

The non-volatile portion of the reaction mixture, which did not contain apo- β -erythroidine, is still under investigation.

Apo- β -erythroidine.—Apo- β -erythroidine was prepared by the method of Sauvage and Boekelheide³ as pale yellow crystals, m.p. 129.5–130.5°, and obtained by recrystallization from ethanol as large colorless prisms, m.p. 132–132.5°; $[\alpha]_D^{20} +1.0$ (c 1.5, benzene). After four crystallizations from methanol–ethyl ether the melting point was unchanged. The observed rotation is within the experimental error of the determination and does not establish optical activity.

Apo- β -erythroidine (1.8 g., pale yellow, m.p. 129.5–130.5°) was also purified by dissolving it in benzene (50 cc.) and passing the resultant solution over a Florisil column (80 \times 30 mm.). A broad pale yellow band appeared and was eluted with benzene (600 cc.). Evaporation of the solvent and crystallization of the residue from ethanol gave colorless prisms (1.04 g.), m.p. 132–132.5°.¹⁵

(15) A Florisil column was first used by Dr. G. L. Sauvage for the purification of apo- β -erythroidine.

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[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY OF LOUISIANA STATE UNIVERSITY]

The Addition of Diphenylketene to *o*-Benzoquinone

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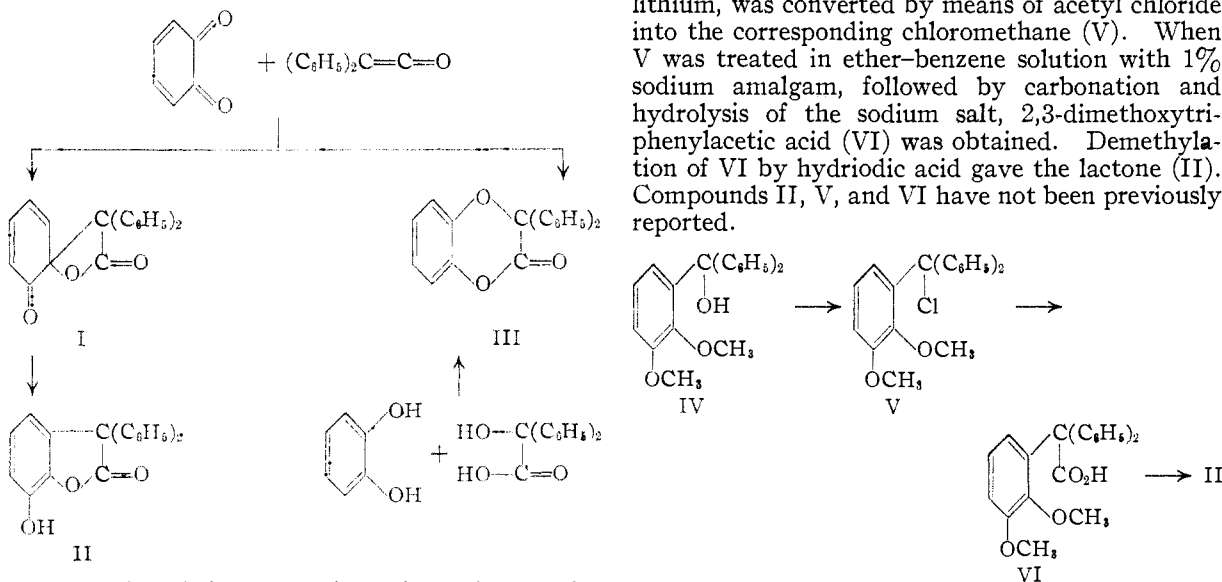
The addition of diphenylketene to *o*-benzoquinone yields diphenyl-*o*-hydroxyphenoxyacetic acid lactone which is identical with the substance obtained by fusing catechol with benzoic acid, but which is described erroneously in the literature as 2,3-dihydroxytriphenylacetic acid lactone. The latter substance may be obtained, however, by the demethylation of 2,3-dimethoxytriphenylacetic acid which can be synthesized by conventional methods. An independent synthesis of diphenyl-*o*-hydroxyphenoxyacetic acid lactone is described whereby hydrogen chloride is eliminated from catechol and diphenylchloroacetyl chloride.

