tracts was washed with 1% aqueous potassium hydroxide. The nitrobenzene solution was treated with 75 g. of anhydrous sodium carbonate, and the resulting mixture was stirred for 18 hours. The dark red, filtered reaction mixture was subjected to distillation until the vapor temperature reached 205°; then it was steam distilled until the nitrobenzene was removed. The dark tars were separated from the aqueous residue in the distilling flask and extracted with benzene for three days in a Soxhlet apparatus. Fresh benzene then replaced the extract solution, and extraction was continued for three additional days. The combined extracts were allowed to flow through a 1 × 18 in. column of activated alumina, and the light yellow solution which emerged from the column was concentrated to 50 ml. On cooling, this solution deposited 5 g. (19%) of a solid mixture which gave evidence of containing at least two compounds, one of which melted at about 175° and the other at about 270°.

One 0.75-g. sample of the solid mixture was chromatographed on a 1 × 20 in. column of activated alumina from 1 l. of carbon tetrachloride solution. The chromatogram was developed with benzene containing 0.2% ethanol. A yellow crystalline solid was obtained, which, after several recrystallizations from *n*-heptane–benzene, yielded white crystals, m.p. 177–183°. This compound corresponded in composition to a trinitroterphenyl.

Anal. Calcd. for $C_{18}H_{11}N_3O_6$: C, 59.18; H, 3.01; N, 11.51. Found: C, 59.38; H, 3.07; N, 11.5.

In the course of several efforts to recrystallize the crude mixed solid product from benzene and from acetic acid, a small fraction of the mixture remained insoluble in the boiling solvents and was collected by filtration. About 0.4 g. of this material was dissolved in 120 ml. of boiling benzene; when the filtered hot solution was allowed to cool, it deposited a gelatinous solid which, when collected by filtration and dried, became a white powder, m.p. 250–256°. Several recrystallizations from "Cellosolve" gave a yellow crystalline solid (about 0.1 g.), m.p. 263–268°. This substance also corresponded in composition to a trinitroterphenyl.

Anal. Calcd. for $C_{18}H_{13}N_3O_6$: C, 59.18; H, 3.01; N, 11.51. Found: C, 59.39; H, 3.30; N, 11.32.

The higher melting isomer appeared more likely to be the one having the structure XXIII; it appears likely that the lower-melting isomer may be 3,5-bis-(2-nitrophenyl)-nitrobenzene or 3-(2-nitrophenyl)-5-(4-nitrophenyl)-nitrobenzene, although no experimental work has been carried out on this isomer.

3,5-Bis-(4-acetamidophenyl)-acetanilide (XVIII). A. From the Trinitroterphenyl XXIII.—About 50 mg. of XXVI, m.p. 263–268°, was dissolved in 1:1 benzene–ethanol and hydrogenated under three atmospheres pressure at room temperature in the presence of Raney nickel for four hours. The solvent was removed on the steam-bath from the filtered solution, the residue was redissolved in benzene and the solution was treated with ketene until precipitation of the acetyl derivative was complete. After two recrystallizations from benzene–ethanol, the product formed light tan needles, m.p. 311.5–313° dec.

Anal. Calcd. for $C_{24}H_{23}N_3O_3$: C, 71.50; H, 5.70; N, 10.40. Found: C, 70.10; H, 5.72; N, 9.37; ash, 0.90.

Apparently a small amount of inorganic material contaminated the analytical samples; there was not enough additional sample for further purification and analysis.

