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ELECTROLYTIC SYNTHESIS OF γ-DIKETONES

A Thesis
Presented to the
Department of Chemistry
Brigham Young University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Leon F. Pahler
May 1972

This thesis, by Leon F. Pahler, is accepted in its present form by the Department of Chemistry of Brigham Young University as satisfying the thesis requirement for the degree of Master of Science.

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I. INTRODUCTION

The carbonyl moiety is the key functional group of many organic syntheses. Carbonyl compounds are susceptible to nucleophilic attack because of the partial polarization of the carbon-oxygen bond. The general reaction of a simple aldehyde or ketone is the 1,2-addition across the carbonyl.

Diketones, in which the carbonyl functions are separated by two or more carbon atoms, generally react as monoketones do. In the case of γ-diketones, the Knorr-Paal synthesis of five membered heterocyclic ring compounds is an exception. Modification of the Knorr-Paal synthesis has led to the synthesis of a number of sterically-crowded 1,2,5-trisubstituted pyrroles (4). This synthetic scheme is also a good method for the synthesis of substituted furans and thiophenes. The availability of the γ-diketones is the limiting factor of this synthesis.

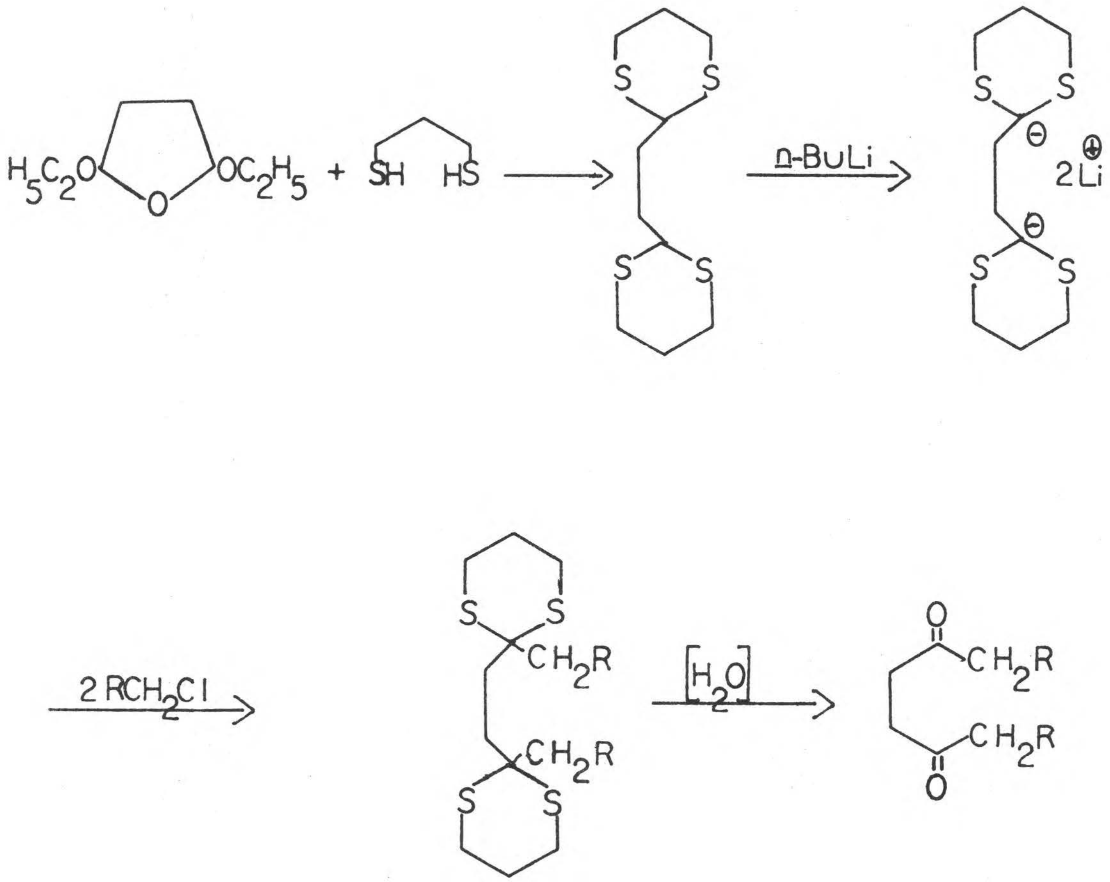
2,5-Hexanedione, which is made by oxidative coupling from acetoacetic ester, is the only commercially available aliphatic γ-diketone. This synthesis does not work for higher homologs of γ-diketones. Aromatic diketones are more readily available and are made by the Friedel-Crafts acylation of an aromatic substrate with a corresponding dicarboxylic acid chloride. The more recent syntheses of γ-diketones have been the acetylenic glycol and bis-

(1,3-dithiane) processes (56). The acetylenic glycol synthesis of γ-diketones is as follows: Acetylenedimagnesium bromide (I) is reacted with an aldehyde, which produces an acetylenic glycol (II). The acetylenic glycol is then hydrogenated yielding a saturated γ-diol (III). The γ-diol is then oxidized to the γ-diketone (IV):

$$\underset{I}{BrMgC\equiv CMgBr + 2RCHO} \longrightarrow \underset{II}{R\text{-}CH(OH)C\equiv C\text{-}CH(OH)R}$$

$$\xrightarrow{(H)} \underset{III}{RCH(OH)CH_2CH_2CH(OH)R} \xrightarrow{(O)} \underset{IV}{RCOCH_2CH_2COR}$$

The bis(1,3-dithiane) synthesis of γ-diketones is as follows:



The diketones made by these two processes are symmetrical diketones (56). Various other syntheses of γ-diketones have been reported but the reactions are cumbersome and often very limited in scope with low yields of desired products.

In 1849, Kolbe obtained ethane and carbon dioxide at the anode during the electrolysis of an aqueous solution of potassium acetate (34).

$$2R\text{-}CH_2\text{-}COO^{\ominus} \xrightarrow{(-2e)} 2RCH_2^{\bullet} + CO_2\uparrow \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}R$$

The term "Kolbe Synthesis" is now understood to imply electrocondensation at the anode of nonsubstituted and substituted carboxylic acids. The condensation product has been termed Kolbe dimer or Kolbe product. However, in most cases the product is called by it's proper name. The general reaction procedure is as follows: The carboxylic acid is placed in the reaction vessel containing sodium metal (2% of the acid weight) dissolved in the reaction solvent. Electrodes (generally platinum) are then positioned in the reaction mixture. A constant current is maintained throughout the reaction. The reaction is run at a temperature less than 50° C and stopped when the reaction mixture reaches a basic pH. The product is then isolated and characterized.

A general procedure, adapting the Kolbe electrolysis synthesis for the preparation of symmetrical γ-diketones, was the main concern for this research.

The following γ-diketones were made by electrolytic condensation of the corresponding β-ketocarboxylic acids:

2,5-hexanedione, 2,2,7,7-tetramethyl-3,6-octanetione, 4,7-decanedione, and 1,4-diphenyl-1,4-butanedione.

II. LITERATURE REVIEW

Kolbe Synthesis

Investigations have shown that the yield of the product in the Kolbe reaction is not only affected by the conditions of electrolysis, but also by acid structure. The electrolysis behavior of various acids in relation to their structure is reviewed below.

Saturated Straight-Chain Acids

Straight-chain fatty acids of varying lengths have been subjected to the Kolbe electrolysis reaction, and have given satisfactory yields in all cases except formic acid.

The decarboxylation of formate ion has been studied using gold, palladium, platinum, and gold-palladium alloy electrodes. The main products were found to be carbon dioxide and hydrogen (9).

The electrolysis of acetic acid has been found to give 90% yields of ethane. Studies have been made on the electrolysis of acetic acid using anodes of different materials. The normal Kolbe products have been ethane and carbon dioxide. However, in the case where the anode was not platinum, the suppression of ethane formation was found (52, 53). The effect of potential pulse techniques (26) and the effect of the current has been studied in the electrolysis of acetic acid(62, 63, 65).

Aqueous solutions of propionic acid were electrolyzed using platinum, lead oxide, and graphite anodes of which only the platinum electrodes gave the normal Kolbe product (7).

Electrolysis of lauric acid using platinum and nickel electrodes produced docosane in yields of 40% in both cases. The addition of measured amounts of potassium hydroxide to the reaction mixture resulted in the decrease of docosane (45). The electrolysis of lauric acid using graphite, lead, tantalum, molybdenium, and iron anodes has been studied and no Kolbe product (docosane) was detected (43). The electrolysis of an aqueous solution of lauric acid was studied. The current needed for the maximum evolution of oxygen was achieved and this procedure gave no Kolbe product (42).

Half-Esters of Dibasic Acids

Alkali-metal salts of dicarboxylic-acid monoesters reacted on electrolysis in an analogous manner to monobasic fatty acids and gave diesters in high yields.

