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PART ONE
THE ADDITION OF DIPHENYLKETONE TO α-BENZOQUINONE

PART TWO
DIAZOKETONES AS REAGENTS FOR
THE IDENTIFICATION OF ORGANIC ACIDS

PART THREE
THE BROMO-2-NITROBENZOIC ACIDS

A Dissertation

Submitted to the Graduate Faculty of the
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in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by
Joseph Martin Dechary
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M.S., Louisiana State University, 1947

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MANUSCRIPT THESSES

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The author is gratefully appreciative of the guidance and encouragement given him by Dr. J. L. E. Erickson who supervised the planning and execution of this investigation. He is indebted to the faculty of the Department of Chemistry for the Charles E. Coates Fellowship for the year, 1951-1952.
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THE ADDITION OF DIPHENYLKETENE TO o-BENZOQUINONE
ABSTRACT
It has been observed that the addition of diphenylketene to p-benzoquinones yielded \( \beta \)-lactones which are stable, colorless compounds. Upon heating, however, these \( \beta \)-lactones decomposed into colored diphenyl-\( \pi \)-quinomethanes and carbon dioxide. The addition of diphenylketene to a second carbonyl group of the p-benzoquinones did not produce the expected di-\( \beta \)-lactones. Instead, their decomposition products, the tetraphenyl-\( \pi \)-quinodimethanes were isolated. The \( \beta \)-lactone obtained from diphenylketene and p-benzoquinone underwent light and gave a benzenoid derivative, 2,5-dihydroxytriphenylacetic acid lactone. Ketene, the simplest member of the series, did not react with the carbonyl groups of p-benzoquinones or \( \alpha,\beta \)-unsaturated ketones.

No reactions of ketenes with \( \alpha \)-quinones have been hitherto reported. The purpose of this work was to study the reaction of diphenylketene with \( \alpha \)-benzoquinone.

The addition of diphenylketene to \( \alpha \)-benzoquinone yielded neither the expected \( \beta \)-lactone, nor its rearrangement product, 2,3-dihydroxytriphenylacetic acid lactone. The addition, which was of the diene-dienophile type, gave diphenyl-\( \alpha \)-hydroxyphenoxacetic acid lactone, a colorless substance which has been obtained previously, but which was erroneously reported in the literature as 2,3-dihydroxytriphenylacetic acid lactone. The latter substance, which was really unknown prior to this investigation, was synthesized by conventional methods starting from 2,3-dimethoxybenzaldehyde.

The substituted benzaldehyde was oxidized by means of potassium permanganate to 2,3-dimethoxybenzoic acid, and the methyl ester of this acid was treated with excess phenyllithium which resulted in the formation of 2,3-dimethoxytriphenylcarbinol. The carbinol, when treated with acetyl chloride, gave the new 2,3-dimethoxytriphenylchloromethane which was then converted into 2,3-dimethoxytriphenylmethylsodium by means of sodium amalgam.
The sodium derivative yielded, upon treatment with carbon dioxide and subsequent hydrolysis of the sodium salt, 2,3-dimethoxytriphenylacetic acid, a new substance. Demethylation of the 2,3-dimethoxytriphenylacetic acid by hydriodic acid yielded the desired 2,3-dihydroxytriphenylacetic acid lactone.

An independent synthesis of the product obtained from diphenylketene and o-benzoquinone was developed which involved the elimination of hydrogen chloride from catechol and diphenylchloroacetyl chloride.

Neither dimethylketene nor ketene gave a successful reaction with o-benzoquinone.
THEORETICAL DISCUSSION
During the course of a remarkable series of researches on the ketenes, Hermann Staudinger examined very extensively the addition of the interesting substance diphenylketene to a variety of p-benzoquinones.

The addition of diphenylketene to p-benzoquinone gave, via 1,2-addition to the carbonyl group, a stable, colorless $\beta$-lactone (I). The $\beta$-lactone lost carbon dioxide when heated and yielded the brownish-yellow diphenyl-$p$-quinomethane (II) which had been previously prepared by Bistrzycki and Herbst. The direct addition of two molecules of diphenylketene to one molecule of p-benzoquinone gave the orange-red tetraphenyl-$p$-quinodimethane (IV), the structure of which followed from an earlier, independent preparation due to Thiele and Balhorn. The intermediate di-$\beta$-lactone (III) postulated by Staudinger was unstable and could not be isolated.

The substituted p-benzoquinones, toluquinone, chloroquinone, and m-di-chloroquinone reacted similarly.
Staudinger observed that the β-lactone (I) underwent an interesting rearrangement when it was irradiated in the solid state or in boiling benzene. It gave the isomeric benzene derivative 2,5-dihydroxytriphenylacetic acid lactone (V). This substance was obtained more conveniently by condensing hydroquinone (VI) with benzilic acid (VII) in the presence of stannic chloride or by fusing the two substances together without solvent or catalyst.

\[
\begin{align*}
\text{I} & \quad \rightarrow \quad \text{V} \\
\text{VII} & \quad \rightarrow \quad \text{VI} \\
\end{align*}
\]

Diphenylketene also added to α,β-unsaturated aldehydes and ketones to give, as final products, diphenylmethylenepolynes.

Dimethylketene gave with p-benzoquinone a colorless addition product, the structure of which was not examined, although Staudinger noted that it regenerated the quinone easily when heated.
Ketene, the parent member of the series, did not react with p-benzoquinone, dibenzalacetone, or benzylideneaniline. Much later, however, Hurd and Thomas, who studied the reaction of ketene with benzaldehyde and furfural, obtained evidence which indicated that ketene does add to the carbonyl group. They obtained reaction mixtures which could be pyrolyzed to give styrene and furylethylene, respectively. No m-nitrostyrene could be obtained with certainty from m-nitrobenzaldehyde and ketene. The production of unsaturated hydrocarbons indicated the presence of $\beta$-lactones.

Staudinger did not extend his researches on the reaction of ketenes with quinones to include any of the o-benzoquinones, presumably since they are much more unstable than the para compounds. With this omission in mind, it was considered of interest to attempt the reaction of diphenylketene with o-benzoquinone itself.

If the behavior of p-benzoquinone is typical, it would be expected that the addition of diphenylketene to o-benzoquinone yields the analogous $\beta$-lactone (VIII) which should either decompose into diphenyl-quinomethane, or rearrange into 2,3-dihydroxytriphenylacetic acid lactone (IX):

![Chemical structures](image.png)
It was found, however, that when o-benzoquinone in benzene suspension was treated with an excess of diphenylketene, the primary addition product (VIII) was not obtained. Instead, there was isolated a colorless substance (X) which was identical with the product obtained from catechol (XI) and benzoilic acid (XII), but which is described in the literature as 2,3-dihydroxytriphenylacetic acid lactone (IX). The substance gave no color with ferric chloride and was insoluble in dilute alkaline solution, behavior which seemed inconsistent with the structure (IX), as well as with the possible isomeric 3,4-dihydroxytriphenylacetic acid lactone.

As a consequence of these observations and for comparison with the product (X) obtained from diphenylketene and o-benzoquinone, the lactone (IX) was synthesised by the following sequence of reactions:

2,3-Dimethoxybentaldehyde (XIII) was oxidised to the corresponding benzoic acid (XIV), and this was converted into methyl 2,3-dimethoxybenzoate (XV). 2,3-Dimethoxytriphenylcarbinol (XVI), prepared from XV and phenyllithium, was converted by means of acetyl chloride into the corresponding chloromethane (XVII). When the chloromethane was treated in an ether-benzene solution with 1% sodium amalgam, followed by carbonation and hydrolysis of the sodium salt, 2,3-dimethoxytriphenylacetic acid (XVIII) was obtained. Demethylation of XVIII by hydriodic acid gave the lactone (IX). Compounds IX, XVII, and XVIII have not been previously reported.
During this investigation there were prepared also 2,3-dimethoxytriphenylmethane and two other members of the series, the methyl ether and the nitrile. The synthesis of the methane was accomplished by formic acid reduction of 2,3-dimethoxytriphenylcarbinol. Methyl 2,3-dimethoxytriphenylmethyl ether was obtained by treating the same carbinol with methanolic sulfuric acid. 2,3-Dimethoxytriphenylacetonitrile was prepared by heating the chloromethane (XVII) with mercuric cyanide. Simultaneous hydrolysis and demethylation of the nitrile by hydriodic acid also yielded the lactone (IX).

As distinguished from the substance (X), m.p. 136-137.5°, obtained by either the reaction of diphenylketene with o-benzoquinone, or from catechol and benzilic acid, the lactone (IX) is quite soluble in dilute alkaline solution, imparts a bluish-green color to the solution, and possesses a much higher melting point, 192.5-193.5°.

Another possible course of the reaction resembles definitely a diene-dienophile type of addition of diphenylketene to o-benzoquinone which yields diphenyl-o-hydroxyphenoxycetic acid lactone (X). This product can also be accounted for by the elimination of two molecules of water from one molecule each of catechol (XI) and benzilic acid (XII). The synthesis of the ether-lactone (X) was conveniently carried out by treating an acetone solution of catechol and diphenylchloroacetyl chloride with potassium carbonate. It proved to be identical in every respect with the product.
resulting from the reaction of diphenylketene with o-benzoquinone and also with the product obtained from the reaction of catechol with benzilic acid. Convincing evidence for the course of the reaction leading to the formation and structure of the ether-lactone \( X \) (by any one of the three routes examined) was obtained when it was treated with hydroiodic acid. There were isolated diphenylacetic acid and catechol, cleavage products compatible only with the structure of diphenyl-o-hydroxyphenoxyacetic acid lactone. The product obtained by von Liebig \( ^6 \) from catechol and benzilic acid and described erroneously as IX must now be assigned the structure \( X \). The ether-lactone ring of \( X \) was easily opened by the reagent, diazomethane, giving methyl diphenyl-o-methoxy-phenoxyacetate, which constitutes further proof for the correctness of the structure \( X \). Spencer and Wright \( ^{12} \) observed a similar opening of the coumarin lactone ring with the methylation of the carboxyl and the phenolic hydroxyl groups.

When this work was substantially complete, it was reported by Horner and co-workers \( ^{13} \) that diphenylketene adds to tetrachloro-o-benzoquinone to give diphenyl-(3,4,5,6-tetrachloro-2-hydroxyphenoxy)-acetic acid lactone. This is in agreement with the results found for o-benzoquinone, and it is suspected that other o-quinones react similarly with diphenylketene, giving pseudo-diene addition products rather than \( \alpha \)-lactones.

The experiments that were carried out with dimethylketene and o-benzoquinone were inconclusive. In several attempts at reactions, the quinone was recovered in the form of an amorphous, yellow polymer which has been described by Willstatter and Muller \( ^{14} \). It is possible that the dimethylketene, which was prepared by the decomposition of dimethylmalonic anhydride, contained traces of acetic acid which may have induced the observed
polymerization of the sensitive quinone.

The results of the investigation on the structure of the product obtained from diphenylketene and o-benzoquinone and the synthesis of the previously unknown 2,3-dihydroxytriphenylacetic acid lactone have appeared in published form elsewhere.

No successful reaction was obtained with ketene and o-benzoquinone or with ketene and β-naphthoquinone. The o-benzoquinone was decomposed immediately, and β-naphthoquinone was unaffected.
EXPERIMENTAL
Silver Oxide. — Silver nitrate, 169.9 g. (1.0 mole), was dissolved in one liter of distilled water, and the solution was slowly added with vigorous stirring to 113 g. (2.0 moles) of potassium hydroxide dissolved in 1500 ml. of distilled water. The precipitate of silver oxide was washed by decantation twelve times with distilled water, six times with acetone and six times with anhydrous ether. The moist oxide was dried in vacuum over paraffin and potassium hydroxide. The yield was 62 g. (94%).

Diphenylketene. — Phenylbenzoyldiazomethane, 22.0 g. (0.1 mole), was dissolved in the minimum required quantity of dry benzene, and the solution was slowly dropped into a 50 ml. Claissen distilling flask which was heated to 100-110° by an oil bath. The azobenzene was thus decomposed and the benzene distilled off at the same time. The residue was distilled in an atmosphere of dry, oxygen-free nitrogen at 3.5-4 mm. pressure, yielding 6 g. of crude diphenylketene. After redistillation, the yield was 5 g. (26%) of reddish-orange ketene, b.p. 117-120° at 3.5-4 mm.

a-Benzocoumarone. — Silver oxide, 23.2 g. (0.10 mole), and 21.3 g. of fused, finely powdered sodium sulfate were placed in a dry 500 ml. glass-stoppered flask and covered with 200 ml. of anhydrous ether. A solution of 5.5 g. (0.05 mole) of catechol (Eastman Kodak Co.) in 100 ml. of anhydrous ether was added and the mixture shaken for exactly two minutes. The deep red mixture was filtered rapidly by suction through a layer of fused, finely powdered sodium sulfate placed in a Buchner funnel with a fritted disc. The ethereal solution then was slowly chilled to -70° by means of an acetone-dry ice mixture. The fine red crystals of the ortho
benzoquinone, which separated out, were washed by decantation three times with cold anhydrous ether, rapidly transferred to a small filter funnel, and weighed at once. The yield was 0.81 g. (15%). The quinone may be kept unchanged for several days by storing in the dark at -70°.

The Addition of Diphenylketene to o-Benzoquinone. — A suspension of 0.7 g. (0.0065 mole) of o-benzoquinone in 35 ml. dry benzene was treated with 5 g. (0.026 mole) of freshly distilled diphenylketene dissolved in 15 ml. of dry benzene. The deep red mixture was decolorized upon standing for two hours, giving a golden-yellow solution. After standing two days in the dark, the solvent was removed in vacuo until fine crystals deposited from the solution; these were collected, washed well with a 1:3 mixture of benzene and low-boiling petroleum ether, and recrystallized from a similar mixture of solvents. The yield was 1.6 g. (82%) of fine white needles, m.p. 136-137.5°. When mixed with the product obtained by the fusion of catechol with benzilic acid, the m.p. was unchanged.