B. By Hydrogenolysis of 2,6-Bis-(2,6-dibromo-4-acetamidophenyl)-4-acetamidoiodobenzene (XVI).—A solution of 1.3 g. of XVI and 1 g. of sodium hydroxide in 150 ml. of ethanol was treated with hydrogen under three atmospheres pressure at room temperature in the presence of Raney nickel for 12 hours. The filtered ethanol solution was concentrated to 25 ml. and poured into 50 ml. of water. The solid product was collected by filtration; the filtrate gave a positive test for iodide ion. The crude solid product (0.6 g., 96%) was dissolved in 200 ml. of benzene, and the solution was treated with ketene to ensure complete acetylation of amino groups present. After concentration of the benzene solution to 30 ml. and cooling, a white solid deposited which, after several recrystallizations from methanol–benzene and from aqueous acetic acid, gave tan needles, m.p. 315° dec., alone or when mixed with a sample prepared as described in the preceding paragraph.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION NO. 1230 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

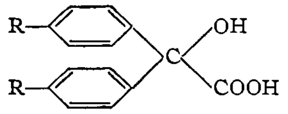
Pyrolysis of Aryl Glycolic Acids. III. The Structure of Langenbeck's Compound[1]

BY HARRY H. WASSERMAN, HERVEY W. ACKERMAN,[2] HERBERT H. WOTIZ[2] AND TIEN-CHUAN LIU

RECEIVED JULY 15, 1954

Langenbeck's compound, formed in the pyrolysis of benzilic acid, has been shown to have the quinodimethan structure VII. Chemical and spectroscopic evidence supporting this structure and the structures of a number of derivatives is presented. An independent synthesis is described which discloses the main structural features of Langenbeck's compound, and suggests a logical reaction sequence for its formation during the pyrolysis. The conclusive proof of structure is based on an unambiguous synthesis of one of the degradation products containing all of the essential features of Langenbeck's compound.

The formation of intensely colored materials during the pyrolysis of benzilic acid (I, R = H) was reported many years ago by Klinger,[3] Nef[4] and others, but Langenbeck[5] was the first to isolate a pure, crystalline, colored substance from among the pyrolytic products. By short energetic heating of benzilic acid in the presence of a small amount of sodium carbonate he obtained a red melt from which brilliant violet-black crystals, m.p. 169°, were isolated. The analysis and molecular weight of this substance appeared to be in accord with the composition $C_{28}H_{20}O_2$ and, based on this molecular formula, Langenbeck assumed that the brilliantly colored product was a dimer of diphenylketene.[6] Although this product was treated with a large variety of reagents, these reactions give little clue as to the structure of this material, since they led to no crystalline derivatives. For example, treatment with alcoholic potassium hydroxide, alcoholic potassium cyanide, zinc and acetic acid,



I

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[1] Presented at the 124th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 11, 1953.

[2] Taken, in part, from the doctoral dissertation of Herbert H. Wotiz, Yale University, 1951, and Hervey W. Ackerman, Yale University, 1952.

[3] H. Klinger and O. Standke, *Ber.*, **22**, 1213 (1889).

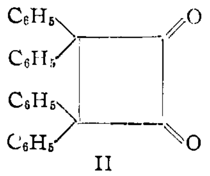
[4] J. U. Nef, *Ann.*, **298**, 242 (1897).

[5] W. Langenbeck and H. Langenbeck, *Ber.*, **61B**, 938 (1928).

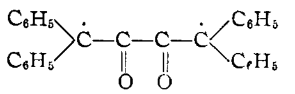
[6] This reasoning was supported by the fact that diphenylketene had earlier[7] been reported to occur among the products of decomposition of benzilic acid.

[7] H. Staudinger, *Ber.*, **44**, 543 (1911).

alcoholic bromine, thionyl chloride, phenyl hydrazine and other reagents led only to the formation of resinous materials. Oxidation with alkaline permanganate or chromic acid yielded benzoic acid and benzophenone as the only degradation products. Based on the yields of benzophenone, and assumptions regarding the oxidative breakdown of benzophenone to benzoic acid, Langenbeck assumed that in the parent compound there were two residues in which two phenyl groups were attached to a single carbon atom, and he proposed structure II for the colored product. Later, Wittig and Lupin[8] suggested a diradical structure, III, for Langenbeck's compound, on the basis of their failure to synthesize analogous tetraaryl cyclobutane derivatives. This diradical proposal was favored by Langenbeck[9] in view of the formation of a thermochromic melt in the pyrolysis of anisilic acid (I, R = OCH_3). The thermochromism in the latter case was considered to be evidence for the formation of free radicals analogous to III. However, Müller[10] shortly afterwards found no paramagnetic susceptibility in Langenbeck's compound and thereby ruled out radical structures such as III. Other formulations proposed for Langenbeck's compound have been IV,[11] based on an analogy with the permanganate colored indanedione IVa,[12] and more recently, V, a di- or tetrapolar representation in which Langenbeck's compound is considered[13] to be a C-enol betaine, analogous to the colored form (VIa) of the spirodinaphthapyran (VI). Formula V recently has received[14] attention as an example of an open-chain analog of the sydnones, compounds which are best represented as a hybrid of a number of ionic forms.