The monoester of adipic acid was electrolyzed using platinum electrodes yielding diethyl decanedioate (diethyl sebacate). The by-products were identified and a mechanism was proposed for the formation of diethyl decandioate (35).

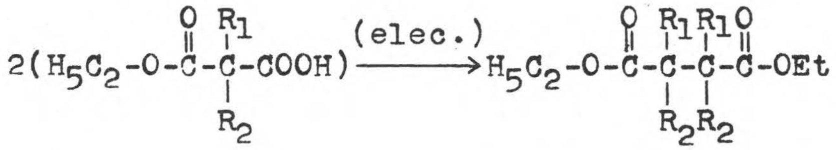
Dialkyl esters (of C_5-C_{10}) were prepared by the electrolysis of monoalkyl esters of shorter-chain dicarboxylic acids in alkaline methanol (36, 54).

Branched-Chain Acids and Half-Esters

The Kolbe electrolysis method has been used for the preparation of α,α-dialkyl and tetraalkyl-substituted succinic esters from half-esters of mono and dialkylmalonic acids. The electrolyses were carried out using methanol as the solvent and platinum electrodes. The products and yields are reported in Table I (15).

TABLE I

THE PRODUCTS AND YIELDS OF THE ELECTROLYSIS OF MONO AND DIALKYL MALONIC HALF-ESTERS



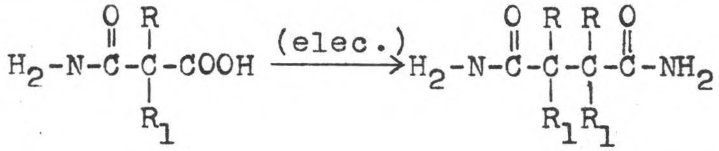
$$2(H_5C_2\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{R_2}{\overset{R_1}{C}}\text{-}COOH) \xrightarrow{(elec.)} H_5C_2\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{R_2}{\overset{R_1}{C}}\text{-}\underset{R_2}{\overset{R_1}{C}}\text{-}\overset{\overset{O}{\|}}{C}\text{-}OEt$$

Substituents on the Malonic Half-Ester	% Yield of Succinate
CH_3, H	34
C_2H_5, H	42
iso-C_3H_7, H	67
neo-C_5H_{11}, H	85
cyclo-C_6H_{11}, H	63
CH_3, CH_3	25
CH_3, C_2H_5	28
C_2H_5, C_2H_5	32
C_2H_5, iso-C_3H_7	22

The steric configurations of the above products are discussed(15). Electrolyses of substituted and nonsubstituted malonamic acids have been studied and the Kolbe products are reported in Table II (16).

TABLE II

THE PRODUCTS AND YIELDS OF THE ELECTROLYSIS OF NONSUBSTITUTED AND SUBSTITUTED MALONAMIC ACIDS



$$H_2\text{-N-}\overset{\overset{O}{\|}}{C}\text{-}\underset{\underset{R_1}{|}}{\overset{\overset{R}{|}}{C}}\text{-COOH} \xrightarrow{(elec.)} H_2\text{-N-}\overset{\overset{O}{\|}}{C}\text{-}\underset{\underset{R_1}{|}}{\overset{\overset{R}{|}}{C}}\text{-}\underset{\underset{R_1}{|}}{\overset{\overset{R}{|}}{C}}\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH_2$$

R, R_1	Total % Yield of Diamide both Racemic and Meso
H, H	56
CH_3, H	14
C_2H_5, H	24
<u>i</u>-C_3H_7, H	43
<u>i</u>-C_4H_9, H	55
C_2H_5, C_2H_5	5

The competition between radical and carbonium ion processes in the Kolbe electrolysis of α-alkylmalonic half-esters of type

$$R\text{-}C(CH_3)_2\text{-}CH(COOR')COOH$$

has been demonstrated, and the results are listed in Table III. The monomer formed was found to result from a carbonium ion process(22).

TABLE III

THE PRODUCTS FROM THE ELECTROLYSIS OF $R(CH_3)_2$-C-CH(COOR')$COO^{\ominus}$

R	R'	Yield of Monomer Fraction %	Total Yield of Dimeric Products %	Ratio Meso/Racemic
C_2H_5	C_2H_5	7	74	1.1
C_3H_7	C_2H_5	16	61	1.7
i-C_3H_7	C_2H_5	3	76	0.82
C_6H_5	C_2H_5	13	48	1.9
C_6H_5	CH_3	16	21	2.0

The electrolysis of methyl hydrogen adipate in methanol was found to produce dimethyl sebacate. However, the production of dimethyl sebacate was suppressed when the reaction was run with the presence of $Cl^{\ominus}$, $Br^{\ominus}$, or $I^{\ominus}$ ions(25).

Anodic oxidation of aqueous solutions of cycloalkanecarboxylates was studied and the production of 1,2-dicyclohexylethane was reported (27). The Kolbe electrolysis of 1-methylcyclohexaneacetic acid using both platinum and carbon anodes was carried out in a 67% methanol-33% pyridine solvent mixture. The dimer, 1,2-bis(1-methylcyclohexyl)ethane, was reported to be the product using both platinum and carbon electrodes. However, the yield using carbon was very low and the yield using platinum was only 4%(50). Electrolysis of 1-adamantaneacetic acid was run and no Kolbe dimer was reported. The products were identified as 1-methoxyhomoadamantane 75% and 1-ethyladamantane (29).

Amino Acids

A diaminodicarboxylic acid (L-α,α'-diaminosuberic acid) was synthesized by hydrolyzing the electrolysis product of L-phthaloylglutamic acid (46).

Aromatic Aliphatic Acids

Electrolysis of phenylacetic acid has been studied and 1,2-diphenylethane was produced in a yield of 50% using a solvent mixture of methanol-pyridine (50) and in a 59% yield when DMF was used as the solvent (49). The electrolysis of phenylacetic acid in the presence of lithium nitrate was found to suppress the Kolbe product completely (1). Electrolysis of 2,4-dinitrophenylacetic acid, 3-nitrophenylacetic acid, 2-nitrophenylacetic acid, and 4,4'dinitroacetic acid did not give any Kolbe dimer. However, 4-nitrophenylacetic acid was found to produce 1,2-bis(4-nitrophenyl)ethane in a 30% yield (70). Using DMF as a solvent, diphenylacetic acid, triphenylacetic acid, and 2,4,6-triisopropylphenylacetic acid were found to give the respective Kolbe dimers in yields of 36% and 31% (49). In another report, the electrolysis using DMF as a solvent of diphenylacetic acid gave a yield of 24% tetraphenylethane (24).

Phenylacetic, 3-phenylpropionic, and 4-phenylbutyric acids in the presence of lithium nitrate did not yield any Kolbe products (1). Electrolysis of aqueous mesitoic acid yielded no Kolbe dimer (38). Electrolysis of 3-phenylpropionic acid in acetic acid did not yield any Kolbe dimer. However, 3,3-diphenylpropionic acid in acetic acid gave a 13% yield of 1,1,4,4-tetraphenylbutane (3).

Unsaturated Acids

Electrolysis of 3-hexenoic and 3-octenoic acids produced the corresponding Kolbe products in 35-40% yields. The products were 3,7-decadiene and 5,9-tetradecadiene, respectively (28).

Keto Acids

Electrolyses of some α-ketocarboxylic acids have been studied. Electrolysis of pyruvic acid in methanol gave no diketone. The main product was found to be methyl acetate(71). α-Oxovaleric and α-oxobutyric acids did not give the Kolbe dimer as products when electrolyzed (71).

Hydroxy Acids

Hydroxy acids generally are not very suitable for the Kolbe reaction because the hydroxyl group is oxidized. However, fair yields of the Kolbe dimer have been reported in the cases of 9-hydroxynonanoic and 11-hydroxyundecanoic acids. The yields were 27% 1,16-dihydroxyhexadecane and 12% 1,20-dihydroxyeicosane, respectively (55).

Halogeno Acids

Electrochemical kinetics of the Kolbe reaction using platinum and gold electrodes have been examined in solutions of potassium trifluoroacetate in trifluoroacetic acid. Hexafluoroethane was produced in high yields (96%) (10, 11). Another study found that at high current densities, bis(trifluoromethyl) peroxide was produced in an 80% yield during the Kolbe electrolysis of trifluoroacetic acid (33).

The electrolysis of 2-fluoro-2-phenylacetic acid did not give any of the desired Kolbe dimer (2).

1,4-Dichlorobutane has been produced in 40-60% yields by the electrolysis of 3-chloropropionic acid. The main by-product was found to be 1,2-dichloroethane. 3-Bromopropionic acid was found to give no Kolbe product (41).