Diphenyl-o-hydroxyphenoxycetic Acid Lactone. — Benzilic acid, 45.6 g. (0.20 mole), and catechol, 22 g. (0.20 mole), were heated together without solvent for one and one-half hours at 225-230°. The red melt was broken up, powdered, and extracted twice with 500 ml. portions of boiling water, followed by two extractions with boiling 5% sodium carbonate solution. The buff-colored powder was air dried, dissolved in benzene, and treated four times with decolorizing charcoal. When an equal volume of low-boiling petroleum ether was added to the filtered, concentrated solution, 32 g. (52%) of the ether-lactone crystallized in glistening, white
needles, m.p. 136-137.5°.

2,3-Dimethoxybenzoic Acid. — 2,3-Dimethoxybenzaldehyde was obtained by distilling the Eastman Kodak product, Technical Grade, and taking the fraction having the b.p. 105-106.5° at 2 mm. The aldehyde, 30 g. (0.18 mole) was boiled under reflux with 300 ml. of water and 35 g. (0.35 mole) of potassium bicarbonate while a hot solution of 22 g. (0.14 mole) of potassium permanganate in 150 ml. of water was slowly added. The mixture was cooled, filtered, and the filtrate acidified with concentrated hydrochloric acid, precipitating the benzoic acid which was collected and washed well with cold water. There were obtained after recrystallization from hot water 25.4 g. (77.8%) of long, stout, colorless needles, m.p. 120-122°.

Methyl 2,3-Dimethoxybenzoate. — In a 500 ml. round-bottomed flask were placed 44.2 g. (0.24 mole) of 2,3-dimethoxybenzoic acid, 125 ml. (3.48 moles) of methanol, and 8.5 ml. of concentrated sulfuric acid. The mixture was boiled under reflux 6 hours, and excess methanol was removed by distillation on the steam bath until the volume was reduced to about one-third of the original volume. The cooled residue was poured into a separatory funnel containing 250 ml. of water, and the ester was extracted with 100 ml. of ether. The ethereal layer was separated, washed with two 50 ml. portions of water, and then shaken with 50 ml. portions of 10% sodium bicarbonate solution until acidification of the bicarbonate layer precipitated no free acid. The ethereal solution was separated, dried over anhydrous sodium sulfate for several hours, decanted from the drying agent, and evaporated to about one-half of its original volume. The addition of an equal volume of low-boiling petroleum ether caused the immediate separation of the ester in a compact mass of huge, colorless
rhombs. The yield of ester, after collecting and washing with 20-30 ml.
of an ether-petroleum ether mixture (1:10), was 36.8 g. (78%), m.p. 48-49°.

2,3-Dimethoxytriphenylcarbinol. — Richtsenhain and Nippus reported
the preparation of 2,3-dimethoxytriphenylcarbinol by the action of phenyl-
magnesium bromide on either 2,3-dimethoxybenzophenone or ethyl 2,3-di-
methoxybenzoate. A larger yield and a purer product was obtained from
phenyllithium and methyl 2,3-dimethoxybenzoate.

To an ethereal solution of phenyllithium (prepared from 7.0 g. of
lithium, 78.5 g. of bromobenzene, and 300 ml. of anhydrous ether) was
added, with occasional cooling and over a period of 45 minutes, 25.5 g.
(0.13 mole) of methyl 2,3-dimethoxybenzoate dissolved in 45 ml. of an-
hydrous ether. The mixture was refluxed for an additional 45 minutes,
poured on to crushed ice, and the product worked up in the usual manner.
The yield of crude material was 31.9 g. (77%). After one crystallization
from ether and three from alcohol, there was obtained 29.3 g. of white
prisms, m.p. 111-112°. Richtsenhain and Nippus reported m.p. 106°.

Anal. Caled. for C_{21}H_{20}O: C, 78.72; H, 6.29. Found: C, 78.85;
H, 6.34.

2,3-Dimethoxytriphenylchloromethane. — 2,3-Dimethoxytriphenylcarbi-
nol, 29.3 g. (0.092 mole), 5 ml. of acetyl chloride and 8.5 ml. of dry
benzene were placed in a 500 ml. round-bottomed flask fitted with a
reflux condenser and calcium chloride drying tube. The mixture was
warmed on the steam bath until a clear solution was obtained, and 11 ml.
of acetyl chloride (16 ml. or 0.23 mole in all) was added through the
top of the condenser. The solution was boiled one-half hour longer,
cooled, and 22 ml. of high boiling petroleum ether added through the top
of the condenser with swirling. The crystals which separated were cooled for two hours in an ice bath, collected, washed quickly with 20 ml. of cold, high-boiling petroleum ether, sucked dry, and stored over soda lime and paraffin. The yield was 28.4 g., nearly quantitative, of the chloromethane, fine white crystals, m.p. 129-130°.

Anal. Caled. for C_{21}H_{10}O_2Cl: C, 74.44; H, 5.65. Found: C, 74.32; H, 5.69.

2,3-Dimethoxytriphenylacetic Acid. — Sodium amalgam (1%), composed of 1.2 g. (0.052 g. atom) of sodium and 120 g. of mercury, was prepared in a dry 250 ml. glass-stoppered flask, and to it was added 7.8 g. (0.023 mole) of 2,3-dimethoxytriphenylchloromethane dissolved in 95 ml. of anhydrous ether and 55 ml. of dry benzene. The mixture was shaken vigorously on the shaking machine for four hours, allowed to stand one-half hour, and then a stream of dry, oxygen-free carbon dioxide was passed in until the red color of the sodium compound disappeared. The carbon dioxide, which was obtained from a Kipp generator, was freed of oxygen by passage over bright copper turnings heated to 400°, and then freed of water by passage over Drierite and phosphorus pentoxide. The yellow solution of the sodium salt was filtered, exhaustively extracted with 10% ammonium hydroxide, and the combined alkaline extracts poured into ice-cold dilute sulfuric acid (1:4). The precipitated acid was collected and washed thoroughly with water. There was obtained 2.7 g. (34%) of crude acid which, after repeated crystallizations from glacial acetic acid, yielded 1.9 g. of 2,3-dimethoxytriphenylacetic acid sintering slightly at 231° and melting at 236-239°.

Anal. Caled. for C_{22}H_{20}O_4: C, 75.84; H, 5.79. Found: C, 75.77; H, 5.63.
2,3-Dihydroxytriphenylacetic Acid Lactone. — Demethylation of 2,3-
dihydroxytriphenylacetic acid lactone (0.2 g.) was accomplished by boil-
with 10 ml. of hydroiodic acid (sp. gr. 1.70), and 5 ml. of glacial acetic
acid for 7 hours. The reaction mixture was cooled, a little saturated
sodium bisulfite solution was added, and the fine crystalline precipi-
tate was collected and washed with water. The yield was 0.18 g. of fine
white crystals, m.p. 192.5-193.5°. The melting point was not raised
after two crystallizations from a mixture of benzene and low-boiling
petroleum ether. Demethylation of the 2,3-dimethoxytriphenylacetic acid
was also accomplished by boiling 0.5 g. of the compound for six hours in
a solution of 2.3 g. of aluminum bromide in 47 ml. of dry benzene. The
aluminum complex was hydrolyzed by pouring the reaction mixture into a
slush of 400 g. of crushed ice and 50 ml. of concentrated hydrochloric
acid. The mixture was warmed on the steam bath for 20-30 minutes,
cooled, and ether added until two phases separated. The benzene-ether
phase was separated and the aqueous phase extracted twice with 25 ml.
portions of ether. The benzene-ether phase and the ethereal extracts
were combined, washed with water, and dried over anhydrous sodium sul-
fate. The ether was removed by warming on the steam bath, and then the
remaining benzene solution was concentrated to a small volume. Upon di-
luting with low-boiling petroleum ether, sandy pink crystals of the lac-
tone crystallized. The yield was 0.37 g., m.p. 192-193°; after two crys-
tallisations (charcoal) from benzene-petroleum ether, m.p. 192.5-193.5°.

H, 4.84.

Diphenyl-β-hydroxyphenoxycetic Acid Lactone. — In a 250 ml. round-
bottomed flask fitted with a reflux condenser and calcium chloride drying
tub® were placed 19.0 g. (0.072 mole) diphenylechloroacetyl chloride, 7.9 g. (0.072 mole) catechol and 60 ml of dry acetone. To this solution was added, in small portions, 9.9 g. (0.072 mole) freshly ignited, finely powdered potassium carbonate. After the mixture ceased evolving carbon dioxide, it was boiled under reflux for 6 hours. The light yellow reaction mixture, which contained some insoluble material, was cooled and enough water (100 ml.) added to dissolve the water-soluble salts present. On further dilution with cold water, a yellow precipitate settled out which was collected on a Buchner funnel. A semi-solid, yellowish-brown oil was removed from the solid material by working with a spatula. The oil and the filtrate, which also contained oily material, were combined, extracted with a total of 125 ml. of ether, and the ethereal extract washed with four 50 ml. portions of 5% sodium carbonate solution followed by four 50 ml. portions of water. The solid material was similarly treated. All ethereal extracts were combined, dried over anhydrous sodium sulfate and the ether evaporated to a small volume. On cooling the solution, large six-sided prisms separated. These were recrystallized from ether to yield 5.5 g. (25%) of the ether-lactone, m.p. 136-137.5°. No depression of the melting point was observed on admixture with the substance obtained from the reaction of diphenylketene with o-benzoquinone, or with the product obtained from catechol and benzilic acid.

The Action of Hydriodic Acid on the Ether-lactone (X) yielded diphenylacetic acid and catechol. One gram of the substance was boiled two and one-half hours with 30 ml. of hydriodic acid and 30 ml. of glacial acetic acid. The solution was cooled and saturated sodium bisulfite solution added to remove iodine. The precipitate which formed upon addition of
water was collected and dried overnight. There was obtained 0.61 g. of
diphenylacetic acid, m.p. 146-148°, m.m.p. 146-147.5°. The filtrate was
extracted five times with 25 ml. portions of ether and the ethereal ex-
tract shaken with a globule of mercury. After removal of the ether,
there remained a sirupy yellow liquid which was dissolved in 5 ml. of
water and treated dropwise with 10% potassium hydroxide solution until
a slight excess was present. Ice was added to the alkaline solution and
then 0.7 ml. of acetic anhydride poured in as quickly as possible. The
mixture was shaken vigorously until the catechol diacetate precipitated.
It was collected, washed thoroughly with water, dried, and crystallized
twice from a small quantity of 70% alcohol. The yield of catechol di-
acetate was 0.21 g., fine white needles, m.p. 62-63°, m.m.p. 62-62.5°.

**Diazomethane** 23. — This compound was prepared in 80% yield from N-
nitroso-β-methylaminoisobutylmethyl ketone and sodium cyclohexoxide in
anhydrous ether according to the directions given in Organic Syntheses.

**The Action of Diazomethane on Diphenyl-α-hydroxyphenoxycetic Acid
Lactone.** — Six and one-tenth grams (0.02 mole) of the ether-lactone was
suspended in a mixture of 40 ml. of anhydrous methanol and 100 ml. of dry
ether. To this was added 250 ml. of ether containing 3.4 g. (0.08 mole)
of diazomethane, and the mixture was immersed in an ice-bath. At the
end of ten days the solution was bright yellow, indicating that an excess
of diazomethane was still present. The diazomethane was destroyed by the
addition of a slight excess of glacial acetic acid, and the ether was
evaporated in vacuum. When the solution had been reduced to a small vol-
ume, 3.1 g. of white crystals, m.p. 128-129°, separated. Further concen-
tration of the mother liquors yielded 1 g. more of white crystals, m.p. 
The residue of uncrystallizable material amounted to 3.1 g. of a light brown oil. Both fractions were combined and recrystallized from ether, yielding 2.8 g. (40%) of methyl diphenyl-<em>o</em>-methoxyphenoxyacetate, m.p. 136-137.5°, m.m.p. 110-121.5° with a sample of the ether-lactone. The compound is insoluble in concentrated, boiling aqueous alkali and soluble in boiling alcoholic alkali.

**Anal.** Caled. for C<sub>22</sub>H<sub>20</sub>O<sub>4</sub>; C, 75.84; H, 5.79; -OCH<sub>3</sub>, 17.82. Found: C, 75.45; H, 5.70; -OCH<sub>3</sub>, 17.82.

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**2,3-Dimethoxytriphenylmethane.** — One gram of 2,3-dimethoxytriphenylcarbinol was boiled for three and one-half hours with 10 ml. of 86% formic acid. After standing several days, the oily product solidified; it was then pulverized, washed thoroughly with water, and dried to give 0.88 g. of crude material, which when crystallized three times from alcohol, yielded glistening white rhombs, m.p. 84.5-85°.

**Anal.** Caled. for C<sub>21</sub>H<sub>20</sub>O; C, 82.86; H, 6.62. Found: C, 82.68; H, 6.76.

**Methyl 2,3-dimethoxytriphenylmethyl ether.** — One gram of 2,3-dimethoxytriphenylcarbinol was dissolved in 10 ml. of boiling methanol; the solution was cooled, three drops of concentrated sulfuric acid was added, and the mixture warmed on the steam bath for 20-30 minutes. When the solvent was removed by evaporation and the oily product was cooled, 0.96 g. of crude methyl ether separated. After three crystallizations from methanol, there were obtained glistening white hexagonal tablets, m.p. 119.5-120°.

**Anal.** Caled. for C<sub>22</sub>H<sub>22</sub>O<sub>3</sub>; C, 79.01; H, 6.63. Found: C, 79.00.
2,3-Dimethoxytriphenylacetonitrile. — Into a 500 ml. round-bottomed flask, fitted with an air condenser and calcium chloride drying tube, were placed 20 g. (0.059 mole) of 2,3-dimethoxytriphenylchloromethane and 18.8 g. (0.073 mole) of mercuric cyanide. The mixture was heated at 150-170° for one and one-half hours in an oil bath, then cooled, and the solid melt powdered and extracted with boiling benzene. The benzene solution was filtered, treated with low-boiling petroleum ether to precipitate oily impurities, and the filtered solution cooled. Upon standing, 4.5 g. (23%) of the crude nitrile crystallised. Recrystallization of the material from a small amount of glacial acetic acid (charcoal) yielded 2.3 g. of colorless leaflets, m.p. 157.5-158°.


