STUDIES OF THE CONDENSATION PRODUCTS OF
ETHYL 3-PHENYL-2,3-DIOXOPROPANOATE
WITH ACTIVE METHYLENE COMPOUNDS

by

FRANK ARCHER MOORE

B. S., Fort Hays Kansas State College, 1942

———

A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE
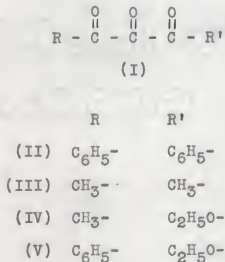
1952

TABLE OF CONTENTS

INTRODUCTION

The reactions of monofunctional organic compounds have been studied extensively, but much less is known about polyfunctional compounds. Knowledge is lacking particularly with regard to the interactions with and effects of neighboring groups upon the reactivity of a single group. This thesis reports the results obtained in a study of condensation reactions of a vicinal tricarbonyl compound (I), ethyl 3-phenyl-2,3-dioxopropanoate (V). This is a continuation of a program initiated several years ago, the objectives of which were to determine the effects of multiple contiguous functions upon certain reactions characteristic of the carbonyl group.

The first tricarbonyl compound (Table 1) was synthesized by de Neufville and von Peckmann (8) when they prepared 1,3-diphenylpropanetrione-1,2,3 (II) in 1891. Ten years later Sachs and Barschall (11) prepared pentanetrione-2,3,4 (III). The mixed ester-diketone type compound ethyl 2,3-dioxobutanoate (IV) was first prepared by Bouveault and Wahl (2), and Wahl (14) synthesized ethyl 3-phenyl-2,3-dioxopropanoate (V).

Tricarbonyl compounds can be prepared from β-keto-esters or β-diketones by direct oxidation with nitrogen oxides or selenium dioxide. Alternatively, β-diketone (or β-keto-ester) is monobrominated, converted to the acetoxy compound with potassium acetate and brominated again. The tricarbonyl compound
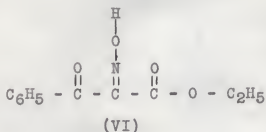
is produced by the elimination of a molecule of acetyl bromide from the acetoxy-bromo compound. The method of Bigelow and Hanslick (1) for the preparation of 1,3-diphenylpropanetrione-1,2,3 involves the treatment of dibenzoyldibromomethane with sodium acetate and hydrolysis of the intermediate compound to give the hydrate of diphenyl triketone. The hydrate of a desired tricarbonyl compound can be dehydrated by vacuum distillation.

Table 1. Representative tricarbonyl compounds.

$$R - \overset{\overset{\text{O}}{\|}}{\text{C}} - \overset{\overset{\text{O}}{\|}}{\text{C}} - \overset{\overset{\text{O}}{\|}}{\text{C}} - R'$$

(I)

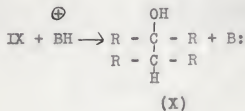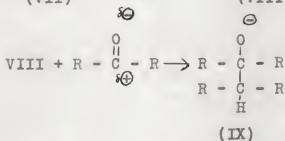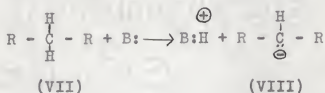|	R	R'
(II)	C_6H_5-	C_6H_5-
(III)	CH_3-	CH_3-
(IV)	CH_3-	C_2H_5O-
(V)	C_6H_5-	C_2H_5O-

Ethyl 3-phenyl-2,3-dioxopropanoate exhibits a general reaction of tricarbonyl compounds in that it forms colorless hydrates and alcoholates. The mono-oxime of this tricarbonyl compound is identical with ethyl iso-nitrosobenzoylacetate and

therefore the structure must be as represented by (VI).
These two reactions demonstrate a hyper-reactivity of the cen-
tral carbonyl group.

$$C_6H_5 - \overset{\overset{\textstyle O}{\|}}{C} - \overset{\overset{\textstyle H}{\underset{\textstyle |}{\overset{\textstyle |}{O}}}}{\underset{\textstyle |}{N}} - \overset{\overset{\textstyle O}{\|}}{C} - O - C_2H_5$$
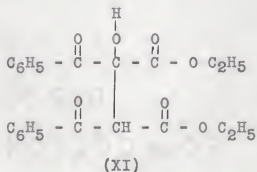
$$(VI)$$

The Knoevenagel reaction (a characteristic reaction of a
carbonyl group), is a base-catalyzed condensation and may be
classed along with other reactions of this type, such as the
aldol, Claisen, and Perkin condensations. The following
mechanism has been postulated for this reaction (15).

$$R - \overset{\overset{\textstyle H}{|}}{\underset{\textstyle |}{C}} - R + B: \longrightarrow B:H^{\oplus} + R - \overset{\overset{\textstyle H}{|}}{\underset{\textstyle \ominus}{C}} - R$$

$$(VII) \qquad\qquad (VIII)$$

$$VIII + R - \overset{\overset{\textstyle O}{\|}}{\underset{\textstyle \oplus}{C}} - R \longrightarrow \begin{matrix} R - \overset{\overset{\textstyle O}{\underset{\textstyle |}{\overset{\textstyle |}{\ominus}}}}{C} - R \\ R - \overset{}{\underset{\textstyle |}{\overset{\textstyle |}{C}}} - R \\ \overset{}{\underset{\textstyle H}{}} \end{matrix}$$

$$(IX)$$

$$IX + BH^{\oplus} \longrightarrow \begin{matrix} R - \overset{\overset{\textstyle OH}{|}}{\underset{\textstyle |}{C}} - R \\ R - \overset{}{\underset{\textstyle H}{\overset{\textstyle |}{C}}} - R \end{matrix} + B:$$

$$(X)$$

The initial step of the reaction is the removal of a proton by the base B: from the active methylene compound (VII) whereby the carbanion (VIII) is generated. This carbanion then attacks the electron deficient carbonyl carbon of the carbonyl compound to form the anion (IX) which in turn abstracts a proton from the conjugate acid of the base, BH^+, to regenerate the basic catalyst, B:, and form the condensation product. According to Remick (10), the following groups, represented above as R' and R", may activate the C-H link when attached directly to the carbon of the methylene group in VII: -NO, -NO$_2$, -CHO, -C(R)=O, -N=NR, -C≡N, -C=NR, -CH=CR$_2$. Of these -CH=CR$_2$ would be the weaker, and -NO and -NO$_2$ would be the stronger in the series.

In light of this mechanism it can be seen that condensations of this type with tricarbonyl compounds would involve reaction of the carbonyl carbon having the greatest electron deficiency with the nucleophilic particle from an active methylene compound. In a tricarbonyl compound, such as ethyl 3-phenyl-2,3-dioxopropanoate (V), it seems reasonable to assume that the electron density on carbons 1 and 3 would be increased by a tautomeric effect in which the benzene ring and the oxygen in the ethoxyl group, respectively, act as electron donors. One limiting structure would be represented by Va.

$$C_6H_5 - \overset{\overset{O}{\|}}{\underset{1}{C}} - \overset{\overset{O}{\|}}{\underset{2}{C}} - \overset{\overset{O}{\|}}{\underset{3}{C}} - O\ Et \longrightarrow C_6H_5 = \overset{\overset{\oplus}{\underset{1}{C}}}{\underset{1}{C}} - \overset{\overset{\ominus}{\overset{O}{|}}}{\underset{\underset{\oplus}{2}}{C}} - \overset{\overset{\ominus}{\overset{O}{|}}}{\underset{3}{C}} = O - Et$$

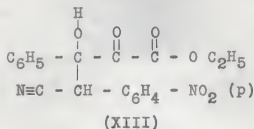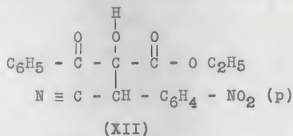(V)   (Va)

Carbons 1 and 3, therefore, would be less susceptible to attack by the carbanion which is produced from the active methylene compound, since the positivity of these carbons has been diminished by the adjacent electron-releasing groups. However, the medial carbon atom would still be an electrophilic center and therefore condensation should occur at this point, and may well occur more readily than with a simple carbonyl compound.

