 (1903).
(193) PERATONER, A., AND TAMBURELLO, A.: Gazz. chim. ital. **36, I**, 33 (1906).
(194) PERATONER, A., AND TAMBURELLO, A.: Gazz. chim. ital. **36, I**, 51 (1906).
(195) PERATONER, A., AND TAMBURELLO, A.: Gazz. chim. ital. **41, II**, 666 (1911).
(196) PETRENKO-KRITSCHENKO, P., AND STANISCHEWSKY, S.: Ber. **29**, 994 (1896).
(197) PHALNIKAR, N., AND NARGUND, K.: J. Univ. Bombay **6**, Pt. II, 97 (1937); Chem. Abstracts **32**, 3763 (1938).
(198) PHILLIPPI, E., AND SEKA, R.: Ber. **54**, 1089 (1921).
(199) POLONOWSKA, N.: Ber. **19**, 2402 (1886).
(200) PRAGER, B.: Ann. **338**, 360 (1904).
(201) PROBST: Ann. **29**, 116 (1839).
(202) PUETZER, B., NIELD, C., AND BARRY, R.: J. Am. Chem. Soc. **67**, 832 (1945).
(203) PUMMERER, R.: Ber. **42**, 3554 (1909).
(204) RAISTRICK, H., BIRKINSHAW, J. H., BRACHEN, A., AND MICHAEL, S. E.: Lancet **2**, 625 (1943).
(205) RAMSTAD, L. E.: Medd. Norsk. Farm. Selsk. **4**, 52 (1942); Chem. Abstracts **37**, 5760 (1943).
(206) RANSTAD, L. E.: Pharm. Acta Helv. **16**, 15 (1941); Chem. Abstracts **35**, 7114 (1941).
(207) RAU, M. A. GOVINDA: Proc. Indian Acad. Sci. **4A**, 687 (1936); Chem. Abstracts **31**, 3353 (1937).
(208) REIBSTEIN, T.: J. prakt. Chem. [2] **24**, 276 (1881).
(209) RIEGEL, E. R., AND REINHARD, M. C.: J. Am. Chem. Soc. **48**, 1334 (1926).
(210) ROBIQUET: Ann. chim. phys. [2] **5**, 276 (1817).

(211) ROBIQUET: Ann. chim. phys. [2] **51**, 236 (1832).
(212) ROBIQUET: Ann. chim. phys. [2] **51**, 246 (1832).
(213) ROBIQUET: Ann. **5**, 90 (1833).
(214) ROBIQUET: Ann. chim. phys. [2] **53**, 428 (1833).
(215) ROBIQUET: Ann. **5**, 95 (1833).
(216) RORDAM, H.: J. Am. Chem. Soc. **37**, 566 (1915).
(217) ROSS, A.: Proc. Roy. Soc. (London) **113A**, 208 (1926); Chem. Abstracts **21**, 360 (1927).
(218) RUHEMANN, S.: J. Chem. Soc. **75**, 253 (1899).
(219) RUHEMANN, S.: J. Chem. Soc. **93**, 433 (1908).
(220) RUHEMANN, S.: J. Chem. Soc. **97**, 459 (1910).
(221) RUHEMANN, S., AND CUNNINGTON, A.: J. Chem. Soc. **75**, 780 (1899).
(222) RYAN, H., AND RYAN, P.: Proc. Roy. Irish Acad. **33**, 105 (1917); Chem. Abstracts **11**, 1826 (1917).
(223) SAITO, K.: Bull. Chem. Soc. Japan **15**, 22 (1940); Chem. Abstracts **34**, 3275 (1940).
(224) SCHENK, J., AND SPIELMAN, M.: J. Am. Chem. Soc. **67**, 2276 (1945).
(225) SCHLENK, W., AND THAL, A.: Ber. **46**, 2847 (1913).
(226) SCHLUBACH, H.: Ber. **48**, 13 (1915).
(227) SCHOTTLE, J., AND PETRENKO-KRITSCHENKO, P.: Ber. **45**, 3230 (1912).
(228) SEGUIN, A.: Ann. chim. phys. [1] **92**, 225 (1814).