Simultaneous hydrolysis and demethylation of the nitrile — was accomplished by boiling 120 mg. of the compound for 34 hours in a solution composed of 2 ml. of hydroiodic acid (sp. gr. 1.70) and 5 ml. of glacial acetic acid. The cooled solution was treated with sufficient saturated bisulfite solution to remove free iodine, and the fine white precipitate was collected, washed with a little water, and dried. There was thus obtained 110 mg. of 2,3-dihydroxytriphenylacetic acid lactone, m.p. 192.5-193°. After two crystallisations from a mixture of benzene and petroleum ether, the melting point was raised to 192.5-193.5°.

Dimethyl Malonic Acid. — In a one liter, three-necked, round-bottomed flask equipped with mechanical stirrer, ice-water condenser, and dropping funnel were placed 50 g. (0.38 mole) of methyl malonate, 113.6
g. (0.8 mole) of methyl iodide, and 200 ml. of anhydrous methanol. The mixture was stirred under reflux and to it was added (two hours) a solution of sodium methyleate prepared from 17.4 g. (0.76 mole) of clean sodium and 300 ml. of anhydrous methanol. An extra 100 ml. of methanol was added to the mixture when about half of the sodium methyleate solution had been dropped in. At the end of three and one-half hours of stirring under reflux, a test drop of the reaction mixture gave no reaction with phenolphthalein. The cloudy solution was evaporated in vacuum until it bumped badly, and the precipitate of sodium iodide, which had formed, was dissolved by the addition of 200 ml. of water. The clear solution was extracted four times with 130 ml. portions of ether, and the ether extract was washed once with water, separated, dried over anhydrous sodium carbonate for two hours, filtered, and evaporated. The crude ester was distilled at a pressure of 2.5 mm., giving 28.6 g. (45%) of colorless methyl dimethylmalonate, b.p. 71°. Saponification of the ester. — The ester was chilled in an ice-bath and then carefully added to an ice-cold solution of 24.5 g. (0.44 mole) of potassium hydroxide and 13 g. of water. The mixture was allowed to stand overnight, chilled again, and then treated with 42 ml. of cold, concentrated hydrochloric acid (sp. gr. 1.19). The mixture was extracted with two 100 ml. portions of ether, followed by five 50 ml. portions of ether. The ethereal solution was separated and evaporated to a sirup from which the solid acid deposited on standing. There was obtained, after recrystallization from ether, 16.5 g. (33%) of dimethyl malonic acid, colorless rhombs, m.p. 184-185° (sublimation).

**Dimethylketene**. — This compound was prepared in 70% yield from dimethyl malonic acid according to the directions given in Organic
Reactions, and was immediately used in the reaction with o-benzoquinone.

Reactions of o-Benzooquinone with Dimethylketene. — A suspension of 2.0 g. (0.19 mole) of o-benzoquinone in 30 ml. dry ether was treated with 2.6 g. (0.30 mole) of freshly prepared dimethylketene, and the mixture was allowed to stand in a dry-ice - acetone mixture. After several hours' standing a bright-yellow precipitate separated, and the reaction mixture was left undisturbed for twelve hours. The precipitate was collected, washed with a little ether - petroleum-ether mixture, and dried in vacuum. There was thus obtained about 1.6 g. of a bright yellow, amorphous substance which resisted all attempts to crystallize it. The substance, apparently a polymeric form of o-benzoquinone, possessed no definite melting point, but sintered at 146° and decomposed completely when the temperature reached 170°.

Ketene. — A ketene generator was constructed according to the directions of Organic Syntheses with modifications which included a dry-ice trap to condense unused acetone and acidic by-products of the pyrolysis and an extra dry-ice trap placed before the reaction vessel. Rubber connections were eliminated throughout the entire apparatus by the use of ground glass joints. The generator was calibrated by absorbing the effluent ketene in standard 5 N alkali and back-titrating the remaining alkali with standard 1 N acid. There was produced 0.18-0.20 mole of ketene per hour.

Reactions of o-Benzooquinone with Ketene. — A suspension of 2.17 g. (0.02 mole) of o-benzoquinone in 95 ml. of dry benzene was treated with a 15 mole excess of ketene over a period of two hours. At first, the reaction mixture became slightly warm, but returned to room temperature.
in a short time, 15 minutes. The reaction mixture was filtered free of a small amount of brown precipitate, and the filtrate was concentrated in vacuum. There was obtained 2.0 g. of amorphous brown powder, apparently decomposed o-benzoquinone.

**Reaction of β-Naphthoquinone with Ketene.** — A solution of 0.5 g. (0.0032 mole) of β-naphthoquinone in 75 ml. of dry benzene was treated with an eight mole excess of ketene over a period of one and one-half hours. The solution appeared much lighter in color at the end of that time. Benzene was removed from the reaction mixture by evaporating in vacuum, and there was obtained about 0.4 g. of amorphous, badly discolored quinone. The experiment was repeated at 0°, using acetone as a solvent and passing in a ten mole excess of ketene. No significant change in color of the reaction mixture was noted, and most of the quinone, about 0.4 g., was recovered in the form of an amorphous brown powder.

**Reaction of o-Benzocquinone with Phenylisocyanate.** — A suspension of 0.5 g. (0.0046 mole) of o-benzoquinone in 75 ml. of dry benzene was cautiously treated with 1.1 g. (0.0093 mole) of phenylisocyanate and the mixture allowed to stand in the dark. At the end of one-half hours' standing, a fine olive-green precipitate separated. It was collected at the end of 24 hours, washed with a little cold benzene and dried. There was obtained about 0.45 g. of amorphous material which was apparently decomposed quinone, since no crystalline material could be obtained from it by any of the usual crystallization procedures.

**Reaction of β-Naphthoquinone with Phenylisocyanate.** — A mixture of 1.6 g. (0.01 mole) of β-naphthoquinone, 3.9 g. (0.03 mole) of
phenylisocyanate, and 50 ml. of dry benzene was allowed to stand for 24 hours. At the end of this time the reaction mixture was filtered free of a dark brown, amorphous precipitate which was washed with a little cold benzene and dried. There was thus obtained about 1.4 g. of amorphous discolored quinone. The experiment was repeated by heating 0.5 g. (0.0032 mole) of β-naphthoquinone, 2 g. (0.015 mole) of phenylisocyanate, and 10 ml. of benzene in a sealed tube at 100-105°C for 48 hours. No significant change was noted in the color of the reaction mixture at the end of the first 24 hours or at the end of the heating period. The reaction mixture was worked up as usual, and there was obtained about 0.35 g. of badly decomposed β-naphthoquinone.
SUMMARY
The addition of diphenylketene to o-benzoquinone yielded diphenyl-o-
hydroxyphenoxyacetic acid lactone which was identical with the substance obtained by fusing catechol with bensilic acid, but which has been des-
eribed erroneously in the literature as 2,3-dihydroxytriphenylacetic acid lactone. The latter substance was obtained, however, by the demethyla-
tion of 2,3-dimethoxytriphenylacetic acid which was synthesized by con-
ventional methods.

An independent synthesis of diphenyl-o-hydroxyphenoxyacetic acid lac-
tone was carried out by eliminating hydrogen chloride from catechol and diphenylehloroacetyl chloride.
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Biskel, H.
**Derivatives of Diphenylacetic Acid and Benzilic Acid.**
Ber., 22: 1337-1339 (1889)

Diphenylchloroacetyl chloride is easily obtained by heating a mixture of one mole of benzilic acid with two moles of phosphorus pentachloride at 120-130°. When the evolution of phosphorus oxychloride ceases, the mass is put into cold water and allowed to solidify. The compound crystallised from ligroin in large, colorless rhombs, m.p. 50°.

Bistrzycki, A. and Herbst, C.
**Diphenyl-p-quinomethane, the Chromogen of the Hydroxytriphenylmethane Dyes.**
Ber., 36: 2333-2339 (1903)

An ethereal solution of p-methoxytriphenylearbinol, when treated with dry hydrochloric acid gas, gave an almost quantitative yield of p-methoxytriphenylchloromethane, \((\text{C}_6\text{H}_5\text{O})_2\text{C}(\text{Cl})\text{C}_6\text{H}-\text{OCH}\), white leaflets, m.p. 122-123°. The chloromethane lost methyl chloride when heated at 180-200° and gave diphenyl-p-quinomethane, brownish-yellow tablets, m.p. 167-168°. Molecular weight determination and quantitative determination of the methyl chloride evolved in the reaction supported the correctness of the quinomethane structure. The quinomethane yielded quantitatively p-hydroxytriphenylmethane when reduced with zinc-glacial acetic acid and p-hydroxytriphenylearbinol when boiled with 70% acetic acid.

Bistrzycki, A. and Nowakowski, L.
**The Condensation of Benzilic Acid with Phenols.**

p-Hydroxytriphenylacetic acid, colorless leaflets, m.p. 212° was prepared by mixing 23 g. (1 mole) of benzilic acid, 115 ml. benzene,
and 11 g. (1 mole) of phenol, and then adding in one portion, 27 g.
staninic chloride (2 moles). The mixture was heated 15 minutes on the
steam bath, then shaken with water, made alkaline with sodium bisarbo-
nate solution, and filtered. Acidification of the aqueous layer gave
a yellow precipitate which collected and crystallised from dilute alco-
hol.

m-Cresol and bensilic acid gave m-tolylidiphenylacetic acid lactone,
white needles, m.p. 126°, and the accompanying product 4-hydroxy-2-
 methylphenylacetic acid; p-cresol and bensilic acid gave p-tolylidiphenylacetic acid lactone, pale yellow prisms, m.p. 130°; similarly
o-cresol gave p-hydroxy-o-tolylidiphenylacetic acid lactone, colorless
plates, m.p. 190°.

Edwards, G. A., Perkin, W. H., Jr., and Stoyle, F. W.
New Synthesis of the Mesonines. XXXI.

The preparation of 2,3-dimethoxybenzoic acid (o-veratric acid)
was best carried out in the following way. o-Veratraldehyde (30 g.)
was kept boiling under a reflux condenser with water (300 ml.) and
potassium bicarbonate (35 g.) while a hot solution of potassium per-
manganate (22 g.) in water was added slowly. The cooled and filtered
solution, on acidification, yielded o-veratric acid, m.p. 120-122°.

Fischer, E. and Fischer, O.
Triphenylmethane and Rosaniline.
Ann., 194: 260 (1878)

Triphenylacetonitrile is obtained in an almost quantitative yield
by heating pure triphenylchloromethane with an excess of mercuric chlo-
ride at 150-170°. The cold, powdered melt is extracted with boiling
benezene, filtered free of mercuric salts and the light brown filtrate carefully treated with ligroin. The greater part of the impurities present is thus precipitated as dirty-yellow flocks. When the clear filtrate is concentrated, the nitrile separates in a rather pure condition. Recrystallization of the substance from hot glacial acetic acid gives colorless, long, three-sided prisms, m.p. 127.5°.

Horner, L., Spietschka, E., and Gross, A.
The Course of the Rearrangement of Diasoketones, o-Quinonediazides and Acid Asides.
Ann., 573: 17-30 (1951)

Anibensil, C₆H₄OO-C(C₆H₄)₂N₂, and tetrachloro-o-benzoquinone reacted in the presence of ultraviolet light and gave an adduct, m.p. 187-188°, the structure of which was established by cleavage with 2 N sodium hydroxide and methylation of the phenolic fragment with diazomethane. There were thus obtained tetrachloroveratrole (II) and benzoic acid (III), cleavage products which correspond to the structure of diphenyl-(3,4,5,6-tetrachloro-2-hydroxyphenoxy)-acetic acid lactone (I). Diphenylketene and tetrachloro-o-benzoquinone also reacted to give the adduct, I.

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\text{O} & \quad \text{O} \\
\text{Cl} & \quad \text{Cl} \\
\text{(C₆H₅)₂} & \quad \text{OCH₃} \\
\text{Cl} & \quad \text{Cl} \\
\text{OCH₃} & \quad \text{HO-C(C₆H₅)₂} \\
\text{I} & \quad \text{II} & \quad \text{III}
\end{align*}
\]

Dimethyketene and tetrachlоро-o-benzoquinone gave a colorless adduct, m.p. 148-149°, the structure of which could not be elucidated.
Aldoketenes did not give adducts with tetrachloro-o-benzoquinone.

Hurd, C. D., and Thomas, C. L.
The Interaction of Ketene with Aromatic Aldehydes and Its Bearing on the Perkins Reaction.

In the presence of a little potassium acetate, ketene reacts exothermically with aromatic aldehydes (benzaldehyde, furfural, m-nitrobenzaldehyde). The primary product was considered to be a non-isolable hydroxyketene, Ar-\(\text{CHOH}\cdot\text{CH}=\text{CO}\), but the chief product isolated was a mixed acetic anhydride Ar-\(\text{CH}=\text{CO}\cdot\text{O}=\text{COCH}_3\). The presence of a \(\beta\)-lactone, Ar-\(\text{CH} \cdot \text{CH}_2\), was indicated in lesser amounts, inasmuch as moderate heating of the reaction product gave rise to arylethylenes, Ar-\(\text{CH} \cdot \text{CH}_2\).

Kauffman, H. and Pannwitz, P.
Triphenylecarbinols. III.
Ber., 45: 766-786 (1912)

Formic acid reduces many triphenylecarbinols so quickly and smoothly that it is the reagent of choice when a pure preparation is desired. When 2,4-dimethoxytriphenylecarbinol is boiled with formic acid, the red color of the solution is discharged in about five minutes, and on cooling the 2,4-dimethoxytriphenylmethane crystallizes. The product is almost pure and is obtained in good yield. The formic acid is oxidized to carbon dioxide, and the course of the reaction can be followed easily by measuring the evolution of the gas. Many carbinols evolve carbon dioxide very quickly, yet, others do so slowly. Triphenylecarbinol belongs in the latter group, giving, after one hour's boiling with formic acid, a mixture of the methane and the carbinol.
Liebig, H. v.
Triphenylmethane - Carboxylic Acids.
Ber., 41: 1645-1648 (1908)

Equimolecular quantities of bensilic acid and resorcinol are heated together without solvent at 180-200° for 1.5-2.0 hours. The melt is extracted with boiling water and the residue crystallised from benzene to give an almost quantitative yield of 2,4-dihydroxy-triphenylacetic acid lactone. This simple procedure allows one to eliminate the use of sulfuric acid or stannic chloride as condensation catalysts and permits the synthesis of o-hydroxyacids in the cases where condensation catalysts give only p-hydroxyacids.