Wahl (14) reported that ethyl 3-phenyl-2,3-dioxopropanoate condensed with ethyl benzoylacetate in the presence of a small amount of piperidine. From this reaction he obtained a compound $C_{22}H_{22}O_7$ which he assumed to have the structure (XI) below.

$$
\begin{array}{c}
\overset{\displaystyle H}{\underset{\displaystyle |}{}} \\
C_6H_5 - \overset{\displaystyle O}{\overset{\displaystyle \|}{C}} - \overset{\displaystyle O}{\overset{\displaystyle |}{C}} - \overset{\displaystyle O}{\overset{\displaystyle \|}{C}} - O\, C_2H_5 \\
C_6H_5 - \overset{\displaystyle O}{\overset{\displaystyle \|}{C}} - CH - \overset{\displaystyle O}{\overset{\displaystyle \|}{C}} - O\, C_2H_5 \\
(XI)
\end{array}
$$

Hudson (6) successfully condensed ethyl 3-phenyl-2,3-dioxopropanoate with malonic acid by means of a Knoevenagel-Doebner type reaction and found that condensation occurred at the medial carbonyl group. Hudson also reported that ethyl 3-phenyl-2,3-dioxopropanoate condensed with p-nitro-phenylacetonitrile in the presence of piperidine. The struc-

ture of this condensation product was not definitely estab-
lished, but experimental evidence supports either (XII) or
(XIII) as possible structures for this condensation product.

$$C_6H_5 - \overset{\overset{\displaystyle O}{\|}}{C} - \overset{\overset{\displaystyle H}{|}}{\underset{\displaystyle |}{\overset{\displaystyle O}{C}}} - \overset{\overset{\displaystyle O}{\|}}{C} - O \; C_2H_5$$
$$N \equiv C - CH - C_6H_4 - NO_2 \; (p)$$

(XII)

$$C_6H_5 - \overset{\overset{\displaystyle H}{|}}{\underset{\displaystyle |}{\overset{\displaystyle O}{C}}} - \overset{\overset{\displaystyle O}{\|}}{C} - \overset{\overset{\displaystyle O}{\|}}{C} - O \; C_2H_5$$
$$N \equiv C - CH - C_6H_4 - NO_2 \; (p)$$

(XIII)

As there were no references in the literature to conden-
sations of ethyl 3-phenyl-2,3-dioxopropanoate with active
methylene compounds other than the three described above, it
seemed desirable to investigate condensations with other
active methylene compounds and attempt to determine the points
of linkage between the addenda. Data of this nature may aid
in an understanding of the electronic nature of this inter-
esting type of compound.

EXPERIMENTAL

Materials Used

The following is a list of the chemicals which were used
during this study for the preparation of the condensation

products: ethyl benzoylacetate (Eastman 2731); nitrogen
dioxide (Matheson Co.); bromine (General Chemical Co. 1473);
potassium acetate (General Chemical Co. 2081); p-nitrophenyl-
acetonitrile (Eastman 1115); pyridine (General Chemical Co.
2165); piperidine (Eastman P687); acetylacetone (Eastman 1088);
ethyl cyanoacetate (Matheson 3011); ethyl acetoacetate (East-
man 111); ethyl malonate (Eastman 121); cyanoacetic acid
(Eastman 3354); and dibenzoylmethane (laboratory preparation).
Acetylacetone, ethyl acetoacetate, ethyl cyanoacetate and ethyl
malonate were all redistilled. Part of the ethyl benzoylacetate
used in synthesis of ethyl 3-phenyl-2,3-dioxopropanoate was re-
fractionated at reduced pressure. Pyridine and piperidine were
dried over potassium hydroxide and distilled before use. Cyano-
acetic acid and dibenzoylmethane were purified by recrystalli-
zation.

Equipment

Special equipment used in this study was an active hydro-
gen analytical apparatus fabricated according to the diagram
given by Siggia (13) and modified for use in quantitative de-
carboxylation determinations, a Beckmann pH Meter, a Fisher
Densitometer, a Fisher-Johns melting point apparatus and a
one-liter three-neck flask with a sintered glass disc and gas
inlet sealed in the bottom.

Preparation of Ethyl 3-Phenyl-2,3-dioxopropanoate

A total of 169 gms of ethyl 3-phenyl-2,3-dioxopropanoate
was prepared. Two different methods were used in the prepara-
tion of this tricarbonyl compound.

Direct Oxidation of Ethyl Benzoylacetate. The first
method employed involved the direct oxidation of ethyl benzoyl-
acetate by nitrogen dioxide as employed by Hudson (6). Liquid
nitrogen dioxide was obtained by passing nitrogen dioxide vapors
from a high pressure cylinder through a low temperature con-
denser cooled by an ice-salt bath. The condensed nitrogen
dioxide was collected in a 250-ml two-neck flask. An ice-salt
bath also was maintained around the flask.

Ethyl benzoylacetate (100 gms, 0.52 mole), acetic anhy-
dride (30 gms) and anhydrous ether (200 ml) were placed in a
one-liter three-neck flask in the bottom of which was a
sintered glass disc and gas inlet. The flask was fitted with
a mechanical stirrer, a thermometer, and a water condenser
equipped with a drying tube filled with 'Drierite', and con-
nected in turn to a gas washer. The flask was cooled by
immersion in an ice-water bath or an ice-salt mixture.

The vapors of nitrogen dioxide (92 gms, 2.0 moles) were
carried into the reaction mixture by passing dried air through
the flask containing the liquid nitrogen dioxide, then through
a sight flask and finally into the reaction flask through the
gas inlet. In two of the eight experiments which were per-

formed using this method, dried nitrogen gas instead of air was used to force the nitrogen dioxide vapors into the reaction mixture. The addition of nitrogen dioxide was regulated so that nearly all of the vapors were absorbed by the reaction mixture. The temperature of the reaction mixture was maintained below 8° C. during the addition of nitrogen dioxide. The ice bath and flask were allowed to warm slowly and to stand overnight at room temperature.

The ethereal solution was transferred to a separatory funnel and washed with ten 50-ml portions of a one-to-one mixture of 20 percent potassium carbonate-saturated sodium chloride solution and then ten 50-ml portions of saturated sodium chloride. The ether and remaining water were removed by evaporation on the steam cone at reduced pressure. The residue was distilled at reduced pressure and a crude fraction was collected having a b.p. 95-205° C.

The crude fractions from eight preparations totaled only 120 gms and represented a 14 percent yield of crude tricarbonyl compound.

Indirect Oxidation of Ethyl Benzoylacetate. In the second method employed for the preparation of ethyl 3-phenyl-2,3-dioxopropanoate, ethyl benzoylacetate was brominated and the resulting dibromo compound was then treated with potassium acetate to obtain the desired tricarbonyl compound. This method is a modified Organic Synthesis preparation (1) as employed by Sharp (12) for the preparation of this compound.