4-Chlorobutyric acid was electrolyzed in methanol using platinum electrodes; 1,6-dichlorohexane was produced in 40-60% yields. 4-Bromobutyric acid was electrolyzed in water and no Kolbe product was found; the product formed was γ-butyrolactone (90%)(41). α-Chloroisobutyric and α-bromoisobutyric acids didn't give the desired Kolbe products (2, 73). The Kolbe electrolysis of heptafluorobutyric produced the desired Kolbe product (tetradecafluorohexane) (6). Electrolysis of 2,2-dichloro-3-phenylcyclopropanecarboxylic acid in methanol and acetic acid or in aqueous methanol with acetic acid gave 3,3-dichloro-1-phenylallyl methyl ether or 3,3-dichloro-1-phenylallyl acetate, depending upon whether the solvent was methanol or acetic acid. No Kolbe product was produced (60).

The electrolysis of 2-chloro and 2-bromopentanoic acid was studied using methanol as a solvent. No Kolbe product was isolated in either case (2, 73).

5-Chloropentanoic acid gave the usual Kolbe product in 40-60% yields (41, 73). 5-Bromopentanoic acid was found to give only 20% 1,8-dibromooctane. 5-Iodopentanoic acid did not give any Kolbe product. Iodine was produced in a quantitative yield (41). The electrolysis of 5,5-difluoropentanoic acid produced the Kolbe product in 56% yields using methanol as the solvent (40).

The electrolysis of 1-bromo and 2-chlorohexanoic acids has been studied and in both cases no Kolbe dimer was isolated (2, 73). 6-Fluorohexanoic acid was electrolyzed in methanol and the yield of the desired Kolbe product (1,10-dichlorodecane) was produced in a 55% yield (55). The electrolysis of 2-fluoro-2-ethylbutanoic acid produced no Kolbe product (2).

The normal Kolbe dimer was not isolated or found when 2-fluoroheptanoic acid was electrolyzed (2). The electrolysis of 7,7-difluoroheptanoic acid (40) and 7-chloroheptanoic acid (55) gave 1,1,12,12-tettrafluorododecane (55%) and 1,12-dichlorododecane (40%). ω-Chlorocarboxylic acids; for example, 9-chlorononanoic, 11-chloroundecanoic, and 13-chlorotridecanoic acids, have been studied and the normal dichlorodimers were produced in good yields (49-52%) (55).

The product 2,2'-(tetrafluoroethylene)bis(heptafluorofuran) was produced when nonafluoro-2-furanacetic acid was electrolyzed using methanol as a solvent (6).

Cyano Acids

Electrolysis of cyanoacetic and *t*-butylcyanoacetic acid in methanol has been studied and the products succinonitrile (24%) and 2,3-di(*t*-butyl)succinonitrile (13%) were characterized (18). Electrolysis of the following cyano acids: isopropyl-, *t*-butyl-, cyclohexyl-, and dimethylcyanoacetic acid in methanol has been studied and the following products listed in Table IV were produced (21).

TABLE IV

THE KOLBE PRODUCTS AND YIELDS OF CYANO ACIDS

α-Cyanoacetic Acids	Dinitrile % Meso	Racemic	Ketenimine %	Methyl Ester %
Isopropyl	13	12	18	--
t-Butyl	13	17	31	35
Cyclohexyl	14	8	8	--
Dimethyl	24	24	6	5

Dicarboxylic Acids

The dicarboxylic acids: azelaic, sebacic, dimethylglutaric, and *trans*-β-hydromuconic acids (*sic*) were electrolyzed in methanol using platinum electrodes. The products were reported as being α, ω-carboxylated polymers. In the case of azelaic acid, the polymer had a mol. wt. of

3200 (44). The electrolysis of *trans*, *trans*, *trans*-1,3-dicarboxy-2,4-dicarbomethoxycyclobutane was found to produce 2,4-dicarbomethoxybicyclobutane in a 15% yield (64). The products cyclopentene and bicyclo(2.1.0)pentane were produced in a ratio of 20:1 when *cis*-1,3-cyclopentanedicarboxylic acid was electrolyzed in methanol (5).

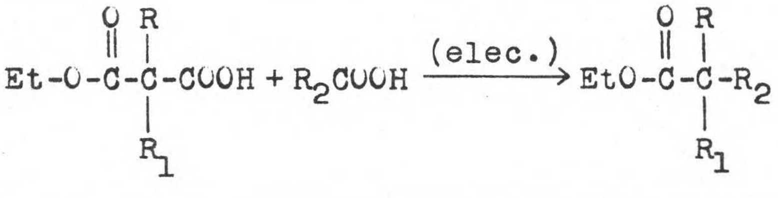
"Crossed" Electrolytic Condensation

Electrolytic condensation of two different carboxylic acids has been termed a "crossed" electrolytic condensation.

Ethyl 18-nonadecenoate was prepared in a 24% yield by the electrolysis of 10-undecenoic acid and ethyl hydrogen sebacate using a platinum anode and a mercury cathode. The solvent for the reaction was methanol (57). The Kolbe electrolysis of a dialkylmalonic half-ester and monocarboxylic acid mixture has been studied. The products are listed in Table V (19).

TABLE V

THE SUBSTRATE, PRODUCTS, AND YIELDS OF THE ELECTROLYSES OF DIALKYLMALONIC HALF-ESTERS



$$\mathrm{Et{-}O{-}\overset{O}{\overset{\|}{C}}{-}\underset{\underset{R_1}{|}}{\overset{\overset{R}{|}}{C}}{-}COOH} + \mathrm{R_2COOH} \xrightarrow{\text{(elec.)}} \mathrm{EtO{-}\overset{O}{\overset{\|}{C}}{-}\underset{\underset{R_1}{|}}{\overset{\overset{R}{|}}{C}}{-}R_2}$$

R, R_1	R_2	Yield
$(C_2H_5)_2$	CH_3	37
$(C_2H_5)_2$	C_2H_5	46

TABLE V--Continued

R,R_1	R_2	Yield
$(C_2H_5)_2$	$\underline{n}$-C_3H_7	39
$(C_2H_5)_2$	$\underline{i}$-C_3H_7	17
$(C_2H_5)_2$	$\underline{t}$-C_4H_9	0
$(C_2H_5)_2$	$(CH_3)_3$-C-CH_2	14
$(C_2H_5)_2$	$(CH_3)_3C$-CH_2-CH_2	26
CH_3,C_2H_5	$\underline{i}$-C_4H_9	36
C_2H_5,$\underline{i}$-C_3H_7	C_2H_5	47
C_2H_5,$\underline{n}$-C_4H_7	CH_3	35
C_2H_5,$(CH_3)_3C$-CH_2	$CH_3OCOCH_2CH_2$	30
C_2H_5,$(CH_3)_3SiCH_3$	CH_3OCOCH_2-CH_2	21

Syntheses of long-chain ω-bromocarboxylic esters were achieved by the electrolysis of mixtures of ω-bromocarboxylic acids and half-esters. The substrates and results are listed in Table VI (72).

$$\underset{\text{I}}{Br(CH_2)_NCOOH} + \underset{\text{II}}{HOOC(CH_2)_MCOOCH_3} \xrightarrow[\text{MeOH}]{\text{(elec.)}} \underset{\text{III}}{Br(CH_2)_{N+M}COOCH_3}$$

$$+ \underset{\text{IV}}{Br(CH_2)_{2N}Br} + \underset{\text{V}}{CH_3OOC(CH_2)_{2M}COOCH_3} +$$

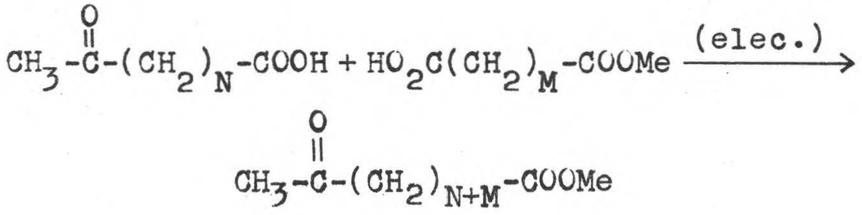
$$\underset{\text{VI}}{Br(CH_2)_NCOOCH_3} + \underset{\text{VII}}{CH_3OOC(CH_2)_MCOOCH_3}$$

TABLE VI

THE RESULTS OF THE ELECTROLYTIC CONDENSATION OF MIXTURES OF ω-BROMOCARBOXYLIC ACIDS AND HALF-ESTERS

Reagents		Product Yield %				
I	II	III	IV	V	VI	VII
N=10	M=4	37	39	39	11	5
N=11	M=4	6	21	51	34	1
N=5	M=8	18	23	1	51	50
N=7	M=8	7	24	6	32	30

Long-chain oxocarboxylic esters have been made by the "crossed" electrolytic condensation of oxocarboxylic acids with half-esters (47).



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_N-COOH + HO_2C(CH_2)_M-COOMe \xrightarrow{(elec.)} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_{N+M}-COOMe$$

The substrates, yields, and products are listed in Table VII.