Under the same conditions, phenol and bensilic acid gave 80-90% of p-hydroxytriphenylacetic acid and 10-20% o-hydroxytriphenylacetic acid. o-Cresol gave 2-hydroxy-3-methyltriphenylacetic acid, m.p. 136-137. m-Cresol gave 2-methyl-4-hydroxytriphenylacetic acid and 2-hydroxy-4-methyltriphenylacetic acid lactone. p-Cresol gave beside the lactone, m.p. 132°, and p-hydroxytriphenylacetic acid, an alkaline-soluble ether of the acid, 2,2-methyl-4,4-hydroxytriphenylacetic acid-5,5-ether, m.p. 245°. Thymol gave p-hydroxytriphenylacetic acid and 2-hydroxy-3-methyl-6-isopropyltriphenylacetic acid lactone. Hydroquinone gave 2,5-dihydroxytriphenylacetic acid lactone, m.p. 200-201°. Catechol gave 2,3-dihydroxytriphenylacetic acid lactone, white leaflets, m.p. 136°.

Perkin, W. H., Jr. and Robinson, R.
Some Derivatives of o-Vanillin. CCCXII.

Methyl 2,3-dimethoxybenzoate, m.p. 47°, was prepared by boiling 2,3-dimethoxybenzolic acid (o-veratric acid) with 5% methanolic H₂SO₄.
The ester crystallized in a mass of colorless rhombs.

Richtschnain, W. and Nippus, P.
Substitution Reactions with Metalorganic Compounds. Part IV.
Reaction of the Grignard Reagent with Aromatic Nitriles Containing Methoxyl Groups.

To the Grignard reagent prepared from 4 g. of magnesium and 23.5 g. of bromobenzene in 100 ml. of ether was added 16.2 g. of 2,3-dimethoxybenzophenone, and the mixture was boiled on the steam bath for 4 hours. On working up the reaction product there were obtained, along with traces of an alkali-soluble substance and starting material, 13.4 g. of 2,3-dimethoxytriphenylcarbinol, colorless prisms, m.p. 106°.

The Grignard reagent prepared from 9 g. of magnesium, 48 g. of bromobenzene and 125 ml. of ether was treated with 22 g. of ethyl 2,3-dimethoxybenzoate, and the mixture was boiled for 4 hours on the steam bath. There were isolated, along with some diphenyl and 2,3-di-methoxybenzophenone, 14.9 g. of 2,3-di-methoxytriphenylcarbinol.

Spencer, E. Y. and Wright, G. F.
The Action of Diazomethane on Lactones and Lignins.

When 1.46 g. (0.01 mole) of coumarin (I), (purified by decomposition of the bisulfite addition product) was dissolved in 30 ml. absolute methanol and treated at 0° with diazomethane from 6.2 g. of nitrosomethylurethan, the yellow color disappeared in one week. One-tenth of the original amount of CH₂N₂ was added, which persisted after 3 days. After filtration from diazomethane polymer, the solution was evaporated under 3 mm. vacuum to leave an oil. When this was dissolved in ether, 0.7 g. of yellow crystals crystallized, 30% of the theoretical amount of 3-carbomethoxy-4-(o-methoxyphenyl)-
pyrasoline (II). No further yield could be obtained from the residual oil. The crystals melted at 94.5° after two recrystallizations from ether.

\[
\text{I} \quad \rightarrow \quad \text{II}
\]

Staudinger, H. and Klever, W.
Ketenes. II. Dimethylketene.
Ber., 39: 968-971 (1906)

Dimethylketene was prepared from bromoisobutyryl bromide and zinc in dry ethylacetate as described. With p-benzoquinone, dimethylketene gave a colorless product, m.p. 104.5°, which regenerated the quinone easily.

Staudinger, H. and Klever, H. W.
Ketenes. VI. Ketene
Ber., 41: 594-598 (1908)

Ketene, \( \text{CH}_2=\text{C} = \text{O} \), did not add to p-benzoquinone, benzylideneaniline, or dibenzalacetone. The reactions were carried out in concentrated, ethereal solutions of the gaseous ketene. Ketene differs from diphenylketene, in that it does not add to the \( \text{C} = \text{O} \), or to the \( \text{C} = \text{N} \) bond.

Staudinger, H.
Ketenes. VIII. The Preparation of Quinonoid Hydrocarbons from Diphenylketene.
Ber., 41: 1355-1363 (1908)

One molecule of diphenylketene added to one molecule of p-benzo-
quinone and gave the stable β-lactone of 4-diphenyl-carboxymethyl-quinol. The β-lactone lost carbon dioxide when heated and gave di-
phenyl-p-quinomethane. When the β-lactone was heated at its melt-
ing point, or in xylene, carbon dioxide was evolved, and p-benzoqui-
none was regenerated, with the consequent formation of tetraphenyl-
p-quinodimethane. The following mechanism was postulated for the
reaction. The β-lactone decomposes into diphenylketene and p-benzo-
quinone, and the ketene adds to the free carbonyl group of the un-
changed β-lactone. The di-β-lactone which is formed decomposes im-
mediately, with loss of carbon dioxide, into tetraphenyl-p-quinodi-
methane. However, no splitting off of diphenylketene could be proved.

The direct formation of tetraphenyl-p-quinodimethane was observed
by reacting two moles of diphenylketene with one mole of p-benzoqui-
none. No di-β-lactone could be obtained, even by working in the
cold. α-Naphthoquinone and diphenylketene gave tetraphenyl-α-naphtho-
quinodimethane, and similarly, p-xyloquinone gave tetraphenyl-p-xylo-
quinodimethane. Anthraquinone gave only a weak reaction with di-
phenylketene, and tetrachloro-p-benzoquinone did not react. Phenyl-
isoncyanate and phenylisothiocyanate, substances similar in structure
to diphenylketene, did not react with p-benzoquinone.

Staudinger, H.
Ketenes. IX. Colored Hydrocarbons from Diphenylketene.
Ber., 41: 1493-1500 (1908)

The addition of diphenylketene to dibenzalacetone proceeded slow-
ly in the cold, but more quickly in boiling toluene. The primary ad-
dition product, the β-lactone, could not be isolated; only its decom-
position product, 3-diphenylmethylene-1,5-diphenylpentadiene-1,4, was
obtained. This compound, \( \text{C}_6\text{H}_5\text{CH} = \text{CH} \), \( \text{O} \text{C} \text{C}_6\text{H}_5 \), may be regarded as an "open" fulvene since the arrangement of its double bonds is similar to that in diphenylfulvene, \( \text{C}_6\text{H}_5\text{CH} = \text{CH} \), \( \text{O} \text{C} \text{C}_6\text{H}_5 \). The yellow color of the pentadiene arises as in the real fulvenes, from the crossed double bonds. The "open" fulvenes are auto-oxidizable, but much less so than the "ring" fulvenes. The primary addition product of oxygen to the pentadiene could not be obtained, nor could the pentadiene be reduced by aluminum amalgam.

Dianisalacetone, p-dichlorodibensalacetone, and dicinnamylideneacetone also reacted with diphenylketene and gave "open" fulvenes which were yellow. Under the same conditions phorone and the methyl and ethyl esters of ketopentadienedicarboxylic acid did not react.

Staudinger, H. and Buchwits, J.

Diphenylketene, in the form of its solid quinoline derivative, was heated with equivalent quantities of various ketones at 130° for 1.5 hours, and the velocity of the reaction was determined by the amount of carbon dioxide eliminated. The reaction proceeds in two stages: the first is the formation of the \( \beta \)-lactone, \( (\text{R})_2\text{C} = \text{O} \), \( \text{C}_6\text{H}_5 \), and the second is the decomposition of the lactone into carbon dioxide and an unsaturated hydrocarbon, \( (\text{R})_2\text{C} = \text{C} \text{C}_6\text{H}_5 \). It was assumed that the second reaction proceeds with an infinitely greater velocity than the first.

The following results were obtained with the ketones, the
formulas of which are given below:

<table>
<thead>
<tr>
<th>Ketone</th>
<th>% Ketone Reacted</th>
</tr>
</thead>
<tbody>
<tr>
<td>R(^{1})'-CO-CH=CH-C(_6)(_5)</td>
<td>82.3</td>
</tr>
<tr>
<td>R(^{1})'-CO-CN</td>
<td>76.3</td>
</tr>
<tr>
<td>R(^{1})'-CO-OH</td>
<td>65.9</td>
</tr>
<tr>
<td>R(^{1})'-CO-C(_6)(_5)</td>
<td>42.5</td>
</tr>
<tr>
<td>R(^{1})'-CO-CH(_3)</td>
<td>32.8</td>
</tr>
<tr>
<td>R(^{1})'-CO-Cl</td>
<td>5.5</td>
</tr>
<tr>
<td>R(^{1})'-CO-O-CO-CH=CH-C(_6)(_5)</td>
<td>5.3</td>
</tr>
<tr>
<td>R(^{1})'-CO-O-C(_2)(_5)</td>
<td>5.4</td>
</tr>
<tr>
<td>R(^{1})'-CO-N=C((_6)(_5))(_2)</td>
<td>0.0</td>
</tr>
<tr>
<td>R(^{2})'-CO-C(_6)(_5)</td>
<td>55.6</td>
</tr>
<tr>
<td>R(^{2})'-CO-CH(_3)</td>
<td>20.7</td>
</tr>
<tr>
<td>R(^{1})=-CH=CH-C(_6)(_5) and R(^{2})=-CH=CH=CH-C(_6)(_5)</td>
<td></td>
</tr>
</tbody>
</table>

The influence of a double linking on the reactivity of the ketone was not marked, but the results indicate that the reactivity of a ketone with diphenylketene is least when an \(-\text{NR}_{2}\) or \(-\text{OR}\) group is attached to the carbonyl group, that is, carboxylic derivatives. The carbonyl group is much more reactive, on the other hand, when attached to \(-\text{H}, -\text{CH}_{3}\), or \(\text{C}_{6}\)\(_5\)- and is most reactive when unsaturated groups, for example, \(-\text{C}==\text{N}\) and \(\text{C}_{6}\)\(_5\)\(\text{CH}=\text{CH}_{2}\), are present. Benzylidenecacetone and diphenylketene gave 1,1,2,4-tetraphenylbutadiene and 3-benzoyl-1,1,2-triphenylcyclobutanone (I):

\[
\text{I. } \quad \begin{array}{c}
\text{C}_{6}\text{H}_{5}-\text{CO-CH} \\
\text{CH(C}_{6}\text{H}_{5})
\end{array} \quad \begin{array}{c}
\text{CO} \\
\text{O(C}_{6}\text{H}_{5})_{2}
\end{array}
\]

Cinnamylidenecacetophenone and diphenylketene gave 1,1,2,6-tetraphenylhexatriene-1,3,5 and 3-benzoyl-1,1-diphenyl-2-styryl-4-cyclobutanone
C₆H₅CH=CH·CH=C(OC₆H₅)₂·O=C. Cinnamoylformonitrile and diphenylketene yielded α-diphenyl-α-styrylacrylonitrile,

C₆H₅CH=CH·C(OC₆H₅)₂. Definite products could not be isolated by heating diphenylketene with either benzylidenacetone, cinnamylidenacetone, methyl cinnamate, or cinnamodiphenylamide.

Staudinger, H. and Endle, R.
Ketenes. XXI. The Similarity of Isocyanates to Ketenes.
Ber., 50: 1044 (1917)

Phenylisocyanate and p-benzoquinone, heated together in a sealed tube at 190°C for fourteen hours, gave impure p-benzoquinonediphenyl-dimine, m.p. 175-180. Fluorenone did not react under similar conditions.

Staudinger, H. and St. Beresa
Ketenes. III. The Reaction of Diphenylketene with Quinones.

Diphenylketene reacts with quinones in much the same manner as with unsaturated ketones. Almost any quinone in which the two ortho-positions with respect to one carbonyl group are unsaturated reacts in the cold with a mole of diphenylketene, yielding β-lactones. Benzoquinone, toluquinone, chlorobenzoquinone and m-dichlorobenzoquinone react in this manner. When there are substituents in the positions ortho to both carbonyl groups, for example, xyloquinone, p-dichlorobenzoquinone, and trichloroquinone, the reaction proceeds very slowly. When all four ortho-positions are substituted, as in chloroanil, the reaction is completely inhibited. These results may be due to "steric hindrance", or to a diminution in the basic character of the oxygen atom of the carbonyl group, but the authors suggest
another explanation. It is known that the unsaturated character of the carbonyl group is increased by the presence of an olefinic linkage, and it is also known that a chlorine substituent diminishes the unsaturated nature of an olefin. The ethylenic bonds in chloroanil are thus less reactive than those in p-benzoquinone, and therefore have a smaller effect in increasing the unsaturated character of the carbonyl groups. In other words, the carbonyl groups in chloroanil are somewhat more saturated than those in p-benzoquinone. 1,4-Naphthoquinone yields a β-lactone less readily than p-benzoquinone, and anthraquinone does not react in the cold with diphenylketene. The β-lactones are quinol derivatives and give the usual carbonyl reactions, e.g., phenylhydrazones which in turn yield aso-derivatives. When the solid β-lactone from p-benzoquinone is exposed to sunlight, or when its benzene solution is boiled in bright sunlight, molecular rearrangement occurs, and the β-lactone of 2,5-dihydroxytriphenylacetatic acid is formed by wandering of the alkyl group. This rearrangement occurs in the absence of water, and is not, therefore, due to addition and subsequent removal of water.