A. Preparation of Ethyl Benzoyldibromoacetate. Ethyl benzoylacetate (96 gms, 0.5 mole) was placed in a two-liter three-neck flask fitted with a stirrer, dropping funnel, and thermometer. The flask was cooled in an ice-bath and bromine (176 gms, 1.1 moles) in chloroform (460 ml) was added by means of the dropping funnel. The hydrogen bromide formed was removed by passing dried air into the flask and out through a drying tube filled with 'Drierite' and thence into a gas washer. Addition of the bromine-chloroform solution required one and a quarter hours during which time the temperature of the reaction mixture was maintained below 15° C. The stirrer remained on and the flow of air was continued for four hours after the addition of bromine was complete. The reaction mixture was allowed to stand overnight after which time the chloroform and excess bromine were removed by evaporation at reduced pressures.

The residual liquid was distilled at 0.4-0.5 mm pressure. A small amount of solid (probably benzoic acid) solidified in the side arm at the start of the distillation. A slight amount of solid carbonaceous residue remained at the end of the distillation. The crude ethyl benzoyldibromoacetate was redistilled and the fraction which distilled at $132-141^\circ$ C. at 0.35-0.60 mm was collected. The refractive index for this compound was n^{21} D 1.5710. Howk and McElvain (4) reported the following physical constants for this compound: b.p. (1 mm) $153-4^\circ$ C; n^{20} D 1.5703. A yield of 149.2 gms was obtained which

represented 85.4 percent of the theoretical yield.

B. Preparation of Ethyl 3-Phenyl-2,3-dioxopropanoate
from Ethyl Benzoyldibromoacetate. Ethyl benzoyldibromoacetate
(149.2 gms, 0.426 mole), which had been obtained in the prepar-
ation described above, was added to a solution of freshly-fused
potassium acetate (88 gms, 0.90 mole) in glacial acetic acid
(250 ml). The mixture was heated on a steam bath overnight.
The precipitated potassium bromide (50 gms, 49 percent of the
theoretical yield) was removed by filtration. The mixture was
then refluxed for one and one-half hours and the additional
potassium bromide which had precipitated was removed. A total
of 82 gms (80 percent of the theoretical yield) of potassium
bromide was obtained.

The acetic acid solvent was removed at reduced pressure
by heating on the steam bath. The residual liquid was dissolved
in 200 ml of ether and washed with five 50-ml portions of sat-
urated sodium chloride. This was followed by washing with
eight 50-ml portions of a one-to-one mixture of 20 percent
potassium carbonate and saturated sodium chloride solution.
Finally the solution was washed with ten 50-ml portions of
saturated sodium chloride and dried overnight over anhydrous
sodium sulfate.

The ether solvent was removed by evaporation on the steam
cone at reduced pressure. Crude ethyl 3-phenyl-2,3-dioxopropa-
noate then was distilled under reduced pressure. The fraction
distilling at 127-190° C. was collected as crude tricarbonyl

compound. Most of the material distilled over at 190° C. A
yield of 50.5 gms of crude ethyl 3-phenyl-2,3-dioxopropanoate
was obtained, which represented 49 percent of the theoretical
yield from ethyl benzoylacetate. This liquid had a red color,
possibly due to the presence of free bromine, and it had a
sharp odor which may have indicated the presence of acetyl
bromide. The vapor above the liquid fumed in moist air indi-
cating that some hydrogen bromide remained in the liquid.

In the second preparation of ethyl 3-phenyl-2,3-dioxopropa-
noate by this method, ethyl benzoylacetate (192 gms, 1.0 mole)
was converted to 120 gms of crude ethyl 3-phenyl-2,3-dioxopro-
panoate with a b.p. 90-190° C. at approximately 75 mm. This
represented an overall yield of 58 percent of the theoretical.

The combined crude tricarbonyl compound from both methods
of preparation was fractionated through a four-foot fraction-
ating column packed with glass helices. A total of 288 gms
was charged to the still and the fraction distilling between
102° C. at 0.7 mm and 115° C. at 2.1 mm was collected as pure
ethyl 3-phenyl-2,3-dioxopropanoate. This material had the fol-
lowing physical constants: refractive index n^{20} D 1.5188 and
density D 26.5°/4° 1.155. Values listed in the literature for
these constants were: b.p. 150-153° C. at 13 mm (15), n^{20} D
1.5191 (12), and density D 20°/4° 1.188 (14). A total of
104.6 gms of this material was obtained.

In a later preparation, ethyl benzoylacetate (192 gms, 1
mole) was employed for the preparation of 101.8 gms (49.3 per-

cent of the theoretical yield) of crude ethyl 3-phenyl-2,3-
dioxopropanoate via ethyl benzoyldibromacetate. This crude
tricarbonyl compound was combined with 23.2 gms of material
prepared previously, and the mixture was fractionated through
a two-foot packed column. A total of 64.4 gms with a b.p.
98-102° C. at 0.55 mm was collected. This material had a
refractive index n^{20} D 1.5181.

<div align="center">

Condensation Reactions of
Ethyl 3-Phenyl-2,3-dioxopropanoate

</div>

All condensations attempted in this study were of the
Knoevenagel (7) (piperidine catalyst) or Doebner (3) (pyridine-
piperidine mixed catalyst-solvent) type.

Condensations of Ethyl 3-Phenyl-2,3-dioxopropanoate with
p-Nitrophenylacetonitrile. A. Doebner Conditions. Attempts
to condense ethyl 3-phenyl-2,3-dioxopropanoate with p-nitro-
phenylacetonitrile by means of the Doebner type reaction were
carried out as follows. Ethyl 3-phenyl-2,3-dioxopropanoate
(3.00 gms, 0.0145 mole) and p-nitrophenylacetonitrile (2.34 gms,
0.0145 mole) were dissolved in pyridine (4.39 gms). A small
quantity of piperidine was added and the mixture was heated on
the water bath or allowed to stand for a period of time. The
reaction mixture was poured into a beaker containing crushed
ice (60 gms) and concentrated hydrochloric acid (20 ml). The
acid solution was stirred mechanically until the ice melted,

and then was extracted with ether or benzene. The solvent
was removed and the residue was recrystallized from benzene
solution. The crystalline material which was obtained under
these conditions could not be purified sufficiently for the
purpose of this study. Table 2 summarizes these unsuccessful
attempts.

Table 2. A summary of attempted condensation reactions in-
volving ethyl 3-phenyl-2,3-dioxopropanoate and
p-nitrophenylacetonitrile in pyridine solution.

Tricarbonyl compd. (gms)	p-Nitro-phenyl-aceto-nitrile (gms)	Piper-idine (gms)	Time of reac-tion (hrs)	Approx-imate tem-perature reaction* ($^\circ$C.)	Extrac-tion sol-vent	Melting point** ($^\circ$C.)	Yield** per-cent
3.00	2.34	0.17	3	100	benzene	171-7	5.6
3.00	2.34	0.10	3	100	ether	–	none
3.00	2.34	0.10	3	100	ether	158-60	12.3
3.00	2.34	0.10	96	25	ether	138-40	13.7
3.00	2.34	2 drops	24	25	***	157-60	26.9
3.00	2.34	3 drops	48	100	benzene	149-54#	20.4

* Reaction at 100° for 5 minutes; at 25° for 48 hours.

** Melting points and yields listed are for the product ob-
tained upon two recrystallizations from benzene.

*** In this experiment the precipitated solids were filtered
off upon addition of ether and this solid material was
recrystallized twice from benzene.

\# In this experiment the yield and melting point are for the
product obtained by one recrystallization from methyl
alcohol.