TABLE VII

THE KOLBE PRODUCTS OF THE ELECTROLYSIS OF THE MIXTURE OF OXOCARBOXYLIC ACIDS AND HALF-ESTERS

N	M	Product Yield %
2	4	32
2	8	29
2	12	25
10	2	16
10	4	--

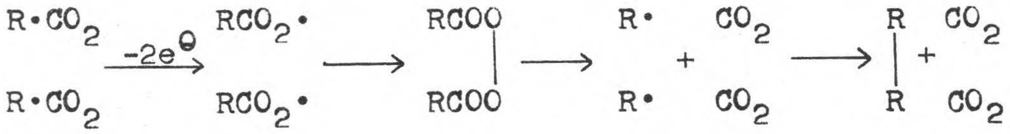
Crossed Kolbe electrolysis of methyl hydrogen _cis_-succinate and acetic acid resulted in a 3.6% yield of methyl _trans_-2-butenate (51). 1-Acetoxy-2_D_-methyl-7-octene has been synthesized by the electrolysis of (+)-4L-methyl-5-acetoxypentanoic acid and 4-pentenoic acid in a 90.5% yield (48).

Mechanism of the Kolbe Electrolysis

There are three mechanisms which have been presented to explain the formation of the products during the Kolbe electrolysis. These mechanisms are: the peroxide theory, the hydrogen peroxide theory, and the radical theory.

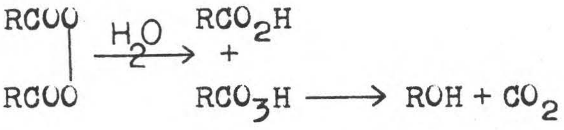
Peroxide Theory

This theory has three intermediates involved in the conversion of carboxylate ions into the final products: discharged anions (I), diacyl peroxides (II), and alkyl radicals (III).



I II III

The by-products are accounted for by the hydrolysis of the peroxide to give a per-acid which decomposes to an alcohol.



Hydrogen Peroxide Theory

This theory depends upon hydrogen peroxide being formed at the anode and then entering into the reaction.

$$2OH^{\ominus} \longrightarrow H_2O_2 + 2e^{\ominus}$$

$$H_2O_2 + 2CH_3CO_2^{\ominus} \longrightarrow C_2H_6 + 2CO_2 + 2OH^{\ominus}$$

This theory required that hydroxyl ions be present and only applies to electrolyses in aqueous solutions. There have been objections to this theory since the addition of concentrated hydrogen peroxide to acetate solutions has been unsuccessful in producing the usual Kolbe product.

Radical Theory

This theory depends upon the formation of free radicals which then dimerize to the products.

$$2RCOO^{\ominus} \xrightarrow{-2e^{\ominus}} 2R\cdot + CO_2 \longrightarrow R\text{-}R + CO_2$$

The by-products have been explained by the formation of carbonium ions.

There have been some papers in the defense of the free radical theory (17, 61). However, ther have been papers in defense of the peroxide theory (discharge ion theory) with new modification (12, 13, 14).

Conclusion

The main reasons the free radical theory is preferred as opposed to the other two theories are: the capacity of the alkyl free radicals (which are formed by the Kolbe electrolysis of carboxylic acids) to initiate the polymerization of styrene and acrylonitrile, and the explanation of the side products.

γ-Diketones

The diester of hexane-2,5-dione-1,6-dicarboxylic acid was produced in a 12% yield by the electrolysis of the ethyl half-ester of 3-oxopentanedicarboxylic acid (69).

γ-Diketones have been prepared by the electrolysis of γ-diketocarboxylic acids with carboxylic acids. Dodeca-2,5-dione was produced in a 30-45% yield by the electrolysis of a mixture of 4,7-diketooctanoic and caproic acids. An array of eleven different γ-diketones have been prepared in an analogous method as 2,5-dodecadione was made but no yields are given (31).

Another electrolytic procedure for the preparation of γ-diketones has been reported (8). The procedure is as follows:

$$CH_2{=}CRY + R_1CO_2H \xrightarrow{(elec.)} (R_1CH_2CR_2Y)_2 \qquad Y{=}\begin{array}{l}COMe\\COEt\end{array}$$

The results are listed in Table VIII. This has been classified as an anodic oxidation of an organic acid in the presence of substrates of type $CH_2{=}CR_2Y$. The Kolbe reaction has been described earlier (page 3) and the electrolysis of a carboxylic acid in the presence of an alkene has not been classified as the Kolbe reaction.

TABLE VIII

THE RESULTS OF THE ELECTROLYSIS OF
$CH_2=CRY+R_1CO_2H$

Substrate	Anion	Products	Yields % Meso	DL
$CH_2=CHCOMe$	$MeCO_2^{\ominus}$	$(MeCH_2CHCOMe)_2$	25	24
$CH_2=C(Me)COMe$	$MeCO_2^{\ominus}$	$(MeCH_2C(Me)COMe)_2$	56	20

Reviews of the Kolbe Electrolysis

There have been a few very good reviews of the Kolbe electrolysis listed in the literature (20, 23, 58, 67, 68).

III. EXPERIMENTAL

General Information

Infrared spectra.--The infrared spectra were recorded on the following spectrophotometers: Perkin-Elmer 457 and 700 models, and Hilger-Watts H1200. All liquids were run as capillary films between NaCl discs. The solids were run by preparing a transparency of the sample in a KBr matrix.

Gas chromatography.--Liquid samples were analyzed on a Varian-Aerograph 1700 gas chromatograph.

Melting points.--All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Acidity and basicity.--pH Hydrian Paper was used in estimating all acidities and basicities.

Power Supplies.--There were two different dc power supplies used in the electrolysis of β-ketoacids. The first was a solid state dc power supply with a capacity of 5 amperes. During an electrolysis reaction, the maximum amperage (0.1--1.0 amperes) obtainable at a potential of 9-10 volts was used. When the first dc power supply was in use, an air stream had to be used in order to keep the power supply from overheating. If a potential over 10 volts was used, overheating occurred. The second (a selenium rectifier) power supply used had a capacity of 30 amperes and 40 volts. There was no heating problem with the second dc power supply.

Experimental Procedure

Preparation of 3-oxobutanoic acid.(37)--A mixture of 52.0 g (0.4 moles) of ethyl acetoacetate (Eastman), 16.0 g (0.4 moles) of sodium hydroxide, and 400 ml of water were stirred at room temperature for 10 hrs. The reaction mixture was then washed three times with 75 ml portions of ether. The resulting aqueous reaction mixture was then cooled to 0° using an ice bath and then acidified to a pH 2 using dil sulfuric acid. The acidic solution was then extracted three times with 75 ml portions of ether. The ether extracts were combined and then the ether was dried using anhyd magnesium sulfate. The ether was then evaporated until 5 ml of ether remained. The resulting yellow liquid was cooled in a Dry Ice-isopropanol bath and the crystals that formed were collected by suction filtration. This gave a yield of 7.9 g of crude material. The now half liquid and half solid product was redissolved in a small portion of ether and recrystallized yielding 4.8 g (11.8%), mp 34--35° (lit., 10% yield, mp 36--37° (37)).

A second reaction was run in which a mixture of 52.0 g (0.4 moles) of ethyl acetoacetate (Eastman), 32 g (0.8 moles) of sodium hydroxide, and 400 ml of water was stirred for

12 hrs at room temperature. The reaction mixture was then washed three times with 75.0 ml portions of ether. The aqueous layer was then cooled to 0^{o} using an ice bath and acidified to a pH 3 with dil sulfuric acid. The acidified aqueous solution was then extracted seven times with 100 ml portions of ether. The ether extracts were combined and then evaporated until about 5 ml of ether remained. The yellow liquid was cooled using liquid nitrogen. White crystals formed and were collected by suction filtration. The yield was 10.0 g (27%).

A third reaction was run in the same manner as the second except 22.2 g (0.56 moles) of sodium hydroxide, and a reaction time of 2 hrs was used. The product 13.0 g, which was 60% 3-oxobutanoic acid determined by titration, was a clear liquid. The actual yield was 7.8 g (19%).

A fourth reaction was run exactly as the second and the product was produced in a yield of 3.67 g. This was 90% 3-oxobutanoic acid which was determined by titration. The total yield was 3.2 g (8.1%).

Preparation of 2,5-hexanedione.--The electrolysis of 3-oxobutanoic acid was carried out as follows: A vessel 10.0 cm high and 3 cm diameter was mounted in a water bath used for cooling. The reaction vessel was then charged with 40 ml methanol, 0.02 g (0.00087 moles) of sodium metal, and 1.0 g (0.0098 moles) of 3-oxobutanoic acid. The anode was a perforated platinum foil cylinder 5.0 cm high with a 2.5 cm diameter (37 cm^2) and the cathode was a platinum wire screen cylinder 5.0 cm high with a 1.3 cm diameter (28 cm^2). The electrodes were positioned into the reaction vessel and a current of 0.15 amperes (a current density of 0.00405 A/cm^2 at the anode) was maintained for 5 hrs at which time the reaction mixture was of a basic pH. The reaction was then stopped. During the reaction, the temperature was maintained at 17°. The reaction was stirred using a magnetic stirrer. The methanol was flashed off until a volume of 20 ml remained. Gas chromatographic analysis using a Porapak Q column indicated a 6.5% yield (based on 0.00893 moles of starting β-ketoacid) of 2,5-hexanedione. An internal standard of methyl isobutyl ketone was used in the gas chromatographic analysis. The theoretical amount of electricity was calculated at 945 coulombs which corresponds to 1.175 hrs at the current applied.