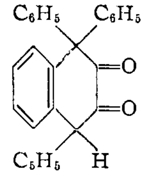
II



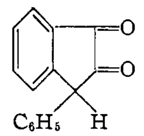
$$(C_6H_5)_2\dot{C}-\underset{\Vert}{C}-\underset{\Vert}{C}-\dot{C}(C_6H_5)_2$$

$$\quad O \quad O$$

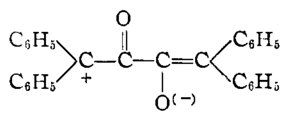
III



IV

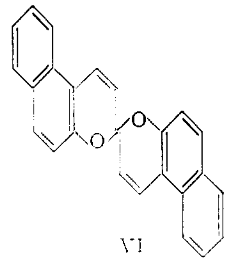


IVa

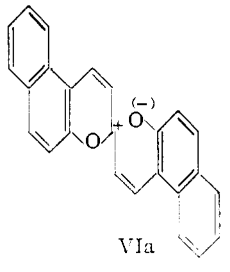


$$(C_6H_5)_2\overset{+}{C}-\overset{O}{\overset{\Vert}{C}}-\underset{O^{(-)}}{\underset{|}{C}}=C(C_6H_5)_2$$

V

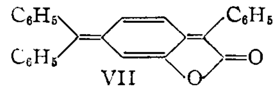


VI



VIa

Formulations II–V, all of which are based on the diphenylketene composition, $C_{28}H_{20}O_2$, and all of which contain essentially the same carbon skeleton, have failed to explain the remarkable color of Langenbeck's compound, its unusual chemical behavior and the mode of its formation in the pyrolysis of benzilic acid. We therefore have reinvestigated the structure of this substance, and are reporting here the degradative and synthetic evidence on which is based a new proposal, that of the quinodimethan, $C_{27}H_{18}O_2$, VII.



VII

Evidence which, at once, cast serious doubt on all previously proposed structures was derived from oxidation studies. Repeated reaction of Langenbeck's compound with neutral or alkaline permanganate, chromic acid and a variety of other oxidizing agents, yielded **only one mole of benzophenone and one mole of benzoic acid per mole of oxidized compound.** Ozonolysis at low temperatures failed to yield any fragments larger than benzophenone. All of the above studies revealed that of the four phenyl groups considered to be present in Langenbeck's compound, only three could be accounted for in the products of oxidation. It appeared that the fourth aromatic ring suffered destruction even under mild oxidative treatment. These results, disclosing an unusual sensitivity of Langenbeck's compound toward oxidation, indicated the presence in the parent compound of only one grouping of atoms wherein two unsubstituted phenyl groups are attached to a single carbon atom, and are not compatible with the carbon skeleton present in either II, III, IV or V. In this connection, it is important to point out that although Langenbeck's structural proposals II and III (as well as the structures IV and V) were based on a molecule containing two diphenylmethylene groupings, Langenbeck actually never obtained two moles of benzophenone per mole of parent compound oxidized. He assumed[5] that a large fraction of the benzoic acid formed during chromic acid oxidation arose from a second-stage breakdown of initially formed benzophenone.

The possibility that one of the aromatic rings in Langenbeck's compound was oxygenated, and thereby susceptible to oxidative destruction, was suggested by two independent lines of evidence arising from (a) periodic acid oxidation of the dipiperidine derivative and (b) reduction.