B. Knoevenagel Conditions. Condensations of the tri-
carbonyl compound with p-nitrophenylacetonitrile were carried
out under Knoevenagel conditions, that is, without the pyri-
dine solvent. The best yield was obtained by carrying the
condensation out as follows. Ethyl 3-phenyl-2,3-dioxopro-
panoate (6.00 gms, 0.0290 mole) and p-nitrophenylacetonitrile
(4.68 gms, 0.0290 mole) were weighed into a 50-ml Erlenmeyer
flask. Ten drops of piperidine were added and the mixture was
agitated after the addition of each drop. The mixture was
warmed for a few seconds on the steam bath, removed and agitated
until it became homogeneous. At this point the mixture turned
a green color and an exothermic reaction occurred. Some of the
heat evolved in the reaction was removed by cooling the flask
under a stream of tap water. The reaction mixture solidified
upon cooling. After standing for two hours the green amorphous
solid was dissolved in several portions of hot benzene.

Excess benzene was then evaporated by passing a stream of
air through a filter flask containing the benzene solution.
The crystalline condensation product was filtered off and
washed with a small amount of benzene. A yield of 7.0 gms
(65 percent of the theoretical) of light green-tinted crystals
possessing a melting point of 169-174° C. was obtained. This
product was recrystallized from benzene and white crystals
were deposited which melted at 177.5-179.0° C. A total of
4.79 gms (44.8 percent yield) of this product was obtained.
Hudson (6) reported a melting point of 179-180° C. for this
compound.

Table 3. A summary of attempted condensation reactions in-
         volving ethyl 3-phenyl-2,3-dioxopropanoate and
         p-nitrophenylacetonitrile in a Knoevenagel type
         condensation.

Tricar- bonyl compd. (gms)	p-Nitro- phenyl- aceto- nitrile (gms)	Piper- idine (drops)	Agitation during heat- ing	Exter- nal cool- ing	Melting point of product (° C.)	Yield per cent
3.00	2.34	5	no	no	178.5-179.0	26.6
3.00	2.34	5*	no	no	178-180	25.8
6.00	4.68	10	yes	yes	177-179	33.5
6.00	4.68	10	yes	yes	177.5-179	37.0
6.00	4.68	10	yes**	yes	177.5-179	44.8

* Piperidine was added after reactants had been heated on
   steam bath.

** Mixture was heated on steam cone for approximately 5
    seconds and then agitated until homogeneous.

Attempted Condensations of Ethyl 3-Phenyl-2,3-dioxopro-
panoate with Cyanoacetic Acid. Attempted condensations of
cyanoacetic acid with ethyl 3-phenyl-2,3-dioxopropanoate were
carried out in the presence of pyridine-piperidine and piper-
idine alone. In each case in which pyridine was used as a
solvent, a yellow or red gummy solid was formed upon addition
of the reaction mixture to the hydrochloric acid-ice mixture.
Upon warming to room temperature the solid melted and attempts
to recrystallize this solid following its extraction by ether
failed. Table 4 summarizes the unsuccessful condensations
with cyanoacetic acid.

Table 4. A summary of attempted condensation reactions of
          ethyl 3-phenyl-2,3-dioxopropanoate with cyano-
          acetic acid.

Tricar-bonyl compd. (gms)	Cyano-acetic acid (gms)	Pyri-dine (gms)	Piper-idine (gm)	Time on steam cone (min.)	Time at room temper-ature	Gas evolved	Solid product (gms)
3.00	1.25	0.00	0.14	15	–	yes	0.0
3.00	1.25	4.39	0.10	5	48 hrs.	yes	0.0
3.00	1.25	0.00	0.08	0	5 days	no	0.0
3.00	1.25	4.39	0.10	2	24 hrs.	yes	0.0
3.00	1.25	4.39	0.10	0	40 min.	no	0.15 acid m.p. 115-124

In one additional reaction ethyl 3-phenyl-2,3-dioxopro-
panoate (3.00 gms, 0.0145 mole) was dissolved in pyridine
(5.1 ml) and cooled in an ice bath. Piperidine (2.2 ml) was
poured onto cyanoacetic acid (1.25 ml, 0.0145 mole) in a 25-ml
flask. A violent reaction occurred and the contents of the
flask turned a red color. The flask containing this mixture
was also cooled in an ice bath. After both flasks were cooled
for 15 minutes, the tricarbonyl-pyridine solution was poured
into the flask containing the piperidine-cyanoacetic acid mix-
ture and the combined reactants were allowed to stand at room
temperature for one hour. In this experiment reaction was
stopped, as before, by pouring the mixture into a beaker con-
taining ice (60 gms) and concentrated hydrochloric acid (20 ml).

The yellow gummy solid noted before appeared again in this
reaction. This solid was dissolved in ethyl acetate (25 ml)
and extracted with the hydrochloric acid solution. The hydro-
chloric acid solution was then extracted with two 25-ml por-
tions of ethyl acetate. The combined ethyl acetate solutions
were then extracted with four 20-ml portions of five percent
potassium carbonate solution. The combined aqueous basic ex-
tracts were then acidified and extracted with two 25-ml por-
tions of ethyl acetate. Excess ethyl acetate was evaporated
and the solid acid allowed to crystallize out. A yield of
0.23 gm of acid which melted up to 123° C. was obtained. This
acid was recrystallized from methyl alcohol to obtain a solid
with a melting point of 123-124° C. A mixed melting point
with this substance and authentic benzoic acid was found to
be 123-124° C.

   Condensation of Ethyl 3-Phenyl-2,3-dioxopropanoate with
Acetylacetone. A typical condensation between ethyl 3-phenyl-
2,3-dioxopropanoate and acetylacetone was carried out as fol-
lows. Ethyl 3-phenyl-2,3-dioxopropanoate (6.00 gms, 0.0290
mole) and acetylacetone (2.90 gms, 0.290 mole) were weighed
into a 25 ml Erlenmeyer flask. Five drops of piperidine were
added. With the addition of the first two drops of piperidine
considerable heat was evolved. The mixture became viscous and
gas bubbles appeared as it was allowed to cool. Crystalliza-
tion was induced by scratching the side of the flask with a
glass rod whereby the entire contents of the flask crystallized.

The solid was removed and washed with ether to give a cream colored solid (8.24 gms) which had a melting point of 94-100° C. This amount represented a theoretical yield of 92.5 percent based upon the calculated molecular weight of 306 for the product (one-to-one addition). This solid was recrystallized twice from ether to yield white crystals which melted with apparent decomposition at 108-117°. A total of 3.29 gms (32.6 percent of theoretical) of this material was obtained.

    Attempted Condensation of Ethyl 3-Phenyl-2,3-dioxopropanoate with Dibenzoylmethane. Condensations of this active methylene compound with ethyl 3-phenyl-2,3-dioxopropanoate were of the Knoevenagel type and were carried out as follows. Ethyl 3-phenyl-2,3-dioxopropanoate (3.00 gms, 0.0145 mole) and dibenzoylmethane (3.25 gms, 0.0145 mole) were weighed into a 25-ml Erlenmeyer flask and five drops of piperidine were added. There was no heat evolved and color of the mixture did not change with the addition of piperidine. The reaction mixture was heated for 45 minutes on a steam cone during which time the mixture turned slightly darker. Upon cooling, a solid substance settled from the mixture. This solid was not isolated as no solvent could be found which would selectively dissolve the sticky impurity which was present, without also dissolving the solid.