A second reaction was run exactly as the first. The gas chromatographic analysis gave a calculated yield of 30% 2,5-hexanedione.

A third reaction was run using exactly the same electrolysis apparatus as in the first reaction. The reaction vessel was charged with 40 ml methanol, 0.1 g (0.00435 moles) sodium metal, and 4.1 g (0.04 moles of 3-oxobutanoic acid). With stirring and maintaining the reaction temperature at 15°, a current of 0.5 amperes (a current density at the anode of 0.0135 A/cm^2) was maintained for 2.5 hrs at which time a pH 8 was detected and the reaction was stopped. The methanol was flashed off leaving a yellow liquid which was fractionally distilled. The fraction collected at 74--75° at 10 torr was analyzed by gas chromatography and was found to be 95% pure 2,5-hexanedione. An ir spectrum of the collected liquid product was run and was the same as that of authentic 2,5-hexanedione. Based on 0.036 moles of starting β-ketocarboxylic acid and 95% of the 0.793 g product yield, a yield of 34% was calculated. A sample of 2,5-hexanedione was distilled and the boiling point was recorded (bp 73--74°/10 torr). The theoretical electrical uptake was 3860 coulombs (2.15 hrs at 0.5 amperes).

A fourth reaction was run using exactly the same electrolysis apparatus used in the first reaction. The reaction vessel was charged with 40 ml of methanol, 0.15 g (0.0065 moles) of sodium metal, and 7.8 g (0.070 moles) of 3-oxobutanoic acid. The electrodes were positioned and a current of 2.8 amperes (a current density at the anode of 0.075 A/cm^2) was maintained for 56 min at which time a pH 8 was reached and the reaction was stopped. The reaction was stirred with a mechanical stirrer instead of the magnetic stirrer and kept at a temperature of 40°. The methanol was flashed off leaving a yellow liquid. The yellow liquid was fractionally distilled, and the fraction at bp 72--74°/10 torr was analyzed on the gas chromatograph using a Porapak Q column. This was found to be 95% pure. An ir spectrum of the liquid was the same as that of 2,5-hexanedione. The theoretical amount of electricity was 7.39 x 10^3 coulombs (44 min at 2.5 amperes). Based on 0.07 moles of starting

β-ketocarboxylic acid and 95% of a 1.35 g crude yield, the yield was calculated to be 32%.

A fifth reaction was run using the same electrolysis apparatus as in the first reaction. The starting materials were: 40 ml methanol, 0.065 g (0.0028 moles) of sodium metal, and 3.29 g (0.0322 moles) of 3-oxobutanoic acid. These starting materials were placed into the reaction vessel. With stirring and keeping the temperature of the reaction at 40° throughout the reaction, the electrodes were positioned and a current of 3 amperes (a current density at the anode of 0.08 A/cm^2) was maintained for 30 min. The reaction was then stopped since a pH 8 was detected. The methanol was flashed off leaving a yellow liquid which was fractionally distilled. The distillate with a boiling point of 73--74°/10 torr was collected and analyzed on the gas chromatograph using a Carbowax 20M column. The liquid was 98--99% pure. The theoretical electrical uptake was 311 coulombs (17 min). A yield of 36% was arrived at based on 0.0294 moles of starting β-keto-acid and 99% of 0.61 g of product.

Preparation of ethyl 2,2-dimethyl-3-oxobutanoate.--A one-liter three-necked round-bottom flask was equipped with a mechanical stirrer, a condenser, and a pressure-equalizing dropping funnel. The flask was charged with 500 ml of anhyd ethanol and then 27.8 g (1.2 moles) of sodium metal was added in small portions. After the addition of the sodium metal was completed, 65 g (0.5 moles) of ethyl 3-oxobutanoate was added drop-wise to the refluxing mixture. With refluxing, 170 g (1.2 moles) of methyl iodide was then added drop-wise. After the addition of methyl iodide, the reaction mixture was stirred at room temperature for an additional 10 hrs. A pH 7 at this point indicated that the reaction was finished. The ethanol was then flashed off and the resulting oil with a precipitate was washed with four 100 ml portions of water. The resulting oil was then dissolved using 100 ml of ether and dried using anhyd magnesium sulfate. The ether was then flashed off and the remaining oil was fractionally distilled. The fraction that came over at bp 79--82^{o}/17 torr was found to be pure by gas chromatograph analysis. The liquid product was produced in a yield of 63.0 g (80%), bp 79--82^{o}/17 torr (lit., bp 184^{o}/760 torr (66)).

Preparation of sodium 2,2-dimethyl-3-oxobutanoate.--A mixture of 8.0 g (0.2 moles) of sodium hydroxide, 150 ml of water, and 31.6 g (0.2 moles) of ethyl 2,2-dimethyl-3-oxobutanoate was stirred at room temperature for 22 hrs. The aqueous layer was then washed two times with 50 ml portions of ether. The water was then flashed off the aqueous mixture leaving a white paste like solid. The temperature was kept below 45^{o} during the evaporation. The yield was 26 g (85%).

Preparation of 2,2-dimethyl-3-oxobutanoic acid.--The sodium salt of 2,2-dimethyl-3-oxobutanoate was acidified to a pH 2 using cold dil sulfuric acid. The aqueous reaction mixture was extracted two times with 50 ml portions of ether. The ether extracts were combined and the ether was dried using anhyd magnesium sulfate. The ether was then flashed off without exceeding a temperature of 40°. A clear, colorless liquid remained (4.6 g or 55%).

A second reaction was run exactly as the first reaction. A portion of the clear, colorless product was titrated with 0.1 N sodium hydroxide and found to be 82% pure.

Attempted preparation of 3,3,4,4-tetramethyl-2,5-hexanedione.--The same electrolysis apparatus used in the preparation of 2,5-hexanedione was used in this reaction. The reaction tube was charged with 2.0 g (0.0132 moles) of sodium 2,2-dimethyl-3-oxobutanoate and 40 ml of methanol. A current of 0.5 amperes (a current density at the anode of 0.0132 A/cm^2) was maintained throughout the reaction. The pH was monitored and a pH 7 was kept throughout the reaction by adding dil hydrochloric acid when a pH 8 or higher was detected. When the pH 7 didn't change, the reaction was stopped. The methanol was flashed off leaving an oil layer on top of an aqueous layer. The oil layer was extracted with ether and the ether was dried using anhyd magnesium sulfate. The ether was flashed off and distillation of the resulting liquid afforded no product.

A second reaction was run using 2.55 g (0.0196 moles) of 2,2-dimethyl-3-oxobutanoic acid, 0.06 g (0.00026 moles) of sodium metal, and 40 ml of methanol. A current of 0.5 amperes was used and the reaction was stopped at a pH 8. The reaction temperature was 11^{o} throughout the reaction. The solvent was flashed off and the remaining liquid was distilled yielding no product.

A third reaction was run the same as the second reaction except 2.29 g (0.017 moles) of 2,2-dimethyl-3-oxobutanoic acid and 0.05 g (0.000227 moles) of sodium metal were used. Distillation yielded no product.

Preparation of ethyl 2-methyl-3-oxobutanoate.--A three-necked one-liter flask was equipped with a condenser, a mechanical stirrer, and a pressure-equalizing dropping funnel. Sodium metal pieces 22.9 g (1.0 moles) were then added slowly to stirring anhyd ethanol 500 ml. Ethyl-3-oxobutanoate 130.0 g (1.0 moles) was then added to the sodium methoxide solution. After the addition was completed, 142.0 g (1.0 moles) of methyl iodide was added drop-wise to the stirring reaction mixture over a 4 hr period. The resulting reaction mixture was then refluxed until a pH 7 was reached and then the reaction was stopped. The solvent was then flashed off leaving an oil with a white precipitate. The oil was extracted from the precipitate by using two portions of 100 ml of ether. The ether extracts were combined and then washed twice with two portions of 50 ml of water. The ether was then dried using anhyd magnesium sulfate and then flashed off. The resulting yellow liquid was fractionally distilled. A yield of 103 g (72%) of ethyl

2-methyl-3-oxobutanoate with a bp of $80^\circ/10$ torr was produced.