The dipiperidine derivative reported by Schönberg and Sina was the only derivative obtainable from

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[8] G. Wittig and F. V. Lupin, *Ber.*, **61B**, 1630 (1928).

[9] W. Langenbeck, *ibid.*, **62**, 962 (1929).

[10] E. Müller, *ibid.*, **68**, 1883 (1935).

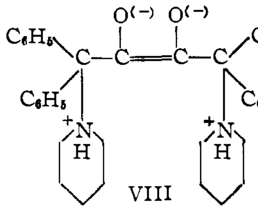
[11] E. Bergmann and O. Blum Bergmann, *J. Chem. Soc.*, 728 (1938).

[12] C. F. Koelsch, THIS JOURNAL, **58**, 1321 (1936).

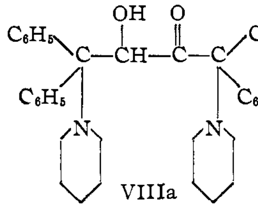
[13] A. Schönberg and A. Sina, *J. Chem. Soc.*, 175 (1947).

[14] W. Baker, W. D. Ollis and V. D. Poole, *ibid.*, 1542 (1950).

Langenbeck's compound up to the present work. Based on its salt-like properties, (high melting point, lack of solubility in organic solvents, etc.) it was assigned the structure VIII, by analogy with the piperidine salts of the spirodinaphthapyrans.[15] Isolation of this product (VIII) was the principal basis for the assignment[13] of the *meso*-ionic structure V to the parent colored compound, and VIII was therefore one of the first products to be reinvestigated in the present work.

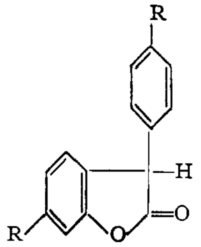

VIII

On the assumption that any molecule such as VIII would exist preferentially in the homopolar form VIIIa and therefore be susceptible to cleavage by ketol-splitting reagents,[16] the piperidine derivative was allowed to react with periodic acid. None of the products (such as α-piperidinodiphenylacetic acid) expected from cleavage of structure VIIIa were obtained in this reaction, but rather a compound $C_{26}H_{20}O_3$, in very small yield, showing properties typical of a phenol, *i.e.*, color with ferric chloride, and weak acidity. The characterization of this product will be described in the later discussion.

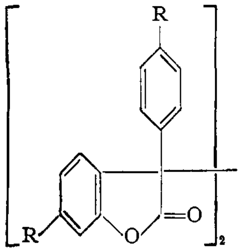

VIIIa

The further evidence suggesting that Langenbeck's compound contained a potential phenolic hydroxyl group came from reactions with reducing agents. By catalytic hydrogenation using platinum oxide, Langenbeck's compound was reduced readily to a mixture of two products, A, m.p. 134–136°, and B, m.p. 214–218°. Compound A, which predominated in the hydrogenation, also could be obtained by reduction with phosphorus and iodine, or by reaction with hydriodic acid. Reaction of Langenbeck's compound with zinc dust and acetic acid, or phosphorus and iodine, also yielded B. Both reduction products A and B showed properties typical of lactones. Lactone A was soluble in aqueous potassium hydroxide, but addition of potassium carbonate or carbon dioxide to the solution resulted in the precipitation of an insoluble potassium salt. On heating with aqueous base, lactone A was converted to a hydroxy carboxylic acid as evidenced by the characteristic bands in the 3 and 5.7 μ region of the infrared spectrum. This acid was unstable, its melting point gradually changing on standing. When heated to 160° it was readily reconverted to lactone A.

An important clue as to the main structural features present in lactones A and B came from a study of their infrared spectra. Both lactones show strong absorption in the 5.5 μ region of the spectrum suggesting the presence of a five-membered enol–lactone system,[17] and in particular, there was observed a striking resemblance between the spectra of A and B, and the spectra of an analogous pair of lactones, IX, R = OCH_3, and X, R = OCH_3, derived from the pyrolysis of anisilic acid.