Thiele, J. and Balhorn, H.
Quinonoid Hydrocarbons.
Ber., 37: 1463-1470 (1904)

Dimethyl terephthalate was added to ethereal phenylmagnesium bromide solution to give the dimethyl ether of tetraphenyl-p-xylyleneglycol, \( (C_6H_5)_2\, O(CH_3)-C_6H_4-(OCH_3)-O(C_6H_5)_2 \), m.p. 181-182.5°. This compound was converted into tetraphenyl-p-xylylenedibromide, m.p. 270-272°, \( (C_6H_5)_2\, O(Br)-C_6H_4-(Br)-O(C_6H_5)_2 \), by treatment with a solution of
bromine in glacial acetic acid. Boiling the bromide in benzene (absence of light) with molecular silver gave tetraphenyl-p-quinodimethane, orange-red needles, m.p. 239-242.

Weygand, C.

Preparation of α-Hydroxybenzophenone.—A mixture of 0.62 g. of 2-methoxybenzophenone, 3.1 g. of aluminum bromide, and 27 ml. of benzene is boiled under a reflux for 4 hours. The reaction mixture is cooled, excess hydrochloric acid is added, the layers are separated, and the aqueous layer is extracted with ether. The phenol is extracted from the combined ether-benzene extracts with 2 N sodium hydroxide, and the alkaline solution is added slowly to hydrochloric acid. After extraction of the phenol with ether and evaporation of the ether, 0.74 g. (96%) of oily α-hydroxybenzophenone is obtained.

Willstatter, R. and Muller, F.
Two Modifications of α-Benzquinone.
Ber., 41: 2580-2586 (1908)

The silver oxide used in the preparation of α-benzoquinone by the oxidation of catechol must not only be carefully washed with water twelve times, but must be dried by washing with acetone six times and then with anhydrous ether six times. The preparation of the colorless modification of α-benzoquinone was carried out by suspending 1.5 g. of silver oxide, and 1.5 g. of fused, powdered sodium sulfate in 7 ml. of anhydrous ether and adding with vigorous shaking a solution of 0.07-0.08 g. of catechol dissolved in 3 ml. of anhydrous ether. After further shaking, 15 seconds, the mixture was filtered through
a layer of fused, powdered sodium sulfate and the bright green filtrate was immediately treated with an equal volume of petroleum ether. After a few seconds a voluminous precipitate of colorless prisms of o-benzoquinone separated. This colorless, labile modification (I) of o-benzoquinone is immediately transformed into the red modification (II) when brought into contact with air, but the transformation is slow enough to observe under the microscope. The formation of o-benzoquinone may be expressed by the reaction scheme given below.

Willstatter, R., and Muller, H. E.
Chloroderivatives of Catechol and of o-Benzoquinone.
Ber., 44: 2187-2188 (1911)

Finely powdered o-benzoquinone dissolves quickly in 2% ethereal hydrochloric acid with decolorization. A quinhydrone is not formed, but a little polymeric quinone settles out as an insoluble powder. The polymer possesses the same percentage composition as does the o-benzoquinone, but shows none of its characteristic reactions. Apparently the yellow compound is a dimer similar to those obtained in the studies carried out earlier with homologous o-benzoquinones.
DIAZOKETONES AS REAGENTS FOR
THE IDENTIFICATION OF ORGANIC ACIDS
THEORETICAL DISCUSSION
This work is concerned with the development of a satisfactory method for the use of dianoketones in the preparation of phenacyl esters which are useful derivatives for the characterization and identification of organic acids.

It was found that the cupric chloride - catalysed decomposition of p-bromo- and p-phenyl-\kappa-diazoacetophenone in dioxane solution in the presence of an organic acid yielded the expected phenacyl esters.

The p-bromo- and p-phenylphenacyl esters of eleven representative organic acids have been prepared and their melting points compared with values obtained in the literature. With two exceptions the melting points for the esters prepared from the dianoketones were identical with or slightly higher than those prepared from the phenacyl halides.

When diazoacetophenone was catalytically decomposed by cupric chloride in the absence of organic acids, dibenzoylethylene was obtained.

Experiments designed to yield phenylketene, or its dimer, by the catalytic decomposition of diazoacetophenone were not successful.
It is usually desirable and in some cases it is necessary to confirm the identification of an organic acid by means of a solid derivative. Solid esters are useful for characterizing organic acids, but with the exception of a number of methyl esters, few esters prepared from the commonly used alcohols are solids. One can then turn profitably to the phenacyl or the substituted phenacyl esters, the majority of which are solid substances.

The p-bromophenacyl and p-phenylphenacyl esters of a large number of organic acids melt in the convenient range of 50-200 °C., and their averaged melting points are higher than that found for the corresponding p-nitrobenzyl esters. The melting points of the p-bromo- and p-phenylphenacyl esters are such that they compare favorably with a number of other derivatives of carboxylic acids.

The phenacyl esters are prepared by treating the salts of the acids with the corresponding phenacyl halides. This method has the advantage that it does not require anhydrous conditions for the formation of the esters.

\[ \text{RCOONa} + \text{BrCH}_2\text{COAr} \rightarrow \text{RGOCH}_2\text{COAr} \]

The preparation of phenacyl esters from the phenacyl halides is subject to two serious shortcomings. First, the reaction requires at least an hour's heating for each carboxyl group present in the acid, and second, the phenacyl halides are disagreeable to use because of their lachrymatory properties. Even the crystalline esters prepared from phenacyl halides frequently adsorb enough halide to cause considerable discomfort. If these shortcomings could be circumvented by the use of other methods of preparation, whereby the use of lachrymators was avoided, the intrinsic value of these solid esters as derivatives could be substantially
increased. A review of the reactions of diazoketones has revealed a method for the preparation of phenacyl esters which apparently achieves this end.

Diazoketones lose nitrogen when catalytically decomposed, and if no opportunities are present for reaction with protonic reagents, the unstable radical which is formed may couple with itself to form an ethylenic compound:

\[ 2\text{RCOCHN}_2 \rightarrow 2\text{N}_2 + 2(\text{RCOCH}) \rightarrow \text{RCOCH}_2\text{CHOOR} \]

If an inorganic acid such as hydrochloric acid is present during the decomposition of diazoketones, \( \alpha \)-chloroketones are formed:

\[ \text{RCOCHN}_2 + \text{HCl} \rightarrow \text{RCOCH}_2\text{Cl} + \text{N}_2 \]

Recently Newman and Beale have shown that \( \beta \)-phenethyl diazomethyl ketone yields di-(4-phenyl-2-ketoethyl) sulfate when treated with concentrated sulfuric acid. With the aid of boron trifluoride as a catalyst they were able to obtain \( \alpha \)-alkoxyacetophenones when diazoacetophenone was decomposed in the presence of alcohols:

\[ 2\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{COCHN}_2 + \text{H}_2\text{SO}_4 \rightarrow (\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{COCH})_2\text{SO}_4 + 2\text{N}_2 \]

\[ \text{C}_6\text{H}_5\text{COCHN}_2 + \text{ROH} \rightarrow \text{RCOCH}_2\text{OR} + \text{N}_2 \]

Bradley and co-workers observed the formation of phenacyl acetate when diazoacetophenone was warmed in glacial acetic acid:

\[ \text{C}_6\text{H}_5\text{COCHN}_2 + \text{CH}_3\text{CO}_2\text{H} \rightarrow \text{C}_6\text{H}_5\text{COCH}_2\text{COCH}_3 + \text{N}_2 \]

These reactions of diazoketones suggested that the decomposition of \( p \)-bromo- and \( p \)-phenyl-\( \alpha \)-diazoacetophenones in the presence of an
aliphatic or an aromatic acid might afford a convenient method for the preparation of \( p \)-bromo- and \( p \)-phenyl-phenacyl esters:

\[
p-\text{Br}-\text{C}_\text{6}H_4\text{-COCH}_2\text{H} + \text{RCO}_2\text{H} \rightarrow p-\text{Br}-\text{C}_\text{6}H_4\text{-COCH}_2\text{-O-COR} + \text{N}_2
\]

\[
p-\text{C}_\text{6}H_5\text{-C}_\text{6}H_4\text{-COCH}_2\text{H} + \text{RCO}_2\text{H} \rightarrow p-\text{C}_\text{6}H_5\text{-C}_\text{6}H_4\text{-COCH}_2\text{-O-COR} + \text{N}_2
\]

Preliminary experiments were carried out by Keeling, who showed that \( p \)-bromo-\( \alpha \)-diazacetophenone yielded the phenacyl esters when the diazoketone was heated with the acids in dioxane solution and in the presence of a small amount of cupric chloride. The cupric chloride served to accelerate greatly the decomposition of the diazoketone, making possible complete reaction in a few minutes.

The details of the development of these exploratory observations into a useful, reliable method for the preparation of phenacyl esters from diazoketones have appeared in published form elsewhere. They also form the major portion of the work on diazoketones described here subsequently.

\( p \)-Phenyl-\( \alpha \)-diazacetophenone, which had not been previously described, was prepared from \( p \)-phenylbenzoyl chloride and diazomethane. The diazoketone was found to be a stable, solid substance which easily decomposed, catalytically, however, in the presence of an organic acid to yield phenacyl esters.

The \( p \)-bromophenacyl and the \( p \)-phenylphenacyl esters of eleven representative organic acids were then prepared from the corresponding diazoketones and their melting points compared with values obtained from the literature. The results are summarized in Table I. It is observed that, with the exception of \( p \)-bromophenacyl formate and \( p \)-phenylphenacyl succinate, the melting points of the esters prepared from the \( \alpha \)-diazacetophenones are identical with, or slightly higher than, the melting point.
of the esters obtained from the sodium salts of acids and phenacyl halides.

p-Bromophenacyl formate and p-phenylphenacyl succinate were prepared from the requisite phenacyl bromides and were found to have exactly the same melting points as the same phenacyl esters prepared from p-bromo-α-diazoacetophenone and p-phenyl-α-diazoacetophenone. Repeated crystalli-

Table I.

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Formic</td>
<td>133.5-134.5</td>
<td>135.2 (11)</td>
<td>75-75.5</td>
<td>74 (14)</td>
</tr>
<tr>
<td>Acetic</td>
<td>85-86</td>
<td>86 (11)</td>
<td>110.5-111</td>
<td>111 (14)</td>
</tr>
<tr>
<td>Propionic</td>
<td>63.5-64</td>
<td>63.4 (11)</td>
<td>103-103.5</td>
<td>102 (14)</td>
</tr>
<tr>
<td>n-Butyric</td>
<td>63.5-64</td>
<td>63 (11)</td>
<td>82-83</td>
<td>82 (15)</td>
</tr>
<tr>
<td>Isovaleric</td>
<td>68</td>
<td>68 (11)</td>
<td>75.5-77</td>
<td>76 (14)</td>
</tr>
<tr>
<td>Benzoic</td>
<td>118.5-119</td>
<td>119 (12)</td>
<td>167-167.5</td>
<td>167 (14)</td>
</tr>
<tr>
<td>Salicylic</td>
<td>140</td>
<td>140 (12)</td>
<td>148.5-149</td>
<td>148 (16)</td>
</tr>
<tr>
<td>Cinnamic</td>
<td>145.5-146</td>
<td>145 (12)</td>
<td>182-183.5</td>
<td>182.5 (14)</td>
</tr>
<tr>
<td>p-Nitrobenzoic</td>
<td>136.5-137</td>
<td>136.5 (13)</td>
<td>181.5-182.5</td>
<td>182 (16)</td>
</tr>
<tr>
<td>p-Toluic</td>
<td>153</td>
<td>153 (12)</td>
<td>165</td>
<td>165 (14)</td>
</tr>
<tr>
<td>Succinic</td>
<td>209.5-210</td>
<td>211 (12)</td>
<td>204-206</td>
<td>208 (14)</td>
</tr>
</tbody>
</table>

zation of these esters (prepared by both methods) from various solvents only served to increase the amount of decomposition as was deduced from
the progressively lowered melting point and the yellow color of the crys-
tal melt.

When diazoacetophenone was catalytically decomposed with cupric chlo-
ride in benzene solution in the absence of organic acids, a 60% yield of
dibenzoylethylene was obtained. The decomposition was carried out using
only 9 mg. of catalyst per gram of diazoketone.

An attempt was made to obtain phenylketene, or its dimer, by decom-
posing diazoacetophenone in the presence of cupric chloride in very dilute,
boiling benzene solution and also by catalytically decomposing the solid
diazoketone in vacuum. Both experiments gave only oily liquids from
which no crystalline material could be obtained. When the decomposition
of the diazoketone was repeated in vacuum, but with alternate chilling
and warming, a slow but smooth reaction set in which yielded a small
amount of dibenzoylethylene.
EXPERIMENTAL
Diazomethane. — This substance was prepared from N-nitroso-\(\beta\)-methylaminoisobutylmethyl ketone and sodium cyclohexoxide in anhydrous ether according to the directions of Organic Syntheses. The yield averaged from many preparations was 80% of theory.

\[ \text{p-Bromobenzoyl Chloride.} \quad - \quad \text{A mixture of 31.1 g. (0.155 mole) of finely divided p-bromobenzoic acid and 33.1 g. (0.159 mole) of phosphorus pentachloride was placed in a one liter, round-bottomed flask fitted with a reflux condenser protected by a calcium chloride drying tube. The mixture was warmed for a few minutes on the steam bath until a spontaneous reaction set in and allowed to heat for one hour. Phosphorus oxychloride was removed by distilling at the water aspirator, a wad of glass wool was put into the flask, and the crude acid chloride was distilled with a free flame. After crystallization from low-boiling petroleum ether, there was obtained 22.1 g. (65%) of fine, white needles of p-bromobenzoyl chloride, m.p. 40-41 \circ.} \]

\[ \text{p-Phenylbenzoyl Chloride.} \quad - \quad \text{p-Phenylbenzoic acid, 19.8 g. (0.1 mole), was suspended in 215 ml. of dry benzene and treated with 27.1 g. (0.13 mole) of phosphorus pentachloride on the steam bath for one hour. The hot solution was treated with decolorizing charcoal and filtered through a small, glass frit-bottomed Buchner funnel protected by a calcium chloride drying tube. Benzene and phosphorus oxychloride were removed by distilling at the water aspirator, and the residue was crystallized from high-boiling petroleum ether. There was obtained 20.1 g. (93%) of fine white needles of p-phenylbenzoyl chloride, m.p. 113.5-115 \circ.} \]

\[ \text{p-Bromo-diazoacetophenone.} \quad - \quad \text{A solution of 8.8 g. (0.04 mole) of p-bromobenzoyl chloride in 40 ml. of dry ether was added with stirring} \]

over a period of 20-30 minutes to an ice-cold ethereal solution (400 ml.) containing 0.10 mole of diazomethane. The reaction mixture was kept at 0-5° for 3-9 hours, allowed to stand at 25° for three hours, and the solvent evaporated in vacuum. The residue was crystallized from an ether— low-boiling petroleum ether mixture yielding 8.3 g. (92%) of fine, yellow needles, m.p. 123.5-124° (gas evolution).