Preparation of 2-methyl-3-oxobutanoic acid.--A mixture of ethyl 2-methyl-3-oxobutanoate 20.0 g (0.0345 moles), sodium hydroxide 11.0 g (0.278 moles), and 100 ml of water was stirred for 1 hr at room temperature. The reaction mixture was then cooled to 0° using an ice bath and then acidified with dil sulfuric acid to a pH 2. The temperature was not allowed to go above 0°. The acidic solution was then extracted with ether, and the extracts were combined. The ether was dried using anhyd magnesium sulfate. The ether was then flashed off keeping the temperature below 40°. A portion of the resulting clear liquid was analyzed by titration and was found to be 76% acid. Based on 76% of 5.26 g, a yield of 4.0 g (25%) was produced.

Attempted preparation of 3,4-dimethyl-2,5-hexanedione.--The same electrolysis apparatus was used in this reaction as in the preparation of 2,5-hexanedione. The reaction vessel was charged with 4.0 g (0.0345 moles) of 2-methyl-3-oxobutanoic acid, 0.065 g (0.00282 moles) of sodium metal, and 40 ml of methanol. A current of 1.0 amperes (a current density of 0.027 A/cm^2) was maintained for 1.25 hrs (theory 55.5 min). The solvent was then flashed off until 2 or 3 ml of methanol remained. The resulting liquid was fractionally distilled with no desired product isolated.

Preparation of ethyl 4,4-dimethyl-3-oxopentanoate. (30)--A mixture of 9.6 g (0.4 moles) of sodium hydride and 23.6 g (0.2 moles) of diethylcarbonate was stirred while 20.0 g (0.2 moles) of pinacolone in 50 ml of ether was added dropwise over a 30 min period. The reaction was kept below 40°. The reaction was stirred for an additional hour at which time it was thought that 80% of the hydrogen had been evolved. The reaction was stopped by the addition of 30 ml of ethanol. It was cooled to 10° and 150 ml of ether was added. While keeping the temperature below 20°, dil hydrochloric acid was added until a pH 4 was reached. The aqueous layer was then extracted twice with 75 ml portions of ether. The extracts were combined, and the ether was dried using anhyd magnesium sulfate. The ether was then flashed off and the resulting oil was fractionally distilled. The product (bp 92--94°/10 torr) was produced in a yield of 5.12 g (14.8%) (lit., bp 96--100°/15 torr (59)).

A second reaction was run in the same manner as the first except 19.2 g (0.8 moles) of sodium hydride, 60 g (0.5 moles) of diethylcarbonate, and 40.0 g (0.4 moles) of pinacolone were used. After the addition of the pinacolone, the reaction was stirred at 40--50° for 7.5 hrs. The product was produced in a yield of 19.6 g (27.5%) with a bp of 92--94°/10 torr.

Preparation of 4,4-dimethyl-3-oxopentanoic acid.--A mixture of 1.2 g (0.03 moles) of sodium hydroxide, 5.0 g (0.029 moles) of ethyl 4,4-dimethyl-3-oxopentanoate, and

50 ml of water was stirred for 2 hrs. The reaction mixture was then extracted twice with 50 ml portions of ether. The resulting aqueous mixture was then cooled to 0° and kept at 0° while dil sulfuric acid was added until a pH 2 was reached. The acidic mixture was then extracted three times with 75 ml portions of ether. The ether extracts were combined and the ether was dried using anhyd magnesium sulfate. The ether was then flashed off leaving a white solid (mp 55--56° dec) with a yield of 2.32 g (55%). The ir spectrum of the white solid showed the COOH band at 3400--2500 cm^{-1} and the two carbonyl bonds 1740 and 1620 cm^{-1}.

A second reaction was run exactly as the first reaction except 2.80 g (0.07 moles) of sodium hydroxide, 10 g (0.058 moles) of ethyl 4,4-dimethyl-3-oxopentanoate, and 75 ml of H_2O were used. The product mp 55--56°, 6.19 g (74% yield), was titrated with 0.1 N sodium hydroxide and found to be 100% acid.

A third reaction was run exactly as the first except 2.0 g (0.05 moles) of sodium hydroxide, 7.1 g (0.041 moles) of ethyl 4,4-dimethyl-3-oxopentanoate, and 75 ml of water were used. The product was produced in a yield of 4.23 g (71.6% yield).

Preparation of 2,2,7,7-tetramethyl-3,6-octanedione.--The same electrolysis apparatus used in the preparation of 2,5-hexanedione was used in this reaction. The reaction vessel was charged with 2.0 g (0.0139 moles) of 4,4-dimethyl-3-oxopentanoic acid, 0.04 g (0.000174 moles) of sodium metal, and 40 ml of methanol. A current of 0.4 amperes (a current density of 0.0108 A/cm^2) was maintained for 2.16 hrs at which time a pH 8 was reached and the reaction was stopped. The solvent was then flashed off and the remaining liquid was fractionally distilled. The product was produced in a yield of 0.3 g (22%) with a bp of 102--105°/9 torr. Gas chromatograph analysis showed the product to be 100% pure. Gas chromatograph analysis using a known sample of 2,2,7,7-tetramethyl-3-octanedione confirmed the structure of the product (lit., bp 106--107°/10 torr (56)).

In the second reaction, 6.0 g (0.046 moles) of 4,4-dimethyl-3-oxopentanoic acid, 0.12 g (0.0052 moles) of sodium metal, and 40 ml of methanol were used and a current of 0.5 amperes (a current density at the anode of 0.0135 A/cm^2) was sustained for 2.8 hrs (theory 2.22 hrs) at which time a pH 8 was detected and the reaction was stopped. The solvent was flashed off and the remaining liquid was distilled. The product was collected in a yield of 1.0 g (24% yield based on 0.041 moles of starting β-ketoacid) with a bp of 103--105°/9 torr (lit., bp 106--107°/10 torr (56)).

A third reaction was run the same as the first reaction except 8.15 g (0.0565 moles) of 4,4-dimethyl-3-oxopentanoic acid, 0.16 g (0.00695 moles) of sodium metal, and 40 ml of methanol were used. The reaction time was 2 hrs (theoretical time 1.5 hrs at 1.0 amperes). The product was produced in a yield of 1.13 g (24% yield based on 0.0496 moles of starting β-ketoacid) with a bp of 101--105°/9 torr.

Preparation of ethyl 3-oxohexanoate.(32)--A three-necked 500 ml round-bottom flask was equipped with a mechanical stirrer and a Dean-Stark trap. A mixture of 80.0 g (1.23 moles) of granular zinc metal, 250 ml of benzene, and a trace of mercuric chloride was brought to a reflux and any water collected in the Dean-Stark trap was discarded. A mixture of 75.9 g (1.1 moles) of butyronitrile (Eastman) and 167.0 g (1.0 moles) of ethyl bromoacetate (Aldrich) was then added drop-wise to the refluxing benzene-zinc mixture over a 45 min period. The resulting reaction mixture was refluxed for an additional hour. The reaction was then brought to a pH 7 using dil sulfuric acid and let set overnight. The reaction mixture was hydrolyzed at a pH 2 for 1 hr and neutralized. The reaction mixture was extracted three times using 75 ml portions of benzene. The extracts were combined, and the benzene was dried using anhyd magnesium sulfate. The benzene was then flashed off, and the remaining liquid was fractionally distilled. A poor yield of the Reformatsky product was collected (18.6 g or 11% yield, bp of 81--82°/10 torr) (lit., bp 90--95°/16 torr, yield 65% (32)).

Preparation of 3-oxohexanoic acid.--A mixture of 9.0 g (0.056 moles) of ethyl 3-oxohexanoic acid, 3.0 g (0.075 moles) of sodium hydroxide, and 60 ml of water was stirred for 2.5 hrs, and then extracted two times with 50 ml portions of ether. The remaining aqueous mixture was cooled to 0° and acidified to a pH 2 using cold dil sulfuric acid. The temperature was not allowed above 5°. The acidic solution was then extracted six times using 75 ml portions of ether. The ether extracts were combined and the ether was then dried using anhyd magnesium sulfate. The ether was flashed off until 10 ml of ether remained. The solution was then cooled using liquid nitrogen and the white solid that formed was collected by suction filtration. The product was produced in a fair yield of 2.57 g (35%) with a mp of 56.5--57.5° dec.

Preparation of 4,7-decanedione.--The same electrolysis apparatus used in the preparation of 2,5-hexanedione was used in this reaction except a mechanical stirrer was used in place of the magnetic stirrer. The reaction tube was charged with 2.25 g (0.0173 moles) of 3-oxohexanoic acid, 0.045 g (0.00195 moles) of sodium metal and 40 ml of methanol. A current of 2.0 amperes was maintained for a period of 20 min (theoretical time was 13.8 min) at which time a pH 8 was reached and the reaction was stopped. The reaction temperature was maintained at 30° throughout the reaction. The solvent was flashed off and the remaining liquid was fractionally distilled. The product was produced in a good yield of 0.52 g (39% based on 0.01535 moles of starting β-ketoacid) with a bp 118--120°/9 torr (lit., bp 62--64°/0.3 torr(56). The diketone was characterized by using the gas chromatograph and by comparing the ir spectrum with that of authentic 4,7-decanedione.