IX



X

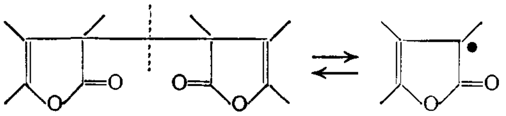
In Table I are listed the two main bands in the spectra of the isocoumaranone (IX, R = OCH_3) and the bislactone (X, R = OCH_3). The corresponding bands in the spectra of lactones A and B are shown for comparison.

TABLE I

PRINCIPAL ABSORPTION BANDS IN THE INFRARED

	μ	
Isocoumaranone (IX, R = OCH_3)	5.51	9.47
Lactone A	5.51	9.47
Bislactone (X, R = OCH_3)	5.55	9.38
Lactone B	5.55	9.37

That lactones A and B might be related as an isocoumaranone and bislactone analogous to the pair IX and X was strongly suggested by the infrared data, and this idea was further supported by the following observations: (a) lactone B exhibits thermochromic behavior (pale blue coloration in hot toluene, colorless solution when cold) as is commonly observed in bislactones of type X, which can take part[17] in the association–dissociation equilibrium



(b) lactone A appeared to undergo partial conversion to lactone B on standing in the presence of acid or basic reagents, possibly through air oxidation, and could be oxidized readily by chromic oxide in acetic acid to lactone B.

A structure which accounts for the formation of isocoumaranone derivatives such as IX and X on treatment of Langenbeck's compound with reducing agents, and which also explains the intense color and sensitivity toward oxidation, is the quinodimethan VII first suggested to us by Professor R. B. Woodward. Formation of VII from benzilic acid at pyrolytic temperatures could take place by condensation of the breakdown prod-

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(15) W. Dilthey and R. Wizinger, *Ber.*, **59**, 1856 (1926).

(16) P. W. Clutterbuck and F. Reuter, *J. Chem. Soc.*, 1467 (1935).

(17) H. H. Wasserman, E. R. Wasserman and T. C. Liu, THIS JOURNAL, **75**, 2056 (1953).

ucts benzophenone and 3-phenylisocoumaranone[18] (IX, R = H) as shown in Chart I.

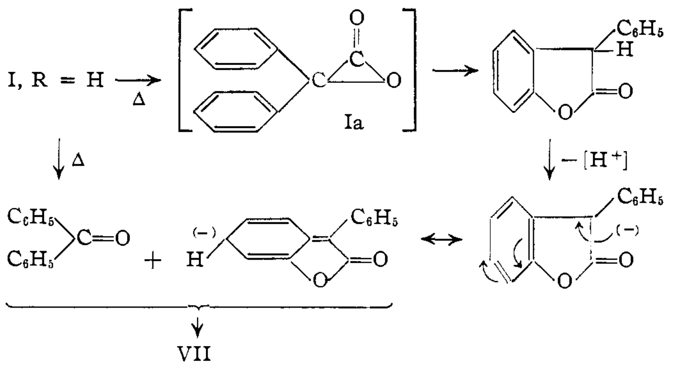


Chart I

The possibility that a reaction scheme such as that pictured above might take place directly by condensing benzophenone with 3-phenylisocoumaranone under conditions approximating those in the pyrolysis of benzilic acid led us to heat these reactants together in the presence of sodium carbonate and with other bases, at varying concentrations, pressures and temperatures. These experiments failed to produce any of the expected purple-black product. When, however, benzophenone dichloride was allowed to react with the sodium salt of 3-phenylisocoumaranone in anhydrous benzene solution, an immediate deep-red coloration developed, and Langenbeck's compound was formed in 25% yield.[19] This synthesis confirmed all of the previous conclusions with respect to the main structural features of Langenbeck's compound, proved that it had the composition $C_{27}H_{18}O_2$, and clearly ruled out any diphenylketene dimer formulations. There remained at this stage of the structure-proof, only one uncertain point, namely, the location of the diphenylmethylene residue.