    Attempted Condensation of Ethyl 3-Phenyl-2,3-dioxopropanoate with Ethyl Acetoacetate. Condensation reactions of ethyl 3-phenyl-2,3-dioxopropanoate with ethyl acetoacetate were also

carried out using the Knoevenagel type reaction. In a typical
condensation ethyl 3-phenyl-2,3-dioxopropanoate (3.00 gms,
0.0145 mole) and ethyl acetoacetate (1.89 gms, 0.0145 mole)
were placed in a 25-ml Erlenmeyer flask, and five drops of
piperidine were added. With the addition of piperidine con-
siderable heat was evolved and the color of the mixture faded.
The mixture was then heated for 15 minutes on the steam cone
during which time it darkened slightly. The contents of the
flask became viscous upon cooling, however, attempts to induce
crystallization of the reaction mixture or to obtain solid
material from benzene solution failed. After standing for a
week no crystals had appeared.

Attempted Condensations of Ethyl 3-Phenyl-2,3-dioxopro-
panoate with Ethyl Cyanoacetate. Results of this condensation
were much the same as those obtained with ethyl acetoacetate.
In this condensation ethyl 3-phenyl-2,3-dioxopropanoate (3.00
gms, 0.0145 mole) was mixed with ethyl cyanoacetate (1.64 gms,
0.0145 mole) and five drops of piperidine were added. Consid-
erable heat was evolved and the mixture turned a red color.
The mixture became viscous, however, attempts to induce crystal-
lization from the reaction mixture or obtain solid material
from benzene solution were unsuccessful.

Condensation of Ethyl 3-Phenyl-2,3-dioxopropanoate with
Ethyl Benzoylacetate. The Knoevenagel type condensation was
employed in the reaction between ethyl 3-phenyl-2,3-dioxopro-
panoate and ethyl benzoylacetate. In this reaction ethyl

3-phenyl-2,3-dioxopropanoate (3.00 gms, 0.0145 mole) and ethyl
benzoylacetate (2.78 gms, 0.0145 mole) were weighed into a
25-ml Erlenmeyer flask. Ten drops of piperidine were added
and a fading of the color of the mixture along with the evolu-
tion of some heat was observed. The mixture was heated for
one hour on the steam cone. During this time the solution
darkened slightly. After the mixture had cooled, crystalliza-
tion was induced by scratching the walls of the flask with a
glass rod. Upon stirring, the mixture solidified forming a
sticky substance which hardened upon standing. The crude con-
densation product was washed with ether and a yield of 4.03 gms
(69.7 percent of the theoretical yield) of white solid was ob-
tained with a melting point of 95-102° C. The product was re-
crystallized twice from ether and gave white needles which
melted at 103.5-105.0° C. A mixed melting point with benzoic
acid was 90-101° C. The yield was 0.78 gm (13.5 percent of the
theoretical yield). Wahl (14) reported a melting point of
109-110° C. for this condensation product.

   Attempted Condensation of Ethyl 3-Phenyl-2,3-dioxopro-
panoate with Ethyl Malonate. In this attempted condensation
ethyl 3-phenyl-2,3-dioxopropanoate (3.00 gms, 0.0145 mole) was
weighed into a flask and ethyl malonate (2.32 gms, 0.0145 mole)
was added. No heat was evolved upon addition of piperidine
(five drops). The color of the solution did not change even
after heating the mixture for one hour on the steam cone. After
standing overnight a few needles had separated from the solu-
tion. The solid was collected on a filter and washed with

ether and the melting point was found to be 232-235° C. This
compound gave a positive nitrogen test upon sodium fusion.

Attempted Structure Proofs of the
Condensation Products

Saponification of p-Nitrophenylacetonitrile Condensation
Product. A total of 4.79 gms of p-nitrophenylacetonitrile
condensation product was saponified by refluxing for three hours
in an excess of approximately 0.5 N sodium hydroxide. At the
end of this time the solution was acidified to a pH of 2 with
3 N hydrochloric acid. This solution was then extracted with
ether and the excess ether was evaporated. The residue from
evaporation of the ether was dissolved in five percent po-
tassium carbonate solution and this was acidified with 3 N
hydrochloric acid. The precipitated acid was filtered off
and dried on a porous plate. A yield of 1.82 gms was obtained.
This acid melted at 221-4° C. with the evolution of a gas.
Hudson (6) reported a melting point of 233-235° C. for this
compound.

The p-nitrophenylacetonitrile condensation product was
also saponified in potassium hydroxide-diethylene glycol
solution. The diethylene glycol solution of potassium hydroxide
was prepared according to Redemann and Lucas (9). Two grams of
condensation product was saponified in 15 ml of this solution
by maintaining the solution at 160° C. for two and one-half

hours. A yield of 0.74 gm of dark yellow acid was obtained. This acid melted with the evolution of a gas at 230-233° C.

Saponification of the p-nitrophenylacetonitrile condensation product also was carried out at room temperature. A portion (2.36 gms) of the product was saponified in a large excess of approximately 0.1 N sodium hydroxide. After standing four days the mixture was acidified to a pH of 7 and extracted with ether. Evaporation of the ether layer yielded only a trace of acidic material. The aqueous solution was acidified further to pH 2 and again extracted with ether. Evaporation of the ether yielded a solid which was dissolved in five percent sodium carbonate solution and acidified. A yellow brown solid with melting point 175-181° C. was obtained in a yield of 1.09 gms. Recrystallization was attempted, however, the material separated as an oil from all of the solvents tried. A small amount of residue from these crystallization attempts was dissolved in five percent sodium carbonate solution and acidified. The solid acid obtained melted at 212-220° C. and a mixed melting point with the acid described above (m.p. 221-4°) was 200-221°.

Quantitative Decarboxylation of the Saponified p-Nitrophenylacetonitrile Condensation Product. A quantitative determination of carboxyl groups present in the dicarboxylic acid obtained in saponification of the condensation product was attempted using the decarboxylation method employed by Hubacher (5).

In this experiment an active hydrogen analytical apparatus as described by Siggia (13) was modified for use in the quantitative decarboxylation. A condenser and a small flask fitted with a ground glass joint and side arm were substituted in place of the reaction flask used in the active hydrogen determination. The side arm of the flask contained a ground glass joint into which was fitted a male joint equipped with a deflagrating spoon.

In making a determination, about 0.15 gm of acid was weighed into the flask and this was dissolved in five ml of redistilled quinoline. The flask was put into place and heated by means of a sand bath up to the initial temperature. Copper carbonate was weighed into the deflagrating spoon and the spoon was placed in the flask. The leveling bulb was adjusted to bring the mercury in the burette to the zero ml mark and the stopcock on top of the burette was turned to isolate the system. The deflagrating spoon was then turned over allowing the copper carbonate catalyst to fall into the reaction mixture. The leveling bulb was regulated to prevent the differential pressure from becoming too great. The bath temperature was raised to the reaction temperature and was maintained as long as any gas was being evolved. At the end of the reaction the bath temperature was allowed to drop to the initial temperature. At this point the final burette reading was made. The volume of gas evolved was corrected to 0° C. and 760 mm. A blank determination was made on the cupric carbonate catalyst,

and it was found that 60.9 percent of the carbon dioxide in
cupric carbonate was evolved. This factor was used in cal-
culation.

Table 5. Results of quantitative decarboxylation experiments.