Preparation of 4-phenyl-3-oxobutanoic acid.--A mixture of 28.8 g (0.15 moles) of ethyl 4-phenyl-3-oxobutanoate, 6.0 g (0.15 moles) of sodium hydroxide, and 100 ml of water was stirred for 1.8 hrs and heated to 80°. The warmed reaction mixture was stirred for an additional hour and then cooled to room temperature. The reaction mixture was extracted two times with 50 ml portions of ether. The aqueous solution was cooled to 0° and while keeping the temperature below 5° was acidified to a pH 2 using dil sulfuric acid. The acidic solution was extracted twice with 100 ml portions of ether. The ether extracts were combined and the ether was dried using anhyd magnesium sulfate. The ether was flashed off leaving a white solid (mp 102--103° dec). The product was produced in a good yield of 5.4 g (22.5%).

In a second reaction, 50.0 g (0.26 moles) of ethyl 4-phenyl-3-oxobutanoate, 18.5 g (0.46 moles) of sodium hydroxide and 100 ml of water were stirred at reflux for 30 min and then stirred for an additional 12 hrs at room temperature. The alkaline mixture was extracted four times with 75 ml portions of ether. The resulting alkaline mixture was cooled to 0° and kept below 5° while acidifing to a pH 2 using dil sulfuric acid. The acidic reaction mixture was extracted with two portions of 100 ml of ether. The extracts were combined, and the ether was dried using anhyd magnesium sulfate. The ether was flashed off leaving a white solid. The yield was 4.6 g (18%) with a mp of 105° dec.

A third reaction was run in which a mixture of 8.0 g (0.0415 moles) of ethyl 4-phenyl-3-oxobutanoate, 1.65 g (0.0415 moles) of sodium hydroxide and 75 ml of water was stirred at room temperature for 2.5 hrs. The reaction mixture was extracted three times with 50 ml portions of ether. The resulting aqueous mixture was cooled to 0° and acidified to a pH 2 using dil sulfuric acid. The temperature was kept below 5° during the acidification. The acidified mixture was extracted three times with 75 ml portions of ether. The ether extracts were combined and the ether was dried using anhyd magnesium sulfate. The ether was flashed off leaving a white solid as the product. The product yield was 2.74 g (40%) with a mp 104° dec.

Preparation of 1,4-diphenyl-1,4-butanedione.--The electrolysis apparatus used in the synthesis of 2,5-hexanedione was used in this reaction. 4-Phenyl-3-oxobutanoic acid 4.9 g (0.03 moles), sodium metal 0.1 g (0.00435 moles), and 40 ml of methanol were placed in the reaction vessel and a current of 0.2 amperes (a current density of 0.0054 A/cm^2) was maintained. After a few minutes, a white film had deposited on the anode causing the current to drop. The anode had to be washed clean of the deposit and then repositioned. This procedure was carried out for 3 hrs and then the reaction was stopped even though a pH 7 was not reached. The reaction was stirred and run at 11°. The reaction mixture was placed in the refrigerator with a temperature of -10°. A yellow solid precipitated and was collected by suction filtration. The solid had a mp of 140--143° and was produced in a yield of 0.90 g (29% based on 0.0256 moles of starting β-ketoacid). An ir spectrum of the solid after crystallization from acetonitrile was the same as that of a known sample of 1,4-diphenyl-1,4-butanedione. The melting point of 144.5--145° was the same as the literature mp of 145° (56).

A second reaction was run in which a solvent system of 20 ml methanol and 20 ml of acetonitrile was used to prevent the film from depositing. The reaction vessel was also charged with 2.0 g (0.0122 moles) of 4-phenyl-3-oxobutanoic acid and 0.04 g (0.000175 moles) of sodium metal. A current of 0.5 amperes (a current density at the anode of 0.0135 A/cm^2) was maintained until a pH 8 was reached without a film being deposited. The reaction was stopped at a pH 8. The reaction was stirred and carried out at 11°. 95% of the solvent was flashed off. The resulting reaction mixture was cooled and the precipitate was collected having a yield of 0.38 g (26% based on 0.0120 moles starting β-ketoacid) with a mp of 143--144°.

In a third reaction, 3.74 g (0.0228 moles) of 4-phenyl-3-oxobutanoic acid, 0.054 g (0.000234 moles) of sodium metal, and a solvent mixture of 10 ml methanol and 30 ml of DMF were placed into the reaction vessel. This was kept at 11° and stirring while a current of 0.8 amperes (a current density at the anode of 0.0216 A/cm^2) was maintained for 1.16 hrs. A pH 8 was reached and the reaction was stopped. 95% of the solvents was flashed off and the resulting mixture was cooled. The precipitate was collected by suction filtration. A yield of 0.25 g (10% based on 0.0205 moles of starting β-ketoacid) with a mp 142--143° was produced which was considered fair.

Preparation of ethyl 3-(2-thienyl)-3-oxopropanoate. (39) --This compound was prepared by Dale Whiting using the Lerone and Hauser method (39).

Preparation of 3-(2-thienyl)-3-oxopropanoic acid.--A mixture of 7.0 g (0.0354 moles) of ethyl 3-(2-thienyl)-3-oxopropanoate, 2.0 g (0.05 moles) of sodium hydroxide and 75 ml of water was stirred at room temperature for 3 hrs and then extracted two times with 50 ml portions of ether. The resulting aqueous mixture was cooled to 0° and was acidified to a pH 2. The temperature was kept below 5° during the acidification. The acidified reaction mixture was extracted three times using 75 ml portions of ether. The ether extracts were combined and the ether was then dried using anhyd magnesium sulfate. The ether was flashed off leaving 5.0 g of a yellowish solid. Recrystallization from benzene resulted in the decomposition of 2 g of the solid. The recrystallized solid 3.05 g had a melting point of 92--93° dec. A yield of 3.05 g (48%) was produced.

A second reaction was run exactly as the first reaction except 10.1 g (0.051 moles) of ethyl 3-(2-thienyl)-3-oxopropanoate, 2.0 g (0.065 moles) of sodium hydroxide, and 75 ml of water were used. The product was produced in a yield of 4.35 g (50%) and had a mp of 91--92° dec.

A third reaction was run exactly as the second reaction but had a yield of 4.2 g (48%) and a mp of 92--93° dec.

Attempted preparation of 1,4-di(2-thienyl)-1,4-butanedione.--The electrolysis apparatus used in the preparation of 2,5-hexanedione was also used in this reaction. The reaction vessel was charged with 2.0 g (0.0117 moles) of 3-(2-thienyl)-3-oxopropanoic acid, 0.04 g (0.000174 moles) of sodium metal, and 40 ml of methanol. An initial current of 0.4 amperes (a current density at the anode of 0.0108 A/cm^2) was maintained for only 5 min at which time a film deposited on the anode stopping the reaction. No product was collected.

A second reaction was run exactly the same as the first except a solvent mixture of 20 ml methanol and 20 ml of acetonitrile was used. A film deposited stopping the reaction.

A third, fourth, and fifth reaction was run exactly as the first except the corresponding solvent systems were used: methanol-ethanol, methanol-benzene, and methanol-THF. They all failed because a film deposited on the anode which stopped the reaction.

The syntheses of γ-diketones by the electrolytic condensation of the corresponding β-ketocarboxylic acids are summarized in Table IX.

TABLE IX

γ-DIKETONES SYNTHESIZED BY ELECTROLYSIS
OF β-KETOCARBOXYLIC ACIDS

Diketone	% Yield Average	Physical State
2,5-hexanedione	34	bp 73--74°/10 torr
2,2,7,7-tetramethyl-3,6-octanedione	23	bp 103--105°/9 torr, mp 22°
4,7-decanedione	39	bp 118--120°/9 torr
1,4-diphenyl-1,4-butanedione	27	mp 144--145°

IV. DISCUSSION

β-Ketocarboxylic Acids

β-Ketocarboxylic acids are unstable in that they tend to spontaneously decompose giving off carbon dioxide and a corresponding ketone. The only β-ketocarboxylic acid that was reported in good detail in the literature was 3-oxobutanoic acid. Undoubtedly, many β-ketocarboxylic acids have been made but the preparation and physical properties are not reported in the literature.

The β-ketocarboxylic acids (3-oxobutanoic, 2-methyl-3-oxobutanoic, and 2,2-dimethylbutanoic acids) were so unstable that they would decompose even when cooled to -10°. These β-ketoacids were hard to purify and use because of the decomposition problem.

The β-ketocarboxylic acids were prepared by saponification of the corresponding esters with sodium hydroxide in an aqueous medium at low temperatures. The alkaline reaction mixtures were then extracted with several portions of ether in order to remove any unreacted ester or organic side products that were not soluble in water. The resulting alkaline reaction mixtures were then cooled to 0° and kept at that temperature while acidifying to pH 2 by addition of dil sulfuric acid. The acidified reaction mixtures were then extracted three to five times using 75 ml portions of ether. The ether extracts were combined and the ether-β-ketoacid solutions were dried using anhyd magnesium sulfate. The ether was flashed off at low temperatures leaving the β-ketoacids.