It has been observed that diphenylketene adds to *p*-benzoquinone to yield a colorless monolactone¹ which can be isolated, although upon heating, it decomposes into diphenyl-*p*-quinomethane and carbon dioxide. This monolactone undergoes rearrangement when illuminated in the solid state, or in boiling benzene, and is transformed into the isomeric benzene derivative, 2,5-dihydroxytriphenylacetic acid lactone.²

If the behavior of *p*-benzoquinone is typical, one might expect the reaction between diphenylketene and *o*-benzoquinone to furnish the analogous monolactone (I) which should either decompose into diphenyl-*o*-quinomethane, or rearrange into 2,3-dihydroxytriphenylacetic acid lactone (II).

isolated a colorless substance which was identical with the product obtained from catechol and benzoic acid, and which is described in the literature³ as 2,3-dihydroxytriphenylacetic acid lactone (II). The substance gave no color with ferric chloride and was insoluble in dilute alkaline solution, behavior which seemed inconsistent with structure (II) as well as with the possible isomeric 3,4-dihydroxytriphenylacetic acid lactone.

In consequence of these observations and for comparison with the product obtained from diphenylketene and *o*-benzoquinone, II was synthesized by the following sequence of reactions: 2,3-Dimethoxytriphenylcarbinol (IV), prepared from methyl 2,3-dimethoxybenzoate and phenyllithium, was converted by means of acetyl chloride into the corresponding chloromethane (V). When V was treated in ether–benzene solution with 1% sodium amalgam, followed by carbonation and hydrolysis of the sodium salt, 2,3-dimethoxytriphenylacetic acid (VI) was obtained. Demethylation of VI by hydriodic acid gave the lactone (II). Compounds II, V, and VI have not been previously reported.



It was found, however, that when *o*-benzoquinone in benzene suspension was treated with an excess of diphenylketene, the primary addition product (I) was not obtained. Instead, there was

(1) H. Staudinger, *Ber.*, **41**, 1355 (1908).

(2) H. Staudinger, *Ann.*, **380**, 248 (1911).

As distinguished from the substance (m.p. 136–137.5°) obtained by either the reaction of diphenylketene with *o*-benzoquinone, or from catechol and benzoic acid, II is quite soluble in dilute alkali,

(3) H. von Liebig, *Ber.*, **41**, 1648 (1908).

imparting 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 dienophile–diene type addition of diphenylketene to *o*-benzoquinone which yields diphenyl-*o*-hydroxyphenoxyacetic acid lactone (III), a product which can also be accounted for by the elimination of two molecules of water from one molecule each of catechol and benzoic acid. The synthesis of the ether-lactone (III) 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 obtained from diphenylketene and *o*-benzoquinone and also with the product resulting from the reaction of catechol with benzoic acid. Convincing evidence for the course of the reaction leading to the formation and structure of III (by any one of the three routes examined) was obtained when III was treated with hydriodic acid. There were obtained diphenylacetic acid and catechol, cleavage fragments compatible only with the structure of diphenyl-*o*-hydroxyphenoxyacetic acid lactone. The product obtained by von Liebig³ from catechol and benzoic acid and described erroneously as II must now be assigned the structure (III).

After this work was completed, we learned that Horner, *et al.*,⁴ only recently reported that diphenylketene added to tetrachloro-*o*-benzoquinone to give diphenyl-(3,4,5,6-tetrachloro-2-hydroxyphenoxy)-acetic acid lactone. This is in agreement with our findings for *o*-benzoquinone, and it is suspected that other *o*-quinones behave similarly with diphenylketene.