Acid (gms)	Basic copper carbonate (gms)	Initial temper-ature ($^\circ$ C.)	Reaction temperature ($^\circ$ C.)	COOH per mole
0.1444	0.0480	285	285	0.525
0.1509	0.0316	305	335	0.552
0.1562	0.0868 (two portions)	118	320-350	1.02
0.1907	Cu° instead of $CuCO_3$	100	310	0.555

The reaction mixtures from three quantitative decarboxyla-
tion determinations were combined and dissolved in approximate-
ly 75 ml of ether. The ethereal solution was washed with five
15-ml portions of 3 N hydrochloric acid and then with two 10-ml
portions of five percent sodium carbonate solution. With the
first three washes, the contents of the separatory funnel was
filtered to remove the precipitated black solid. Ether was
evaporated from the neutral fraction and the red solid remain-
ing was recrystallized from ethyl alcohol. A small quantity
of red brown material with a melting point of 124-133° C. was
obtained. There was not a sufficient quantity of this material
for another recrystallization. Only a trace of acid material

was obtained from the sodium carbonate wash.

Carbon-Hydrogen Analysis of Acetylacetone Condensation
Product. The following values were obtained from carbon-hydro-
gen combustion microanalysis of the acetylacetone condensation
product. Calculated values for the compound $C_{16}H_{18}O_6$ which
would be formed by condensation of one mole of acetylacetone
with one mole tricarbonyl compound are carbon 62.75 percent
and hydrogen 5.92 percent. Analysis showed 62.54 and 62.41
percent carbon, and 6.08 and 6.01 percent hydrogen.

Saponification Equivalent of Acetylacetone Condensation
Product. Acetylacetone condensation product (0.2196 gm) was
saponified by refluxing for two hours in 25 ml of 0.2706 N
alcoholic sodium hydroxide. A total of 42.36 ml of 0.1096 N
sulfuric acid was required to neutralize the excess sodium
hydroxide.

$$\text{Sap. Eq.} = \frac{0.2196 \times 1000}{(25.00 \times 0.2706) - (42.36 \times 0.1096)} = 103.4$$

A second sample (0.0886 gm) was saponified by refluxing
for two hours in 25 ml of 0.3229 N alcoholic sodium hydroxide.
A total of 65.80 ml of 0.1096 N sulfuric acid was required to
reach the end point.

$$\text{Sap. Eq.} = \frac{0.0886 \times 1000}{(25.00 \times 0.3229) - (65.80 \times 0.1096)} = 104.0$$

Calculated for $C_{16}H_{18}O_6$ (tribasic) 102.

Carbonyl Group Determination of the Acetylacetone Conden-
sation Product. A carbonyl determination was made on the
acetylacetone condensation product by the method described by
Siggia (13). The condensation product (0.5481 gm) was weighed
into a 250 ml Erlenmeyer flask and 30 ml of hydroxylamine hydro-
chloride in ethanol and 100 ml of bromphenol blue indicator in
pyridine-alcohol solution were added. The solution was heated
three hours and allowed to cool to room temperature. The mix-
ture required 2.51 ml of 0.6750 N alcoholic sodium hydroxide
to reach the end point. The carbonyl group was calculated as
the percent of the sample that contained one carbonyl group.

$$\frac{2.51 \times 0.6750 \times 306.3 \times 100}{0.5481 \times 1000} = 94.3 \text{ percent carbonyl}$$

Calculated as a "carbonyl equivalent" these data show the
equivalent weight to be 324.

$$\frac{0.5481 \times 1000}{2.51 \times 0.6750} = 324$$

Carbon Hydrogen Analysis of Ethyl Benzoylacetate Product.
The following results were obtained from a carbon hydrogen
analysis of this condensation product. Calculated values for
the compound $C_{22}H_{22}O_7$ (one-to-one addition) were carbon 66.32
percent and hydrogen 5.57 percent. Analysis showed 66.80 and
67.02 percent carbon and 5.50 and 5.25 percent hydrogen.

Saponification Equivalents of Ethyl Benzoylacetate Product.
Three different saponification equivalents were determined. In
one of these, condensation product (0.1154 gm) was dissolved

in 25 ml of 0.0996 N base and saponified by standing at room
temperature 18 hours. Back titration required 14.12 ml of
0.1096 N sulfuric acid. Saponification equivalent was 122.5.
In two other determinations in which the condensation product
was refluxed in 0.0996 N sodium hydroxide, saponification
equivalents were found to be 123.4 and 121.6. These and addi-
tional values are summarized in Table 6.

Table 6. Saponification equivalent of ethyl benzoylacetate
condensation product.

Condensation product (gms)	Vol. NaOH 0.0996 N (ml)	Vol. H_2SO_4 0.1096 N (ml)	Reflux time (hrs)	Reaction: at room temp. (hrs)	Saponification equivalent
0.1154	25.00	14.12	0	18	122.5
0.1926	27.07	10.54	2	-	123.4
0.1254	25.00	13.31	2	-	121.6
0.2701	*	41.80	1 2/3	-	122.1
0.1251**	*	52.63	2	-	125.5
0.1614**	***	50.40	1 1/2	-	128.1

* Saponified in 25 ml of 0.2706 N alcoholic sodium hydroxide.

** Condensation product dried for 48 hours in vacuum desiccator.

*** Saponified in 25 ml of 0.2706 N alcoholic sodium hydroxide.
    Back titration required 0.19 ml of 0.0996 N sodium
    hydroxide.

Sample Calculations

General Formulas used in calculations of the results are given below with the calculations to which they apply.

Saponification Equivalent:

Sap. Eq. = $(A \times 1000) / (B \times C) - (D \times E)$

where   A = weight of sample in grams

         B = volume in milliliters of standard base used

         C = normality of base

         D = volume in milliliters of standard acid used

         E = normality of standard acid

Quantitative Decarboxylation:

$$F = A \times \frac{D}{760} \times \frac{273}{E}$$

A = B - C volume of carbon dioxide (ml)

B = final burette reading (ml)

C = initial burette reading (ml)

D - barometer reading, millimeters of mercury

E = temperature of gas (degrees Absolute)

F = volume of carbon dioxide (corrected) (ml)

$$\frac{\dfrac{F \times 1000}{22,400}}{\dfrac{H}{359}} = \frac{G \times 0.609 \times 1000}{221} = COOH \text{ groups/mole}$$

G = weight of cupric carbonate catalyst in grams

0.609 = fraction of cupric carbonate decomposing to give carbon dioxide

221 = equivalent weight of cupric carbonate

H = weight of acid sample in grams

359 = molecular weight of sample

Carbonyl Group Determination:

$$\frac{A \times B \times C \times 100}{D \times 1000} = \text{percent carbonyl compound}$$

$$\frac{D \times 1000}{A \times B} = \text{"carbonyl equivalent"}$$

A = volume of milliliters of standard base used

B = normality of base

C = molecular weight of compound
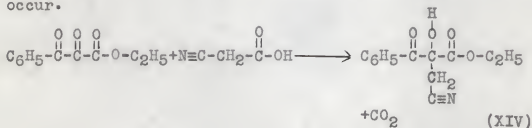
D = weight of sample in grams

DISCUSSION AND CONCLUSION

Preparation of ethyl 3-phenyl-2,3-dioxopropanoate by means of direct oxidation of ethyl benzoylacetate by nitrogen dioxide proved unsatisfactory in that large quantities of benzoic acid were obtained along with only a small amount of the desired compound.

Preparation of ethyl benzoyldibromoacetate followed by treatment of this compound with potassium acetate and hydrolysis of the resulting diacetoxy derivative to give the desired tricarbonyl hydrate proved to be a more practical method for the preparation of ethyl 3-phenyl-2,3-dioxopropanoate.