Analysis: Caled. for \( C_{8}H_{7}ON_{2}Br \): C, 42.7; H, 2.2. Found: C, 42.8; H, 2.2.

\( \text{p-Phenyl-\( \alpha \)} \)-diazooacetophenone was prepared from \( \text{p-phenylbenzoyl chloride} \) and diazomethane in 95% yield by much the same method as that given for \( \text{p-bromo-\( \alpha \)} \)-diazooacetophenone, except that the acid chloride was dissolved in 120 ml. of a solution composed of 30 ml. of dry ether and 90 ml. of dry benzene. The diazoketone crystallized from benzene in fine, pale yellow needles, m.p. 117.5-118.5° (gas evolution).

Analysis: Caled. for \( C_{8}H_{10}ON \): C, 75.7; H, 4.5. Found: C, 76.0; H, 4.7.

Preparation of Phenacyl Esters of Organic Acids. — Three millimoles of the acid was dissolved, by warming if necessary, in 10 ml. dioxane placed in an 8 inch test-tube. The mixture was cooled to room temperature and 2 millimoles of the diazoketone added. After the diazoketone had dissolved, 2-4 mg. solid cupric chloride was added and the mixture warmed until the evolution of nitrogen was steady. Heating was discontinued when the clear yellow solution became light brown in color (an intermediate change to light green was usually observed) and a vigorous evolution of gas set in. After a few minutes the evolution of gas ceased, and the solution was boiled for one minute and then poured into a well-
stirred mixture containing 100 ml. water, 5 ml. 10% aqueous potassium carbonate, and some ice. The crystals of the ester which formed were collected on a Witt filter plate, washed with a liberal quantity of water, sucked dry, and crystallized from ethyl alcohol. A preliminary filtration was made to remove cupric chloride and decolorizing charcoal which was used when necessary. Phenacyl esters of the lower aliphatic acids were best crystallized from aqueous ethyl alcohol, while benzene or acetone was usually found to be more satisfactory for the phenacyl esters of aromatic acids. Dioxane was found to be suitable for crystallizing the phenacyl succinates. The yield of crude air-dried esters varied from 61% to 100%, depending upon the acid used.

20

of Diaoacetophenone. — To a well-stirred, ice-cold solution of diazomethane, 5.0 g. (0.12 mole) in 365 ml. of dry ether, and 12.2 g. (0.12 mole) of anhydrous triethylamine was added (20-30 minutes) 16.9 g. (0.12 mole) of freshly distilled benzoyl chloride dissolved in 25 ml. of dry ether. The mixture was stirred at 4-5° for approximately 11 hours and filtered free of triethylamine hydrochloride. The weight of triethylamine hydrochloride recovered, 14.4 g. (0.11 mole), corresponded to 88% of theory. Ether was removed by evaporating at reduced pressure, and when the solution had been concentrated to a small volume and chilled to -15 to -20°, 14.6 g. of crude diazoketone separated. The material was recrystallized from a mixture of low- and high-boiling petroleum ethers (3:1), yielding 13.7 g. (73%) of bright yellow needles, m.p. 48-49.5°.

Dibenzoylethylene. — A solution of 4.4 g. (0.030 mole) diazoacetophenone in 30 ml. dry benzene was warmed with 40 mg. cupric chloride by means of a water bath maintained at 45° until a steady evolution of gas
was produced. The water bath was then removed and the reaction mixture cooled occasionally in an ice bath. After 20-30 minutes the evolution of gas had ceased, and the reaction mixture was warmed at 50-60° for a short time. Removal of the solvent under reduced pressure yielded 2.1 g. (60%) crude dibensoylethylene. After two crystallizations from ethyl alcohol, bright yellow needles were obtained, m.p. 109.5-110°. The following derivatives were prepared: Dibenzoylethane was obtained by reducing 100 mg. of dibensoylethylene with 0.5 g. of zinc dust in 7 ml. of glacial acetic acid. The crude ethane was precipitated by the addition of water and recrystallized several times from alcohol, yielding about 30 mg. of fine white crystals, m.p. 142-143°. 3,6-Diphenylpyridazine was obtained by treating 120 mg. of dibensoylethylene dissolved in 4.5 ml. of glacial acetic acid with an excess of hydrazine hydrate. The crude amine was precipitated by the addition of water and by chilling. Recrystallization from alcohol (decolorizing charcoal) yielded 40 mg. of colorless plates, m.p. 222-223°.

A similar experiment with diazoacetophenone and cupric chloride was carried out at a lower temperature (6°). A somewhat lower yield of the ethylenic compound was obtained, and irradiation of the mother liquors from which the compound crystallized yielded 10 mg. of silky, white needles of the higher melting isomer, m.p. 134°.

Cupric Chloride - Catalyzed Decomposition of α-Diazoacetophenone in Dilute Solution. — A solution of 1 g. (0.0064 mole) of α-diazoacetophenone in 25 ml. of dry benzene was slowly added over a period of two hours to 500 ml. of vigorously stirred and refluxed benzene containing 10 mg. of cupric chloride. The solution was filtered free of a small amount of amorphous material, and the filtrate was evaporated in vacuum.
There remained a small amount of red-brown, oily liquid from which no crystalline material could be isolated.

Cupric Chloride - Catalyzed Decomposition of Solid $\alpha$-Diazoacetophenone in Vacuum. — Solid $\alpha$-diazoacetophenone, 1.5 g. (0.0096 mole), and 5 mg. cupric chloride were warmed in a 50 ml. modified Claisen flask which was connected to one small (50 ml.) and one large (500 ml.) distilling flask, both of which were chilled in an ice-hydrochloric acid bath. The entire system was evacuated to 1 mm. pressure prior to the addition of the catalyst. An immediate reaction set in, and after a few minutes an oily, brown liquid was obtained which did not yield any crystalline material. The experiment was repeated with 1 g. of diazoketone and 2.3 mg. of cupric chloride, and the decomposition was controlled by alternate chilling and warming over a period of one and one-half to two hours. A small amount of reddish-brown oil remained in the reaction flask. The oil was taken up in ether and chilled to $-15^\circ$, precipitating a small amount of dibenzoylethylene.
SUMMARY
The cupric chloride-catalyzed decomposition of several \( \alpha \)-diazooacetophenones in dioxane solution in the presence of an organic acid yielded phenacyl esters. The \( p \)-bromo- and \( p \)-phenylphenacyl esters of eleven representative organic acids have been prepared by the use of two new reagents, \( p \)-bromo- and \( p \)-phenyl-\( \alpha \)-diazooacetophenone, and their melting points have been compared with values obtained from the literature.

In the absence of protonic reagents the cupric chloride-catalyzed decomposition of diazoacetophenone yielded dibenzoylethylene.
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ANNOTATED AND SELECTED

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Diazomethane and o-Nitro Compounds. II. N-Hydroxyisatin from o-
Nitrobenzoyl Chloride.
Ber., 60B: 1364-70 (1927) C.A., 21: 2897-2898 (1927)

The reaction of o-nitrobenzaoyl chloride and diazomethane affords
80% of the $\alpha$-diaz-o-nitroacetophenone, m.p. 105-106$^\circ$, light yellow,
becomes rapidly reddish-brown and weathers in air. It deflagrates
violently on dry distillation, evolves nitrogen with dilute acids,
and with HCl or HBr it gives N-hydroxyisatin and $\alpha$-NO$_2$C$_6$H$_4$COCH$_2$Cl
or the Br- analog.

Bradley, W., and Robinson, R.
CLIXIV. The Interaction of Benzoyl Chloride and Diazomethane to­
gether with a Discussion of the Reactions of the Diazenea,

Diazacetophenone undergoes quantitative and smooth decomposi­
tion when it is warmed with glacial acetic acid. The product was
isolated by ether extraction and crystallized from light petroleum
in tablets melting at 48-49$^\circ$. The melting point of the substance
was not depressed by admixture with an authentic sample of $\alpha$-ace­
toxyacetophenone.

Bradley, W., and Schwartsenbach, G.
Acylation of Diazomethane. Effects of Variations in the Conditions
on the Extent of Formation of Chloroacetophenone from Benzoyl Chlo­
ride.

C$_6$H$_5$CH$_2$COCl and CH$_2$N$_2$ in ether at -10$^\circ$ give a viscous oil which
decomposes at 90-100$^\circ$, evolves nitrogen and reacts with p-NO$_2$C$_6$H$_4$CO$_2$H
to give p-nitrobenzoyloxymethyl ketone, m.p. 120$^\circ$. p-NO$_2$C$_6$H$_4$-COCl
and CH$_2$N$_2$ give $\alpha$-diaz-p-nitroacetophenone, m.p. 116-117$^\circ$ which loses
nitrogen at 120-125$^\circ$. Similarly $\alpha$-diaz-3,4-diacetoxyacetophenone,
m.p. 76-77°, lemon yellow, was prepared from the corresponding acid chloride.

**Glibben, D. A. and Nierenstein, N.**
The Action of Diazomethane on some Aromatic Acyl Chlorides.

The acid chlorides were dissolved in dry ether and treated with an ethereal solution of diazomethane. The ether was removed and the residue fractionally distilled in vacuum. Chloromethylketones were the products.

**Grundmann, C.**
The Decomposition of Diazoketones.
*Ann.,* 536: 29-36 (1938)

α-Diazoacetophenone decomposes in the presence of cupric oxide to give trans-dibenzoylethylene (I), m.p. 110°. Similarly:

\[
\begin{align*}
C_6H_5CH_2COCH_2 & \rightarrow C_6H_5CH_2COCH=CHCOCH_2C_6H_5 + N_2 \\
CH_3COCH_2 & \rightarrow CH_3COCH=CHCOCH_3 + N_2 \\
C_6H_5COCH_2 & \rightarrow C_6H_5COCH=CHCOCH_2C_6H_5 + N_2 \\
C_6H_5CO(C_6H_5)N_2 & \rightarrow C_6H_5CO(C_6H_5)N=N=(C_6H_5)COOC_6H_5 + N_2 \\
C_6H_5COCH_2 & \rightarrow C_6H_5CO-CH-CH-COCH_3 + N_2 \\
\end{align*}
\]

The mechanism of the formation of cyclopropane derivatives from diazoketones is possibly similar to the formation of tricarboxycyclopropanes from diazoacetic esters:
For general purposes, the p-bromophenacyl esters are more useful for identification than the p-chloro- or the p-iodophenacyl esters. On comparing 18 of the p-bromophenacyl esters with the corresponding p-nitrobenzyl esters, the yields in both cases averaged 80%, while the average melting point of the p-bromophenacyl ester is 118.8° and that of the p-nitrobenzyl ester is 84.1°, giving 34.7° in favor of the former.

In every case, the p-bromophenacyl ester melted higher than the corresponding p-nitrobenzyl or phenacyl ester. p-Bromophenacyl bromide gave very poor results with dibasic acids, but for monobasic acids, especially those of the formic acid series, it gave better results than any other reagent thus far tried.

The p-halogen phenacyl esters were hydrolyzed to their corresponding alcohols; p-bromophenacyl alcohol melted at 136.6°. The alcohols are very soluble in ether, hot water, and hot alcohol.

Newman, M. S. and Beal, P.
An Improved Method for the Preparation of Aromatic Diazoketones.

Tertiary amines are used to remove hydrochloric acid formed in the reaction, RCOCl + CH₉N₂ (I) → RCOCHN₂ (II) + HCl, and thereby prevent destruction of a second mole of I.
Benzoyl chloride (0.1 mole) in 25 ml. ether was added over a period of 20 minutes to a cold solution of 0.1 mole diazomethane and 0.1 mole triethylamine in 235 ml. ether (ice-salt bath). After 12 hours in the cold, 86% of Et₃HCl was collected, and from the filtrate and washings 86% of crude C₆H₅COCHN₂ (11.8 g.) was isolated.

4-MeO-C₆H₄COCHN₂ was similarly prepared in 73% yield, m.p. 86-89°, crystallised from ligroin. Similarly, CH₃(CH₂)₃CH₂COCHN₂ and (CH₃)₃C-COCHN₂ were prepared in 69% and 98% yield (crude) respectively.

Newman, M. S. and Beal, P. F.
A New Synthesis of α-Alkoxy Ketones.

The decomposition of α-diazoketones is shown to be non-protonic acid (boron trifluoride) catalysed. In the absence of alcohols, only tar results from this treatment, but in the presence of typical primary, secondary and tertiary alcohols, the corresponding alkoxy ketones are obtained. For example, methanol and diazacetoephonone yield α-methoxyacetophenone; similarly isopropyl alcohol gives α-isopropoxyacetophenone, and tertiary butyl alcohol gives α-t-butoxyacetophenone. In an attempt to prepare β-tetralone by treatment of β-phenethyl diazomethyl ketone with ethereal sulfuric acid, there was obtained dI-(4-phenyl-2-ketobutyl) sulfate, the first example of this class of compound.

Ralston, A. W. and McCorkle, M. R.
4,4'-Diaminodiphenylmethane as a Reagent for the Identification of Monobasic Saturated Aliphatic Acids.

4,4'-Diaminodiphenylmethane has been found to give diamides of
aliphatic acids by heating the theoretical equivalent of the diamine with the respective acids:

\[ \text{CH}_2(\text{C}_6\text{H}_5\text{NH})_2 \cdot 2\text{RCOOH} \rightarrow \text{CH}_2(\text{C}_6\text{H}_5\text{NHCO})_2 + \text{H}_2\text{O} \]

Because of the ease of preparation and purification and their high melting points, these compounds served as excellent derivatives for the identification of aliphatic acids. With the lower members there was considerable depression of the mixed melting point with the next highest homolog, but this became increasingly smaller as the series was ascended.