The highest yields of 3-oxobutanoic, 2-methyl-3-oxobutanoic, and 2,2-dimethyl-3-oxobutanoic acid were achieved when the saponification was run at room temperature and the reaction time was in the range of 12 hrs. The other β-ketoacids: 4-phenyl-3-oxobutanoic, 3-oxohexanoic, 4,4-dimethyl-3-oxopentanoic, and 3-(2-thienyl)-3-oxopropanoic acid were produced in high yields with a saponification reaction time of 2--3 hrs. The reaction temperature was 23°.

Electrolysis of β-Ketoacids

The general electrolysis procedure was as follows: A reaction vessel was mounted in a water bath used for cooling. A β-ketocarboxylic acid was placed in the reaction vessel containing sodium metal (2% of the β-ketoacid wt) dissolved in the reaction solvent (generally 40 ml of methanol). The reaction vessel was equipped with a magnetic stirrer which was used during the reaction. The cylindrical platinum electrodes were then positioned in the reaction mixture and a constant current was maintained throughout the reaction. The reaction was run at a temperature less than 50° and stopped when the pH of the electrolyte dropped to 8. The solvent was then evaporated, and the product was isolated and characterized. The γ-diketones synthesized by this method are listed in Table IX.

Attempted Preparation of 3,4-Dimethyl and 3,3,4,4-Tetramethyl-2,5-Hexanedione

The general electrolysis procedure was followed in the electrolysis of both 2-methyl and 2,2-dimethyl-3-oxobutanoic acid, but no product was isolated in either case. The failure of these two reactions was not unexpected since reviews (20, 23, 58, 67, 68) of the Kolbe electrolysis showed low yields (less than 5%) or no yields of Kolbe dimer produced when α-mono and α, α-dialkyl substituted acids were electrolyzed.

L. Ebersen (17, 20) has shown that the ionization potential of the intermediate radical R• is the dominant parameter in determining the ease of further oxidation of the radical. Radicals with high ionization potentials (i.e. >8 eV) are fairly resistant towards oxidation to carbonium ions; thus, the radical mechanism will be favored in these cases. The radicals with low ionization potentials (i.e.< 8 eV) are oxidized further and a carbonium mechanism is followed. The ionization potentials of a variety of radicals are listed in Table X.

TABLE X

IONIZATION POTENTIALS

Radical	Potential (eV)
Methyl	9.95
Ethyl	8.78
Propyl	8.33
Butyl	8.64

TABLE X--Continued

Radical	Potential (eV)
Isobutyl	8.35
$\cdot CH_2CN$	10.87
$Me_2\dot{C}CN$	9.15
Isopropyl	7.90
_t_-Butyl	7.42
Cyclobutyl	7.88
Cyclopentyl	7.80
Cyclohexyl	7.60
Benzyl	7.76
Benzhydryl	7.32

Ionization potentials for radicals of type $R_2\dot{C}COOEt$ (15) and $R_2\dot{C}CONH_2$ (16) are not known. However, the good to moderate yields of the Kolbe products is an indication that these radicals belong to the high ionization potential group.

The α-mono and α, α-dialkyl substituted β-ketocarboxylic acids when electrolyzed, produce radicals that are isopropyl and _t_-butyl radicals, respectively.

The structure and experimental data of the α-mono and α, α-dialkyl substituted β-ketocarboxylic acids indicated that the two radicals formed during electrolysis have low ionization potentials and are further oxidized to a carbonium ion which doesn't yield Kolbe products as experimentally reported.

The ionization potentials of α-keto radicals resulting from the spontaneous decarboxylation of β-ketocarboxylic acids have not been reported. It isn't possible to speculate if a radical or carbonium mechanism should have been followed.

2-Oxo-1,1-dimethylpropyl and 2-oxo-1-methylpropyl radicals have a carbonyl function α to the radical and experimentally haven't produced the desired Kolbe product. Even though there are structural differences between these α-keto and alkyl radicals, experimental results indicate that they are analogous in that no Kolbe dimer was synthesized in either case.

Attempted Preparation of 1,4-di(2-thienyl)-1,4-butanedione

Preparation of 1,4-di(2-thienyl)-1,4-butanedione using the general electrolysis procedure with methanol as the solvent failed because a non-conducting product or by-product formed was not soluble and deposited out on the anode stopping the reaction. The white film was thought to be a product that was insoluble in methanol. The former preparation of 1,4-diphenyl-1,4-butanedione from 4-phenyl-3-oxobutanoic acid was accomplished by using a solvent system of acetonitrile and methanol after giving evidence of failing for the same reasons as the thienyl analog when methanol only was used as the solvent. Since 3-(2-thienyl)-3-oxopropanoic acid is somewhat analogous to 4-phenyl-3-

oxobutanoic acid, the same solvent system of acetonitrile and methanol was used. This attempt failed like the first and for the same reason.

A third, fourth, and fifth electrolysis reaction was carried out using solvent systems of methanol-benzene, methanol-ethanol, and methanol-THF, respectively, but all three failed in the same way the first reaction failed.

All attempts to prepare 1,4-di(2-thienyl)-1,4-butanedione have failed. The reason for the failure was attributed to the insolubility of the product or by-products formed which deposited on the anode and in turn caused a current drop stopping the reaction.

Limitations of the Electrolysis of β-Ketoacids

The Kolbe electrolysis of β-ketoacids in the case where they are α-mono or α-dialkyl substituted do not yield the desired Kolbe products. However; since no other groups in the α position were studied, there is a theoretical possibility that other α-substituted β-ketoacids could yield Kolbe dimers upon electrolysis.

A second limitation was found to be the electrolysis of 3-(2-thienyl)-3-oxopropanoic acid which failed to yield the desired Kolbe product.

A third limitation is the availability of β-ketoesters that are needed to prepare β-ketoacids. The only two readily available β-ketoesters were ethyl acetoacetate and ethyl benzoylacetate.

A fourth limitation is the nature of β-ketoacids themselves in that they tend to decompose. The lower the atomic weight of a β-ketocarboxylic acid, the easier the β-ketoacid appears to decarboxylate.

V. SUMMARY

Electrolysis of β-ketocarboxylic acids.--The electrolysis of β-ketoacids yielding the desired γ-diketones was successful in four cases. The γ-diketones synthesized were: 2,5-hexanedione, 4,7-octanedione, 3,3,7,7-tetramethyl-2,5-hexanedione, and 1,4-diphenyl-1,4-butanedione. They were produced in good yields.

The electrolysis of β-ketoacids resulted in three failures; two of which were not unexpected. The two reaction failures for which more precedent exists were the electrolyses of 2-methyl and 2,2-dimethyl-3-oxobutanoic acid. The third reaction that failed was the electrolysis of 3-(2-thienyl)-3-oxopropanoic acid. The failure of the third reaction was attributed to the insolubility of the product or by-products which deposited on the anode and then caused a current drop to 0.0 amperes.

Literature cited.--The literature review covered the electrolysis of substituted and nonsubstituted carboxylic acids from 1958 through 1971.

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ELECTROLYTIC SYNTHESIS OF γ-DIKETONES

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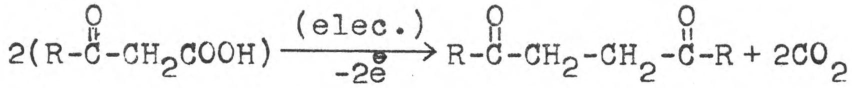
ABSTRACT

Four γ-diketones were synthesized by using a modification of the Kolbe electrolytic condensation of β-ketocarboxylic acids.



$$2(\mathrm{R}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{CH_2COOH}) \xrightarrow[-2e^{\ominus}]{\text{(elec.)}} \mathrm{R}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{CH_2}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{R} + 2\mathrm{CO_2}$$

The following γ-diketones were synthesized in moderate yields: 2,5-hexanedione, 4,7-decanedione, 2,2,7,7-tetramethyl-3,6-octanedione, and 1,4-diphenyl-1,4-butanedione (34, 39, 23, and 27, respectively). However, attempted preparation of the following γ-diketones failed: 3,4-dimethyl-2,5-hexanedione, 3,3,4,4-tetramethyl-2,5-hexanedione, and 1,4-di(2-thienyl)-1,4-butanedione.

Attempts to electrolytically condense α-alkyl and α, α-dialkyl substituted monocarboxylic acids have been reported and all attempts have ended in failure; similarly, the attempts to synthesize 3,4-dimethyl and 3,3,4,4-tetramethyl-2,5-hexanedione from 2-methyl and 2,2-dimethyl-3-oxobutanoic acid, respectively, failed.

The preparation of 1,4-di(2-thienyl)-1,4-butanedione failed because the product or side product was not soluble in the solvents tried and this resulted in precipitation of a non-conducting white product film on the electrodes, thus, preventing further electrolysis.