In the condensation reaction between ethyl 3-phenyl-2,3-

dioxopropanoate and p-nitrophenylacetonitrile only enough heat
to initiate the reaction was required; upon additional heating
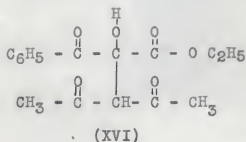the yield of the desired compound decreased.

Cyanoacetic acid appeared to condense with ethyl 3-phenyl-
2,3-dioxopropanoate since a colored solid precipitated upon
addition of the reaction mixture to a hydrochloric acid-ice
mixture. Also in instances where the reaction mixture was heated
a gas was evolved. Hudson (6) observed the evolution of carbon
dioxide in condensations of malonic acid with ethyl 3-phenyl-
2,3-dioxopropanoate. Although cyanoacetic acid itself could
decompose to liberate carbon dioxide this appears unlikely
since the decomposition temperature of the pure acid is 160° C.
If condensation of ethyl 3-phenyl-2,3-dioxopropanoate with
cyanoacetic acid involved the medial carbonyl group with loss
of carbon dioxide then the following reaction would probably
occur.

$$
\underset{}{C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-O-C_2H_5} + N\equiv C-CH_2-\overset{O}{\overset{\|}{C}}-OH \longrightarrow
\begin{array}{c}
H \\
C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-C_2H_5 \\
CH_2 \\
C\equiv N
\end{array}
$$

$$+CO_2 \qquad (XIV)$$

Compound XIV might be expected to be liquid or a low melt-
ing solid. This appears to be the case since no solid conden-
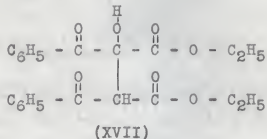sation products were obtained.

Acetylacetone readily condensed with ethyl 3-phenyl-2,3-
dioxopropanoate. Carbon and hydrogen analysis indicated a one-
to-one addition product. Assuming that condensation occurred

at the medial carbon of the tricarbonyl compound, XVI is sug-
gested as the structure of this product. It is further sug-
gested that alkaline hydrolysis of this compound occurs at
three points, indicated by arrows in XVI, which would account
for the observed saponification equivalent being one-third of
the molecular weight. The fact that only one carbonyl group
was noted by analysis is anomolous, since a value of three
would be expected for a compound of structure XVI. Insuf-
ficient time was available to investigate this compound more
completely.

$$
\begin{array}{c}
\quad\quad\quad\quad\quad\quad\overset{\text{H}}{\underset{|}{}} \\
C_6H_5 - \overset{O}{\underset{\|}{C}} - \overset{\overset{O}{|}}{\underset{|}{C}} - \overset{O}{\underset{\|}{C}} - O\ C_2H_5 \\
CH_3 - \overset{O}{\underset{\|}{C}} - CH - \overset{O}{\underset{\|}{C}} - CH_3 \\
(XVI)
\end{array}
$$

Ethyl 3-phenyl-2,3-dioxopropanoate and dibenzoylmethane
did not appear to react in the cold in the presence of piperi-
dine catalyst. Upon heating, a reaction seemed to occur,
however, the solid (which could not be isolated from the re-
action mixture) may have been dibenzoylmethane. Condensa-
tions appeared to occur between ethyl 3-phenyl-2,3-dioxopro-
panoate and both ethyl acetoacetate and ethyl cyanoacetate
even though solid condensation products could not be isolated.
This assumption is based upon the evolution of heat, the change
of color of the reaction mixture, and the fact that the mix-
tures also became viscous upon cooling.

Ethyl 3-phenyl-2,3-dioxopropanoate condensed with ethyl benzoylacetate to give the compound $C_{22}H_{22}O_7$ reported by Wahl (14). Assuming again that condensation involved the medial carbonyl group XVII is suggested as the structure of this compound.
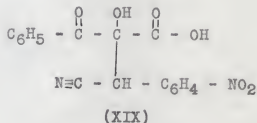
$$C_6H_5 - \overset{\overset{O}{\|}}{C} - \overset{\overset{H}{\overset{|}{O}}}{\underset{|}{C}} - \overset{\overset{O}{\|}}{C} - O - C_2H_5$$
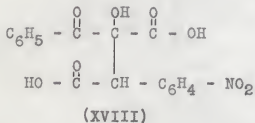$$C_6H_5 - \overset{\overset{O}{\|}}{C} - CH - \overset{\overset{O}{\|}}{C} - O - C_2H_5$$

(XVII)

The average saponification equivalent for the compound was found to be 123.9, which is intermediate between the theoretical 99.5 (tetrabasic) and 136.7 (tribasic). It would appear that incomplete saponification occurred in these experiments and little can be said further. Carbon and hydrogen analysis values observed were a little high, compared to the expected values.

Ethyl 3-phenyl-2,3-dioxopropanoate did not appear to react with ethyl malonate either in the cold or when heated on the steam bath for one hour. Apparently condensation did not take place and more rigorous conditions would be required, perhaps, for the condensation of ethyl malonate with this tricarbonyl compound. The small quantity of solid nitrogen-containing compound obtained was assumed to be a compound of piperidine.

Upon saponification of the p-nitrophenylacetonitrile con-
densation product Hudson (6) obtained a dicarboxylic acid
(neutral equivalent 166.6). Benzoic acid was not recovered
from this saponification as in the saponification of the ma-
lonic acid condensation product. It was thought that with
more stringent conditions benzoic acid could be cleaved from
the p-nitrophenylacetonitrile condensation product molecule.
However, two and one-half hours at 160° C. in a diethylene
glycol-potassium hydroxide solution was not sufficient to pro-
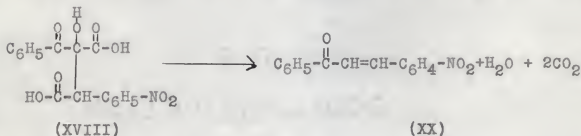duce cleavage beyond that which had been produced in aqueous
medium.

Saponification of this condensation product in aqueous
alkali at room temperature apparently gave a mixture of two
acids; possibly XVIII and XIX below.

$$C_6H_5 - \overset{O}{\underset{}{C}} - \overset{OH}{\underset{|}{C}} - \overset{O}{\underset{}{C}} - OH$$
$$HO - \overset{O}{\underset{}{C}} - CH - C_6H_4 - NO_2$$
$$(XVIII)$$

$$C_6H_5 - \overset{O}{\underset{}{C}} - \overset{OH}{\underset{|}{C}} - \overset{O}{\underset{}{C}} - OH$$
$$N{\equiv}C - CH - C_6H_4 - NO_2$$
$$(XIX)$$

A mixture of these acids was indicated since the melting
point of the acid recovered was much lower than that for the
acid presumed to be XVIII which was obtained upon heating the
condensation product in aqueous alkali.

It was hoped that decarboxylation of the dicarboxylic
acid XVIII by quinoline and either copper or basic cupric

carbonate might bring about the formation of 4-nitrochalcone
(XX) which is a known compound. In the formation of 4-nitro-
chalcone (XX) from the above acid (XVIII) it was presumed
that the acid would undergo base-catalyzed dehydration due to
the action of quinoline. The reaction would proceed as follows:

$$C_6H_5-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{\underset{\underset{HO-\overset{\overset{O}{\|}}{C}-CH-C_6H_5-NO_2}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OH \longrightarrow C_6H_5-\overset{\overset{O}{\|}}{C}-CH=CH-C_6H_4-NO_2+H_2O + 2CO_2$$

(XVIII)   (XX)

In order to find out more about this reaction a quanti-
tative decarboxylation was run on XVIII. After three attempts
in which the calculated carboxyl group per mole ratio was too
low, one more determination was made using a double portion of
basic cupric carbonate catalyst. From this determination 1.02
carboxyl groups per mole was found. A possible explanation
for obtaining a result of one, rather than two, carboxyl groups
per mole is that at such high temperatures in the presence of
quinoline, more profound alterations of structure may have
occurred.