The diamides were prepared as follows: 4,4'-diaminodiphenylmethane (0.005 mole) and slightly more than 0.01 mole of the acid are heated at the boiling temperature until water ceases to be evolved (one hour for the lower aliphatic members and five minutes for stearic acid) and the products are crystallized from benzene-methanol or benzene-butanol mixtures.

<table>
<thead>
<tr>
<th>Diamides of 4,4'-Diaminodiphenylmethane</th>
<th>Melting Point °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic</td>
<td>227-228</td>
</tr>
<tr>
<td>Propionic</td>
<td>212-213</td>
</tr>
<tr>
<td>Butyric</td>
<td>197-198</td>
</tr>
<tr>
<td>Valeric</td>
<td>188-189</td>
</tr>
<tr>
<td>Caproic</td>
<td>185-186</td>
</tr>
<tr>
<td>Neptulic</td>
<td>183-184</td>
</tr>
<tr>
<td>Caprylic</td>
<td>182-183</td>
</tr>
<tr>
<td>Pelargonic</td>
<td>176-177</td>
</tr>
<tr>
<td>Capric</td>
<td>178-179</td>
</tr>
<tr>
<td>Undecylic</td>
<td>175-176</td>
</tr>
<tr>
<td>Lauric</td>
<td>174-175</td>
</tr>
<tr>
<td>Tridecylic</td>
<td>172-173</td>
</tr>
<tr>
<td>Myristic</td>
<td>170-171</td>
</tr>
<tr>
<td>Pentadecylic</td>
<td>167-168</td>
</tr>
<tr>
<td>Palmitic</td>
<td>167-168</td>
</tr>
<tr>
<td>Margaric</td>
<td>164-165</td>
</tr>
<tr>
<td>Stearic</td>
<td>164-165</td>
</tr>
</tbody>
</table>
Reid, E. E.
The Identification of Acids.

p-Nitrobenzyl bromide serves as a convenient reagent for the identification of acids. Benzoic acid and its substitution products yield esters with this reagent in practically quantitative yield. The lower aliphatic monobasic acids, except acetic acid, gave rather low melting esters but in good yield. The yields and purity of esters of polybasic acids left much to be desired.

The p-nitrobenzyl esters are prepared by dissolving the required amount of the sodium or potassium salt of the acid in 5 ml. of water and then adding 10 ml. of 95% alcohol and 1.0 g. of p-nitrobenzyl bromide. The mixture is boiled under reflux for one hour (two hours for dibasic acids) and the ester precipitated by cooling. The esters are recrystallized from alcohol to a constant melting point.

<table>
<thead>
<tr>
<th>p-Nitrobenzyl Ester</th>
<th>Melting Point, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formate</td>
<td>31</td>
</tr>
<tr>
<td>Acetate</td>
<td>76</td>
</tr>
<tr>
<td>Propionate</td>
<td>31</td>
</tr>
<tr>
<td>Butyrate</td>
<td>35</td>
</tr>
<tr>
<td>Benzoate</td>
<td>89</td>
</tr>
<tr>
<td>o-Toluate</td>
<td>90.7</td>
</tr>
<tr>
<td>o-Nitrobenzoate</td>
<td>111.8</td>
</tr>
<tr>
<td>o-Chlorobenzoate</td>
<td>106</td>
</tr>
<tr>
<td>Anthranilate</td>
<td>205</td>
</tr>
<tr>
<td>p-Bromobenzoate</td>
<td>139.5</td>
</tr>
<tr>
<td>2,4-Dinitrobenzoate</td>
<td>142.0</td>
</tr>
<tr>
<td>Phenylpropiolate</td>
<td>83</td>
</tr>
<tr>
<td>Thiocyanate</td>
<td>85</td>
</tr>
<tr>
<td>Oxalate</td>
<td>204</td>
</tr>
<tr>
<td>Malonate</td>
<td>85.5</td>
</tr>
<tr>
<td>Tartrate</td>
<td>163</td>
</tr>
<tr>
<td>Citrate</td>
<td>102</td>
</tr>
</tbody>
</table>
Veibel, S. and Lillelund, H.
Bensyliothiourea and its Application to the Identification of Organic Acids.

The synthesis of bensyliothiourea hydrochloride is described. A table of the melting points of the salts of 23 organic acids and bensyliothiourea is included. For the preparation of bensyliothiourea hydrochloride, 76 g. of thiourea is dissolved in 200 ml. of hot water, the solution is diluted with 135 ml. of alcohol and 126.5 g. of benzyl chloride is added. After refluxing on the water bath until the benzyl chloride is dissolved, the mixture is heated for an additional half-hour and with occasional stirring. On cooling the mixture, a large fraction of the bensyliothiourea hydrochloride separates. The mother liquors from the filtration of the compound yielded more material, and a total yield of 186 g. (92%) of bensyliothiourea hydrochloride, m.p. 149-150°, was obtained.

The following method is suggested for the preparation and purification of salts employed in the characterization of the organic acids listed below: One hundredth gram equivalent of the acid is dissolved in 10 ml. of water, or in the minimum amount of hot water if the acid is slightly soluble, and a few drops of methyl red indicator are added. Sufficient 1 N sodium hydroxide solution is added to change the color of the indicator, and then two or three drops of 1 N hydrochloric acid is added in excess. The solution is then mixed with a solution containing 2 g. of bensyliothiourea hydrochloride in 10 ml. of water, and the mixture is chilled until the salt separates completely from the solution. The salt may be crystallized from the smallest quantity possible of alcohol or dilute alcohol, depending on the solubility of
Dibasic acids react frequently to form neutral salts with two molecules of benzylisothiourea, although this is not invariably the case. Thus, fumaric acid yields a neutral salt, while maleic acid yields an acid salt. Oxalic acid, ethylmalonic acid, and benzoic-o-sulfonic acid yield neutral salts, while malonic acid yields only an acid salt with benzylisothiourea.

<table>
<thead>
<tr>
<th>Benzylisothiourea Salts</th>
<th>Melting Point °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formate</td>
<td>150-151</td>
</tr>
<tr>
<td>Acetate</td>
<td>135-136</td>
</tr>
<tr>
<td>Propionate</td>
<td>151-152</td>
</tr>
<tr>
<td>Glycolate</td>
<td>146-147</td>
</tr>
<tr>
<td>Oxalate</td>
<td>195-196</td>
</tr>
<tr>
<td>Malonate</td>
<td>145-146</td>
</tr>
<tr>
<td>Ethylmalonate</td>
<td>120-121</td>
</tr>
<tr>
<td>Benzoate</td>
<td>166.5-167.5</td>
</tr>
<tr>
<td>Cinnamate</td>
<td>178-179</td>
</tr>
<tr>
<td>o-Bromobenzoate</td>
<td>170-171</td>
</tr>
<tr>
<td>Salicylate</td>
<td>147-148</td>
</tr>
<tr>
<td>Anisate</td>
<td>184-185</td>
</tr>
<tr>
<td>Anthranilate</td>
<td>142-143</td>
</tr>
<tr>
<td>Amygdalate</td>
<td>164-165</td>
</tr>
<tr>
<td>Benszenesulfonate</td>
<td>148-149</td>
</tr>
<tr>
<td>o-Toluenesulfonate</td>
<td>170-171</td>
</tr>
<tr>
<td>p-Toluenesulfonate</td>
<td>182-183</td>
</tr>
<tr>
<td>Sulfosalicylate</td>
<td>203-204</td>
</tr>
<tr>
<td>Sulfanilate</td>
<td>187-188</td>
</tr>
<tr>
<td>Benzoate-o-sulfonate</td>
<td>205-206</td>
</tr>
<tr>
<td>Benzoate-m-sulfonate</td>
<td>163-164</td>
</tr>
</tbody>
</table>
THE BROMO-2-NITROBENZOIC ACIDS
ABSTRACT
3-Bromo-2-nitrobenzoic acid has been previously prepared, but in very low yield. The synthesis of 6-bromo-2-nitrobenzoic acid has not been hitherto described. During the course of this investigation these two isomeric bromo-2-nitrobenzoic acids were prepared in good yield and from readily available synthetic intermediates. 6-Amino-2-nitrobenzoic acid served as starting material for the preparation of both 3-bromo- and 6-bromo-2-nitrobenzoic acid. The amino acid was obtained in 44% overall yield by a four-step synthesis which began with 3-nitrophthalic acid: the diammonium salt of 3-nitrophthalic acid was fused to eliminate ammonia and water, and the 3-nitrophthalimide thus formed was treated with aqueous alkali which gave 3-nitrophthalamic acid. The 3-nitrophthalamic acid, when treated with potassium hypobromite, yielded 6-amino-2-nitrobenzoic acid.

The bromination of 6-amino-2-nitrobenzoic acid gave the new 6-amino-3-bromo-2-nitrobenzoic acid which was deaminated by treatment of its diazonium chloride with hypophosphorous acid. The 3-bromo-2-nitrobenzoic acid was thus obtained in 54% yield.

6-Amino-2-nitrobenzoic acid was converted into the hydrobromide which, upon treatment with nitrous acid, gave the diazonium bromide. The addition of the diazonium salt to cuprous bromide solution yielded 86% of the new 6-bromo-2-nitrobenzoic acid.
THEORETICAL DISCUSSION
o-Nitrobenzoic acid is capable of yielding four bromo-2-nitrobenzoic acids. This investigation involves the preparation of 3-bromo-2-nitrobenzoic acid, which has been reported previously by other workers, and 6-bromo-2-nitrobenzoic acid, which has not been reported at all in the literature.

It is expected that work on the two remaining members of the series, the 4-bromo- and the 5-bromo-2-nitrobenzoic acids, which has been carried on in this Laboratory, will be reported by Mr. T. R. Pullig at a later date.

No satisfactory method for the preparation of 3-bromo-2-nitrobenzoic acid has been described in the literature. From the crude nitration product of m-bromobenzoic acid only 3.5% of the compound has been isolated, although it has been determined by phase equilibrium studies that 11.4% is present. Friedlander and co-workers described a more convenient method for the isolation of the 3-bromo-2-nitrobenzoic acid from the nitration product but gave no information as to yield. A very small yield of 3-bromo-2-nitrobenzoic acid has been obtained by the neutral permanganate oxidation of a mixture of 3-bromo- and 4-bromo-2-nitrotoluenes, and an unspecified amount was prepared by the oxidation of a pure sample of 3-bromo-2-nitrotoluene.

In the present work the preparation of the 3-bromo-2-nitrobenzoic acid and the 6-bromo-2-nitrobenzoic acids has been accomplished in good yields and from readily available starting materials.

An attractive route to both the 3-bromo- and the 6-bromo-2-nitrobenzoic acid was provided by 6-amino-2-nitrobenzoic acid (I) which was obtained from 3-nitrophthalic acid by the following reaction sequence: The diammonium salt of 3-nitrophthalic acid was fused to eliminate water and
ammonia, thus giving 3-nitrophthalimide. When the 3-nitrophthalimide was treated with aqueous potassium hydroxide, the imide ring was opened, and 3-nitrophthalamic acid was obtained. The Hofmann degradation of the 3-nitrophthalamic acid yielded 6-amino-2-nitrobenzoic acid (I).

The overall yield of 6-amino-2-nitrobenzoic acid prepared from 3-nitrophthalic acid was about 44%, which is a very satisfactory yield considering the number of reaction steps involved and the inexpensiveness of the starting material.

The bromination of 6-amino-2-nitrobenzoic acid in glacial acetic acid gave 72% of the new 6-amino-3-bromo-2-nitrobenzoic acid (II), and when this was diazotized in hydrochloric acid and the diazonium salt treated at 0° with hypophosphorus acid, 54% of 3-bromo-2-nitrobenzoic acid (III) was obtained:

Diazotization of 6-amino-2-nitrobenzoic acid in hydrobromic acid gave a diazonium bromide which was converted in the presence of cuprous bromide
into 86% of the new 6-bromo-2-nitrobenzoic acid (IV):
EXPERIMENTAL
3-Nitrophthalimide. — A two liter round-bottomed flask was charged with 158 g. (0.75 mole) of 3-nitrophthalic acid and a solution of 148 ml. (2.25 moles) of concentrated ammonium hydroxide (sp. gr. 0.9) in 225 ml. of water. The aqueous solution of diaminium 3-nitrophthalate was evaporated to dryness by heating the flask in an oil bath maintained at 110° for two days, after which the dry salt was decomposed by heating it for eight hours at 180°, and then finally at 210-220° until the fused mass ceased to evolve ammonia. The melt was cooled, broken up, and extracted with 1300 ml. of acetone. The acetone extract was treated twice with decolorizing charcoal, filtered, and evaporated to 400 ml. On adding 200 ml. of alcohol and cooling, the crude imide separated. It was recrystallized from a mixture of acetone and alcohol (2:1), yielding 53.8 g. (58%) of bright, yellow needles, m.p. 215-216°.

3-Nitrophthalamic Acid. — Finely powdered 3-nitrophthalimide, 23.2 g. (0.21 mole) was dissolved by stirring for two hours in a solution of 39.8 g. (0.41 mole) of potassium hydroxide in 890 ml. of water. The light yellow solution was allowed to stand for two hours, after which it was chilled and carefully acidified with 35 ml. of cold, concentrated hydrochloric acid. The 3-nitrophthalamic acid, which separated immediately, was collected, washed with a little ice-water, and dried. The yield was 27.8 g. (82%) of colorless platelets, m.p. 153-154°, with resolidification and remelting at 213-215°.