For a product, $C_{27}H_{18}O_2$, formed in the reaction of 3-phenylisocoumaranone with benzophenone dichloride there are several possible structures, VII, XI, XII (or the corresponding *ortho* isomer XIIa) and XIII, as shown in Chart II. Products VII, XI, XII, and XIIa would result from attack at one of the *ortho* or *para* positions of either the substituted or the unsubstituted aromatic ring of the 3-phenylisocoumaranone. Formation of the radical XIII would be analogous to the reaction claimed by Schlenk and Mark[20] to take place between benzophenone dichloride and sodium triphenylmethyl, leading to the stable radical, pentaphenylethyl.

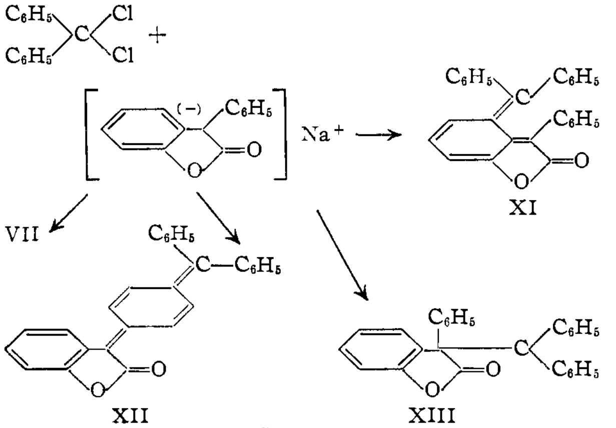
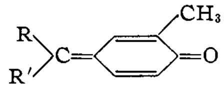


Chart II

Structures XII and XIIa can be ruled out immediately since neither compound would account for the fact that one mole of benzoic acid always is isolated per mole of oxidized material. The radical structure, XIII, is also untenable in view of the lack of the paramagnetic behavior shown by Langenbeck's compound. Dr. S. I. Weissman kindly measured the paramagnetic resonance absorption of the colored compound and his results[21] confirmed Müller's previous conclusions[10] that this product is not a free radical.

Of the two remaining structures VII and XI, both of which fit the physical and chemical properties of Langenbeck's compound, VII definitely is preferred on the basis of the fact that the attack of benzophenone dichloride on the isocoumaranone system would be expected to take place at the less hindered *para* position. There are many analogies for such preferential *para* attack, as in the reaction of 1-naphthylphenyldichloromethane with *o*-cresol where the *p*-quinomethan XIV is formed exclusively.[22] Furthermore, attempts to effect condensation between benzophenone dichloride and an isocoumaranone where the *para* position is blocked (*o*-hydroxy-*p*,*p*′-dimethoxydiphenylacetic acid lactone (IX, R = OCH_3)) resulted only in recovered starting materials and decomposition products.



XIV

In order to prove conclusively that the colored quinodimethan contains *para* substitution, as in VII, there was needed a synthesis either of Langenbeck's compound or of one of the degradation products, in which the location of the diphenylmethylene residue was known. The synthesis of lactone A therefore was attempted by the condensation of *m*-diphenylmethylphenol with mandelic acid or its nitrile. Although this method had proven to be useful for the preparation of other related isocoumaranone derivatives,[17,23] no lactone A could be obtained in this way, and attention was therefore directed to the only other degradation product on hand containing four phenyl rings, the phenolic ketone $C_{26}H_{20}O_3$.

The phenolic ketone obtained in very low yields

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[18] The isolation of isocoumaranones during pyrolysis of aryl glycolic acids has been reported recently in the case of anisilic acid where the main product has been shown[17] to be IX, R = OCH_3; moreover, in the present work the intermediate 3-phenylisocoumaranone (IX, R = H) has been detected in small amounts when benzilic acid (I, R = H) is subjected to slow, controlled breakdown.

[19] This experiment was carried out by H. R. Wetherell, Jr.

[20] W. Schlenk and H. Mark, *Ber.*, **55B**, 2285 (1922).