Our experiments with dimethylketene and *o*-benzoquinone were inconclusive. In several experiments the quinone was recovered in the form of an amorphous, yellow polymer.⁵ It is possible that our dimethylketene, which was prepared by the decomposition of dimethylmalonic anhydride, contained traces of acetic acid which may have induced polymerization of the sensitive quinone.

Experimental⁶

***o*-Benzoquinone.**—Silver oxide,⁷ 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 chilled slowly to –70° by means of an acetone–Dry Ice mixture. The fine red crystals of the *o*-benzoquinone, which separated, 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. of dry benzene was treated with 5 g. (0.028 mole) of

freshly distilled diphenylketene⁸ 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 benzoic acid,³ the m.p. was unchanged.

Anal. Calcd. for C₂₀H₁₄O₃: C, 79.5; H, 4.7. Found: C, 79.4; H, 5.1.

2,3-Dimethoxytriphenylcarbinol (IV).—Richtzenhain and Nippus⁹ reported the preparation of IV by the action of phenylmagnesium bromide on either 2,3-dimethoxybenzophenone or ethyl 2,3-dimethoxybenzoate. We have obtained a larger yield and a purer product 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 anhydrous ether. The mixture was then refluxed for an additional 45 minutes, poured onto crushed ice, and the product worked up in the usual manner. The yield of crude material was 1.9 g. (77%). After one crystallization from ether and three from alcohol, there was obtained 29.3 g. of white prisms, m.p. 111–112°. Richtzenhain and Nippus⁹ reported m.p. 106°.

Anal. Calcd. for C₂₁H₂₀O₃: C, 78.72; H, 6.29. Found: C, 78.85; H, 6.34.

2,3-Dimethoxytriphenylchloromethane (V) was prepared from 29.3 g. (0.092 mole) of IV according to the procedure given by Bachmann for the preparation of triphenylchloromethane.¹⁰ The yield of product (28.4 g., m.p. 129–130°) was nearly quantitative.

Anal. Calcd. for C₂₁H₁₉O₂Cl: C, 74.44; H, 5.65. Found: C, 74.32; H, 5.69.

2,3-Dimethoxytriphenylacetic Acid (VI).—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 V 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 VI sintering slightly at 231° and melting at 236–239°.

Anal. Calcd. for C₂₂H₂₀O₄: C, 75.84; H, 5.79. Found: C, 75.77; H, 5.63.

2,3-Dihydroxytriphenylacetic Acid Lactone (II).—Demethylation of VI (0.2 g.) was accomplished by boiling with 10 ml. of hydriodic 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 precipitate 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 VI* was also accomplished by boiling 0.5 g. of the compound for six hours

(8) Diphenylketene was prepared in 63% yield from diphenylchloroacetyl chloride by means of zinc, according to the method of H. Staudinger, *ibid.*, **38**, 1735 (1905). This method appears to be superior to the one described in *Org. Syntheses*, **20**, 47 (1940).

(9) H. Richtzenhain and P. Nippus, *Chem. Ber.*, **82**, 416 (1949).

(10) W. E. Bachmann, *Org. Syntheses*, **23**, 100 (1943).

(4) L. Horner, E. Spietschka and A. Gross, *Ann.*, **573**, 24 (1951).

(5) R. Willstätter and H. E. Müller, *Ber.*, **44**, 2187 (1911).

(6) All melting points are uncorrected.

(7) R. Willstätter and F. Müller, *Ber.*, **41**, 2581 (1908).

in a solution of 2.3 g. of aluminum bromide¹¹ 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 washed 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 sulfate. The ether was removed by warming on the steam-bath, and then the remaining benzene solution was concentrated to a small volume. Upon diluting with low-boiling petroleum ether, sandy pink crystals of the lactone (II) crystallized. The yield was 0.37 g., m.p. 192–193°; after two crystallizations (charcoal) from benzene-petroleum ether, m.p. 192.5–193.5°.