(229) SEVERINI, F.: Gazz. chim. ital. **26**, II, 337 (1896).
(230) SIMON, L.: Compt. rend. **130**, 255 (1900).
(230a) SIMON, L., AND GUILLAUMIN, A.: Compt. rend. **175**, 1208 (1922).
(231) SIMONSEN, J.: J. Chem. Soc. **93**, 1025 (1908).
(232) SKRAUP, H., AND PRIGLINGER, J.: Monatsh. **31**, 365 (1910).
(233) SMIRNOFF, A.: Helv. Chim. Acta **4**, 599 (1921).
(234) STENHOUSE, J.: Ann. **49**, 18 (1844).
(235) STENHOUSE, J.: Ann. **123**, 191 (1862).
(236) STOLL, A., HOFMANN, A., AND KREIS, W.: Helv. Chim. Acta **17**, 1334 (1934).
(237) TAKAHASHI, T., AND ASAI, T.: J. Agr. Chem. Soc. Japan **10**, 604 (1934); Chem. Abstracts **28**, 6519 (1934).
(238) TAKAHASHI, T., AND ASAI, T.: Zentr. Bakt. Parasitenk. II Abt. **93**, 248 (1936); Chem. Abstracts **30**, 3460 (1936).
(239) TAMBURELLO, A.: Gazz. chim. ital. **33**, II, 264 (1903).
(240) THOLE, F., AND THORPE, J.: J. Chem. Soc. **99**, 2208 (1911).
(241) THOMS, H., AND PIETRULLA: Pharm. Monatshefte **1**, 146 (1920); Chem. Abstracts **15**, 1510 (1921).
(242) THORPE, J., AND WOOD, A.: J. Chem. Soc. **103**, 1569 (1913).
(243) TICKLE, T., AND COLLIE, J. N.: J. Chem. Soc. **81**, 1006 (1902).
(244) TOMAS AND LE FEVRE: Bull. soc. chim. **50**, 193 (1888).
(245) TORTORICI, R.: Gazz. chim. ital. **30**, II, 16 (1900).
(246) TORTORICI, R.: Gazz. chim. ital. **30**, I, 523 (1900).
(247) TSCHELINZEFF, W.: Bull. soc. chim. [4] **35**, 751 (1924).
(248) VASIL'EV, V. G., AND SYRKIN, J. K.: Acta Physicochim. U.R.S.S. **6**, 639 (1937); Chem. Abstracts **32**, 4029 (1938).
(249) VERKADE, P.: Rec. trav. chim. **44**, 82 (1925); Chem. Abstracts **19**, 1546 (1925).
(250) VORLÄNDER, D.: Ann. **341**, 64 (1905).
(251) VORLÄNDER, D., AND MEYER, G.: Ber. **45**, 3355 (1912).
(252) VOTOCEK, E., AND MALACHTA, S.: Chem. Listy **31**, 201 (1937); Chem. Abstracts **31**, 7872 (1937).
(253) WAKSMAN, S. A., HORNUNG, E. S., AND SPENCER, E. L.: Science **96**, 202 (1942).
(254) WALDEN, P.: Ber. **34**, 4196 (1901).
(255) WALKER, J.: Ber. **34**, 4116 (1901).
(256) WERNER, A.: Ber. **34**, 3309 (1901).

(257) WERNER, A.: Ann. **322,** 300 (1902).
(258) WIELAND, H., HESSE, G., AND MEYER, H.: Ann. **493,** 272 (1932).
(259) WILDE, C.: Ann. **127,** 165 (1863).
(260) WILLSTÄTTER, R., AND PUMMERER, R.: Ber. **37,** 3743 (1904).
(261) WILLSTÄTTER, R., AND PUMMERER, R.: Ber. **38,** 1462 (1905).
(262) WISLICENUS, W., AND SCHOLLKOPF, K.: J. prakt. Chem. [2] **95,** 295 (1917).
(263) WISLICENUS, W., AND VON WRANGELL, M.: Ann. **381,** 383 (1911).
(264) WOOD, J.: J. Chem. Soc. **83,** 575 (1903).