To date, proof of structure of the p-nitrophenylacetoni-
trile condensation product by simple degradative means has
been unsuccessful. A structure proof of this compound would
best be obtained by an independent synthesis by unequivocal
methods, a task of difficult nature. The ethyl benzoylacetate
and acetylacetone condensation products may yield to the tech-

nique employed by Hudson (6) in characterizing the condensation product of ethyl 3-phenyl-2,3-dioxopropanoate with malonic acid, however, insufficient time prevented more detailed studies by this writer.

A future study of these products could consist of (1) carbon-hydrogen analyses, (2) saponification equivalents, (3) active hydrogen determinations, (4) carbonyl group determinations, and (5) identification of the fragments obtained by saponification of the condensation products.

SUMMARY

Ethyl 3-phenyl-2,3-dioxopropanoate was condensed with acetylacetone, ethyl benzoylacetate, and p-nitrophenylacetonitrile in the presence of piperidine as a catalyst. Condensations with p-nitrophenylacetonitrile and ethyl benzoylacetate have previously been reported in the literature.

The condensation product of ethyl 3-phenyl-2,3-dioxopropanoate and p-nitrophenylacetonitrile was saponified to obtain an acid previously shown to be a dibasic acid with a molecular formula $C_{17}H_{13}O_8N$. Attempted quantitative decarboxylation of this acid indicated that reactions other than decarboxylation probably occurred and therefore data thus obtained could not be used in determining the structure of the acid.

Ethyl 3-phenyl-2,3-dioxopropanoate was condensed with ethyl benzoylacetate to give a solid condensation product.

Evidence supported the formula $C_{22}H_{22}O_7$ for this condensation product.

A molecular formula $C_{16}H_{18}O_6$ was indicated by analysis for the condensation product of ethyl 3-phenyl-2,3-dioxopropanoate with acetylacetone. This product was cleaved readily in hot alkali, and appeared to be tribasic, as indicated by saponification equivalent values.

Condensation reactions were attempted with ethyl 3-phenyl-2,3-dioxopropanoate and the following active methylene compounds: cyanoacetic acid, ethyl acetoacetate, ethyl cyanoacetate, dibenzoylmethane, and ethyl malonate. In all cases no solid condensation products were isolated, but evolution of heat and pronounced color changes indicated that some reaction occurred in each case except with dibenzoylmethane and ethyl malonate.

ACKNOWLEDGMENT

BIBLIOGRAPHY

(1) Bigelow, L. A., and R. S. Hanslick.
        Diphenyl triketone. Organic Synthesis. 13: 38-40.
        1933.

(2) Bouveault, L., and A. Wahl.
        Preparation des ethers ⍺-β-dicetoniques. Compt.
        rend. 138: 1221-1223. 1904.

(3) Doebner, O.
        Synthese der Sorbinsaure. Deutsch. Chem. Gesell.
        Ber. 33: 2140-2142. 1900.

(4) Howk, B. W., and S. M. McElvain.
        The reaction of organic halides with piperidine:
        II Certain alpha-bromo-beta-ketonic esters. Amer.
        Chem. Soc. Jour. 54: 282-289. 1932.

(5) Hubacher, M. H.
        Determination of carboxy groups in aromatic acids.
        Analyt. Chem. 21: 945-947. 1949.

(6) Hudson, G. V.
        The chemistry of vicinal tricarbonyl compounds:
        Condensation reactions of ethyl 3-phenyl-2,3-
        dioxopropanoate. Unpublished data from Master's
        Thesis, Kansas State College, Manhattan, Kansas.
        1950.

(7) Knoevenagel, E.
        Condensation von Malonsaure wit aromatischen
        Aldehyden durch Ammoniak and Amine. Deutsch. Chem.
        Gesell. Ber. 31: 2596-2619. 1898.

(8) de Neufville, R., and H. von Peckmann.
        Uber das Diphenyltriketone. Deutsch. Chem. Gesell.
        Ber. 23: 3376-3379. 1890.

(9) Redemann, C. E., and H. J. Lucas.
        Rapid saponification of esters by potassium hydroxide
        in diethylene glycol. Indus. and Engg. Chem., Analyt.
        Ed. 9: 521. 1937.

(10) Remick, A. E.
        Electronic interpretations of organic chemistry.
        2nd ed. New York: John Wiley and Sons. 1949.

(11) Sachs, F., and H. Barschall.
          Ueber triketone. Deutsch. Chem. Gesell. Ber. 34:
          3047-3052. 1901.

(12) Sharp, D. B.
          A mechanism for the cleavage of certain phenyl-
          hydrazones by bromine. Amer. Chem. Soc. Jour. 71:
          1106-1108. 1949.

(13) Siggia, S.
          Quantitative organic analysis via functional groups.
          New York: John Wiley and Sons. 1941.

(14) Wahl, M. A.
          Sur le benzoylglyoxalate d'ethyle. Compt. rend.
          144: 212-214. 1907.

(15) Watson, H. B.
          Reaction mechanisms. Annual Reports on the Progress
          of Chemistry. (Chem. Soc. London). 36: 210-215.
          1939.

STUDIES OF THE CONDENSATION PRODUCTS OF
ETHYL 3-PHENYL-2,3-DIOXOPROPANOATE
WITH ACTIVE METHYLENE COMPOUNDS

by

FRANK ARCHER MOORE

B. S., Fort Hays Kansas State College, 1942

———————————

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1952

In an attempt to determine the interactions between the functional groups in a vicinal tricarbonyl compound, a series of condensation reactions were attempted with ethyl 3-phenyl-2,3-dioxopropanoate and various active methylene compounds. Several experiments then were employed in an effort to determine the structure of each condensation product.

Solid condensation products were obtained when ethyl 3-phenyl-2,3-dioxopropanoate condensed in the presence of piperidine with each of the following active methylene compounds: acetylacetone, ethyl benzoylacetate, and p-nitrophenylacetonitrile. Condensations of this tricarbonyl compound with p-nitrophenylacetonitrile and ethyl benzoylacetate have been reported previously in the literature.

The condensation product of ethyl 3-phenyl-2,3-dioxopropanoate and p-nitrophenylacetonitrile was saponified to obtain a dibasic acid previously shown (Hudson) to have a molecular formula $C_{17}H_{13}O_8N$. Attempted quantitative decarboxylation of this acid indicated that reactions other than decarboxylation were occurring and therefore data thus obtained could not be used in determining the structure of the acid.

Ethyl 3-phenyl-2,3-dioxopropanoate condensed with ethyl benzoylacetate to give a solid condensation product. Analytical evidence supported the formula $C_{22}H_{22}O_7$ for this condensation product. A molecular formula $C_{16}H_{18}O_6$ was indicated

for the condensation product of ethyl 3-phenyl-2,3-dioxopro-
panoate and the active methylene compound, without loss of a
mole portion of water as often occurs in this type of conden-
sation.

Condensation reactions were attempted with ethyl 3-phenyl-
2,3-dioxopropanoate and the following active methylene com-
pounds: cyanoacetic acid, ethyl acetoacetate, ethyl cyano-
acetate. dibenzoylmethane, and ethyl malonate. In all these
experiments no solid condensation products were isolated.