6-Amino-2-nitrobenzolic Acid. — A solution of 21 g. (0.1 mole) of 3-nitrophthalamic acid in 100 ml. of 1 N potassium hydroxide was chilled in an ice bath and an ice-cold solution of 15.6 g. (0.1 mole) of bromine in 200 ml. of 1 N potassium hydroxide was quickly added. After mixing,
300 ml. of ice-cold 1 N potassium hydroxide was added rapidly with swirling, and the solution was immersed immediately in a large, vigorously boiling water bath for 40 minutes. At the end of this time, the flask was removed from the bath and plunged directly into an ice-bath. When the temperature of the deep red, alkaline solution had dropped to 4-5°, 205 ml. of ice-cold 2 N hydrochloric acid was carefully added. The amino acid separated immediately, giving 15 g. (83%) of crude material, m.p. 176-176.5°. Recrystallization from hot water yielded 12.6 g. of large, golden-yellow needles, m.p. 184°.

**6-Amino-3-bromo-2-nitrobenzoic Acid.**—In a one liter, three-necked, round-bottomed flask fitted with a mechanical stirrer, thermometer, and dropping funnel were placed 21.4 g. (0.12 mole) of finely powdered 6-amino-2-nitrobenzoic acid and 400 ml. of glacial acetic acid. The mixture was cooled to 10° with stirring, and then about half of a solution of 38.4 g. (0.24 mole) of bromine in 100 ml. of glacial acetic acid was slowly added from the dropping funnel, care being taken to keep the temperature at 15-20°. Then 21.4 g. (0.12 mole) more of the amino acid and 100 ml. of glacial acetic acid were added to the mixture, and the remainder of the bromine-acetic acid solution was dropped in as before. The reaction mixture was stirred for an additional 15 minutes, 34 g. (0.25 mole) of sodium acetate trihydrate dissolved in 50 ml. of water was added, and the clear solution was poured with constant stirring into 2 liters of water containing 500 g. of ice. The bright yellow precipitate of the bromo compound was collected, washed free of acetic acid with cold water, and dried to give 36 g. of crude product, m.p. 196-201°. Working up the mother liquors yielded 9.2 g. more material, m.p. 195-197°, giving a crude total yield of 45.2 g., 72% of theory. Recrystallization of a
sample of the material twice from dilute alcohol and once from 50% aqueous acetic acid gave bright yellow needles, m.p. 201-202.5°.

Anal. Calcd. for C_7H_5BrN_2O_4: C, 32.21; H, 1.93; N, 10.73; Br, 30.61.
Found: C, 32.21; H, 2.48; N, 10.68; Br, 30.75.

3-Bromo-2-nitrobenzoic Acid. — In a one liter, three-necked, round-bottomed flask fitted with a mechanical stirrer, thermometer, and dropping funnel were placed 41.8 g. (0.016 mole) of finely powdered 6-amino-3-bromo-2-nitrobenzoic acid, 130 ml. of concentrated hydrochloric acid (sp. gr. 1.18), and 85 ml. of water. The mixture was stirred for 4 hours, and the insoluble light yellow precipitate of amine hydrochloride which formed was cooled to 0° in an ice-salt bath. Sodium nitrite, 11.3 g. (0.016 mole) dissolved in 50 ml. of ice-water was added with stirring to the amine hydrochloride over a period of 1 hour. The fine precipitate of cream colored diazonium salt this produced was stirred for one-half hour, and 420 ml. of 30% hypophosphorous acid (14 mole excess) pre-cooled to 0°, was dropped in with stirring and strong cooling. A vigorous evolution of nitrogen occurred immediately. The suspension was stirred at 0° for 24 hours and then filtered. The filter cake was washed with a little cold water, dried and crystallized from dilute alcohol (decolorizing charcoal) to give 21.5 g. (54%) of 3-bromo-2-nitrobenzoic acid, m.p. 241-246°.
Two recrystallizations from dilute methanol yielded fine, white needles, m.p. and m.m.p. 247-249.5°.

6-Bromo-2-Nitrobenzoic Acid. — In a 500 ml. round-bottomed, three-necked flask fitted with a mechanical stirrer, thermometer, and dropping funnel were placed 18.2 g. (0.1 mole) of 6-amino-2-nitrobenzoic acid and 58 ml. (0.5 mole) of 48% hydrobromic acid. The mixture was stirred for
one hour when the amine was converted into a thick, yellow mush of the hydrobromide. On adding 155 ml. of water and stirring at 65°-70° for a few minutes, a clear, deep-orange solution of the amine hydrobromide was obtained. It was chilled with stirring to -5° to separate the amine hydrobromide in the form of a fine, yellow precipitate, and a cold solution of 6.9 g. (0.1 mole) of sodium nitrite in 40 ml. of water was added over a period of 30 minutes. The thin, yellow suspension of the diazonium salt which formed was stirred at -5° for one hour and then poured rather rapidly (15 minutes) with vigorous stirring into a cold solution (20-25°) of cuprous bromide which was made in the following manner: A solution of 31.4 g. (0.13 mole) of cupric sulfate pentahydrate in 110 ml. of hot water was prepared in a one liter round-bottomed flask, and to it was added 15.4 g. (0.15 mole) of solid sodium bromide. To the deep green solution of cupric bromide thus obtained was added 6.8 g. (0.065 mole) of sodium bisulfite and 4.5 g. (0.12 mole) of sodium hydroxide dissolved in 55 ml. of hot water. The cuprous bromide, which separated immediately as a fine, white precipitate, was cooled, washed with water twice by decantation, and dissolved in 45 ml. of 47% hydrobromic acid.

After the addition of the diazonium salt solution to the cuprous bromide was complete, the mixture was stirred at room temperature for two hours, and then at 50-60° for an additional two hours to insure complete decomposition of the diazonium salt-cuprous bromide complex. The light tan precipitate of the 6-bromo-2-nitrobenzoic acid was collected, pressed free of liquid, and washed thoroughly with 50 ml. of cold 10% hydrobromic acid and then with 50 ml. of ice water. The crude air-dried acid was extracted with 100 ml. of 7% potassium hydroxide solution; the solution of the potassium salt was filtered and just neutralized with concentrated
excess of hydrochloric acid was added to the filtered solution, and the free 6-bromo-acid was collected, washed with a little cold water and dried. The yield was 21.2 g. (86%) of lightly colored material, m.p. 177-177.5°. After crystallisation from very dilute methanol (decolorising charcoal), there were obtained large, white needles, m.p. 177.3-177.5°.

Anal. Calcd. for C\textsubscript{7}H\textsubscript{4}O NBr: C, 34.17; H, 1.64; Br, 32.48; N, 5.59. 
Found: C, 34.44; H, 1.82; Br, 32.27; N, 5.55.
3-Bromo-2-nitrobenzoic acid was prepared in 54% yield by a method which involves the deamination of 6-amino-3-bromo-2-nitrobenzoic acid.

6-Bromo-2-nitrobenzoic acid, which has not been described previously in the literature, was obtained in 86% yield by diazotizing 6-amino-2-nitrobenzoic acid in hydrobromic acid and treating the diazonium salt with cuprous bromide.
ANNOTATED AND SELECTED

BIBLIOGRAPHY

ALPHABETIZED ACCORDING TO AUTHOR
In the preparation of 6-nitro-2-aminobenzoic acid by the Hofmann degradation of 3-nitrophthalamic acid it is essential to keep the solutions cold until the necessary amount of alkali and bromine has been added. The cold solution should then be placed directly on a boiling water bath and heated up as rapidly as possible, the close of the reaction (30-40 min.) being indicated by the solution turning a rich, red color, when it should be cooled down as rapidly as possible in an ice-bath; it is then carefully acidified with the calculated amount of HCl. The amino acid separates in beautiful yellow needles which are practically pure. If the heating and cooling proceed slowly, the product will be darker in color and smaller in amount. When not perfectly pure, its tendency is to separate in a granular condition. In case the acid does not separate from the cold solution on shaking, it can generally be precipitated by the addition of a little salt. The yield is 80-85% of the weight of amino acid taken.

For the preparation of 3-nitrophthalimide, the 3-nitrophthalic acid is treated with an excess of ammonia and evaporated to dryness at 110°. The temperature is then raised to 170-180° until no more NH₃ is evolved and then to 210° until fusion occurs. When the fused mass has ceased to effervescence, the temperature is raised for a few minutes to 216°, and the melt allowed to cool. The crude imide from the neutral ammonium salt melts at 210-216° and is easily purified by crystallization from alcohol, yielding large, yellow, lustrous
needles, m.p. 216°.

Burton, H., Hammond, F., and Kenner, J.
CCXVII. Mercuriation of o-Nitrotoluene.

Ten grams of a mixture of 3- and 4-bromo-2-nitrotoluenes was oxidized by a boiling solution of KMnO₄ (30 g.) and MgSO₄ (20 g.) in water (1500 ml.). A mixture of 3- and 4-bromo-2-nitrobenzoic acids was obtained from which the 4-bromo- isomer was separated by boiling in water, in which it is soluble. Two and one-half grams of the 3-bromo- isomer was obtained. No yield was given for the 4-bromo- isomer.

Friedlander, P., Brukner, S., and Deutsch, G.
Bromo and Methoxy Derivatives of Indigo.
Ann., 363: 39 (1912)

The m-bromobenzoic acid is dissolved in concentrated H₂SO₄ and nitratated with the corrected amount of HNO₃-H₂SO₄ below 40°. The crystalline precipitate is collected and washed with cold 1:1 sulfuric acid-water and dried. The separation of the 5-bromo-2-nitrobenzoic acid is carried out by boiling in hot benzene in which it is soluble; the 3-bromo-2-nitrobenzoic acid is not soluble in hot benzene. Traces of the easily soluble acid can be removed by boiling with water. No yields are given for either isomer.

Holleman, A. F.
Rec. Trav., 20: 206-234 (1901)

The nitration of m-bromobenzoic acid is carried out using four
times the quantity of concentrated nitric acid necessary and keeping the temperature at 25° or at 0°. One can also use nitric acid having a sp. gr. of 1.52. The separation of the isomers is based on the fact that the 3-bromo-2-nitrobenzoic acid is not soluble in cold 65% alcohol while the 5-bromo-isomer is soluble. Furthermore, the 3-bromo-isomer is less soluble in water than the 5-bromo-isomer. No yields based on isolation are given for either isomer, but from the melting point of the crude nitration mixture and the phase diagram for the two isomers prepared from known mixtures of the pure isomers, the author was able to determine that the nitration of m-bromobenzoic acid at 0° yielded a product containing 11.6% of the 3-2-1 isomer. At -30°, 11.6% of the 3-2-1 isomer was obtained.

Hubner, H., Ohly, J. and Philipp, O.
The Isomerism of Aromatic Acids
Ann., 143: 239 (1867)

3-Bromo-2-nitrobenzoic acid, m.p. 246-248° is obtained in 3.5% yield by the nitration of m-bromobenzoic acid, 120 g. of the m-bromo-
benzoic yielding only about 4 g. of the 3-bromo-2-nitrobenzoic acid.
It appears that if one keeps the temperature down during the nitra-
tion, the yield might be increased.

Hubner, H. and Petermann, A.
The Isomerism of Aromatic Acids. III. Conversion of Benzoic Acid
into Anthranilic Acid and Salicylic Acid.
Ann., 149: 132 (1869)
The yield of 3-bromo-2-nitrobenzoic acid obtained from the nitra-
tion of m-bromobenzoic acid is very small since it cannot be separated completely from the accompanying 5-bromo-2-nitrobenzoic acid.
3-Nitrophthalic acid was prepared as follows: To a mixture of 175 g. of phthalic anhydride and 175 ml. of concentrated HNO₃ in a 3-liter round-bottomed flask, there was slowly added with shaking 175 ml. of concentrated H₂SO₄. The mixture was heated for 3 hours on the steam bath, after which it was cooled and poured with constant stirring into 500 ml. of cold water. An additional 60 ml. of water was used to rinse the flask. The suspension was cooled to 10°, filtered, and pressed as dry as possible with the aid of a rubber dam. The filter cake was thoroughly stirred for a few minutes with 200 ml. of ice-water and the precipitate was crystallized from 200 ml. of glacial acetic acid. The solution was allowed to stand at room temperature for 24 hours to insure complete precipitation. The yield of small, hard prisms, m.p. 216–218° (vac.) was 70 g. (26%).
VITA
Joseph Martin Deehary was born in Youngsville, Louisiana, on March 6, 1922. His elementary education was received in the parochial and public schools of Plaquemine, Louisiana, and he graduated from Plaquemine High School in May of 1939.

In September of 1940 he entered Louisiana State University and graduated in August of 1943 with the Degree of Bachelor of Science in Chemistry. While an undergraduate he was made a member of Phi Eta Sigma, honorary scholastic fraternity; Phi Lambda Upsilon, honorary chemistry fraternity; and Kappa Mu Epsilon, honorary mathematics society.

He entered the Graduate School of Louisiana State University in August of 1943, and in June of 1944 his graduate studies were interrupted for a period of service in the Armed Forces of the United States. After a term of service in the European Theater of Operations, he was honorably discharged from the Army of the United States on April 9, 1946.

In June of 1946 he re-entered the Graduate School of Louisiana State University and received the Degree of Master of Science in Chemistry in August of 1947. He resigned his Graduate Assistantship in the Department of Chemistry of Louisiana State University in February of 1948 to take a position as research chemist in the Oil, Fat and Protein Division of the Southern Regional Research Laboratory of the United States Department of Agriculture in New Orleans, Louisiana.

He is a member of Sigma Xi and the American Chemical Society, and has published in the fields of nutrition, plant pigments, and organic synthesis.

In September of 1950 he returned to the Graduate School of Louisiana State University and was awarded the Charles E. Coates Fellowship in Chemistry for the academic year, 1951-1952. He is now a candidate for the Degree of Doctor of Philosophy in Chemistry.
PUBLICATIONS
"Diazoketones as Reagents for the Identification of Organic Acids",

"The Addition of Diphenylketene to o-Benzquinone",

"2,3-Dimethoxytriphenylmethane and Some of Its Derivatives",

"The Bromo-2-nitrobenzoic Acids",
Candidate: Joseph M. Dechary

Major Field: Chemistry

Title of Thesis: PART I THE ADDITION OF DIPHENYLketene TO o-BENZOQUINONE
PART II DIAZOKETONES AS REAGENTS FOR THE IDENTIFICATION OF ORGANIC ACIDS
PART III THE BROMO-2-NITROBENZOCIC ACIDS

Approved:

J. L. E. Frickman
Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination: May 6, 1952