Anal. Calcd. for $C_{20}H_{14}O_3$: C, 79.45; H, 4.67. Found: C, 79.75; H, 4.84.

Diphenyl-*o*-hydroxyphenoxyacetic Acid Lactone (III).—In a 250-ml. round-bottomed flask fitted with a reflux condenser and calcium chloride drying tube were placed 19.0 g. (0.072 mole) of diphenylchloroacetyl chloride, 7.9 g. (0.072 mole) of catechol and 60 ml. of dry acetone. To this solution was added, in small portions, 9.9 g. (0.072 mole) of 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.

(11) C. Weygand, "Organic Preparations," Interscience Publishers, Inc., New York, N. Y., 1945, p. 196.

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 (III), 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 benzoic acid.

The action of hydriodic acid on III yielded diphenylacetic acid and catechol. One gram of III was boiled 2.5 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 extract 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 diacetate was 0.21 g., fine white needles, m.p. 62–63°, m.m.p. 62–62.5°.

BATON ROUGE 3, LOUISIANA RECEIVED OCTOBER 20, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Chemistry of Carbon Suboxide. I. Reaction with Phenylmagnesium Bromide

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When phenylmagnesium bromide reacts with carbon suboxide in equal molar proportions, there is formed upon decomposition of the complex, acetophenone, 3-benzoyl-6-phenyl-1,2-pyran-2,4(3H)-dione (II) and 2,4,6-trihydroxytrimesophenone (III). All three compounds probably have benzoylketene or an analogously constituted Grignard complex as a common precursor, II being a dimer and III a trimer of this ketene. When phenylmagnesium bromide and carbon suboxide react in a two-to-one molar proportion, respectively, and the resulting complex is decomposed, there results benzophenone, triphenylcarbinol and β,β -diphenylhydracrylic acid. Five other unidentified compounds were isolated from the reaction mixture and characterized: $C_{15}H_{10}O_2$, $C_{18}H_{12}O_2$, $C_{27}H_{18}O_3$, $C_{36}H_{14}O_2$ and $C_{16}H_{18}O_4$.

The reaction of carbon suboxide with methylmagnesium iodide was studied by Billman¹ who reported the isolation of triacetylphloroglucinol as a product of the union of three moles of each of the two reactants. The current investigation was undertaken to explore further the reaction of the Grignard reagent with this oxide of carbon.

The addition of carbon suboxide to phenylmagnesium bromide produced a complex, decomposition of which gave a mixture from which were isolated acetophenone, β,β -diphenylhydracrylic acid (I), benzophenone, triphenylcarbinol, 3-benzoyl-6-phenyl-1,2-pyran-2,4(3H)-dione (II), 2,4,6-trihydroxytrimesophenone (III), diphenyl and five unidentified compounds: $C_{15}H_{10}O_2$, $C_{18}H_{12}O_2$, $C_{27}H_{18}O_3$, $C_{36}H_{14}O_2$ and $C_{16}H_{18}O_4$. The unidentified compounds have been characterized. Although the balance of products appeared to differ when the proportion of oxide to Grignard reagent was varied,

the nature of the products did not change markedly.

The course of the reaction becomes apparent from the compounds that were isolated and identified. The first mole of Grignard reagent added to carbon suboxide to produce an ion-pair of indeterminate geometry, the anion being a resonance hybrid. Decomposition of this complex with acid probably produced benzoylactic acid which decarboxylated under the conditions of the reaction to give acetophenone. The presence of I among the products indicates that when two moles of Grignard reagent become involved with one mole of carbon suboxide, one mole must have added one-two and the other added one-four² to the oxide molecule. Apparently the complex formed from two moles of Grignard reagent was unstable and partially decomposed in the dry ether solution to benzophenone, which

(2) The two negative charges would tend to become distributed as far as possible from one another in the anion of the double complex that was formed.

(1) J. H. Billman and C. Smith, THIS JOURNAL, **61**, 457 (1939).