[21] S. I. Weissman, Washington University, St. Louis, Mo., private communication.

[22] W. Bockemüller and R. Geier, *Ann.*, **542**, 185 (1939).

[23] A. Bistrzycki and J. Flatau, *Ber.*, **28**, 989 (1895).

from the reaction of periodic acid with the dipiperidine derivative of Langenbeck's compound is soluble in alkali, gives a strong ferric chloride coloration, reacts with 2,4-dinitrophenylhydrazine to give an unstable product, and exhibits bands at 2.8 and 6.13 μ in the infrared. Its infrared spectrum shows considerable similarity in the 2 and 6 μ regions to that of *p*-hydroxybenzophenone. The above evidence strongly suggested that this oxidation product was the hydroxy phenolic ketone XVII, and a synthesis of XVII therefore was carried out as described below, and summarized in Chart III.

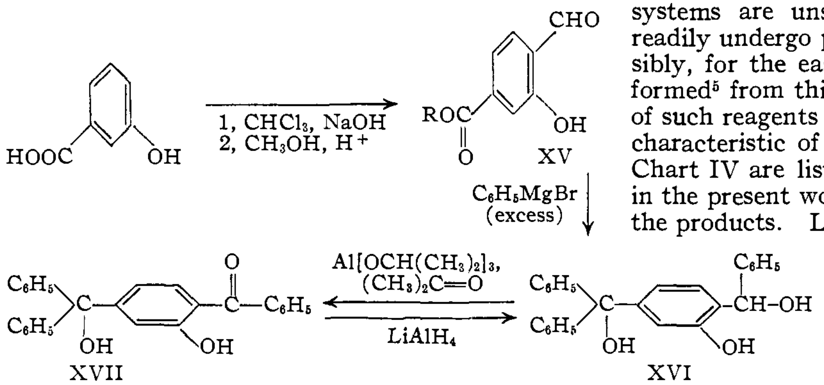


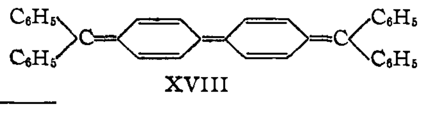
CHART III

The known[24] 3-hydroxy-4-formylbenzoic acid (XV, $R = H$) was prepared by a Reimer–Tiemann reaction using *m*-hydroxybenzoic acid. The methyl ester (XV, $R = CH_3$) then was treated with excess phenylmagnesium bromide to form the triol XVI. The latter compound was converted by Oppenauer oxidation to a crystalline ketone identical in every respect with the phenolic ketone XVII derived by degradation of Langenbeck's compound. The infrared spectrum of the synthetic triol XVI was superimposable upon that of the triol obtained by lithium aluminum hydride reduction of the ketone XVII.

The above unambiguous synthesis of the phenolic ketone XVII, which contains all of the essential structural features of Langenbeck's compound, confirms the conclusions derived from the previous synthetic and degradative evidence, and clearly establishes the structure of the colored pyrolysis product as the quinodimethan VII.

Formation of VII during the pyrolysis of benzilic acid probably takes place by a condensation reaction analogous to that pictured in Chart I, although it is worth considering that the diphenylmethylene fragment formed by decarboxylation of a diradical derived from Ia may be the important intermediate involved in the attack on the aromatic ring. It is planned to devote further study to this phase of the problem.

The intense, purple-black color of Langenbeck's compound is consistent with its formulation as a quinodimethan, related systems, such as the Tschitschibabin hydrocarbon XVIII exhibiting similar intense absorption in the visible region of the spectrum.[25]



XVIII

The chemical behavior of Langenbeck's compound also is consistent with that expected of the reactive conjugated system present in VII. Such systems are unstable toward oxidation,[26,27] and readily undergo polymerization[28,29] accounting, possibly, for the ease with which tars and resins are formed[5] from this compound. The ready addition of such reagents as hydrogen and piperidine is also characteristic of the quinodimethan system.[28] In Chart IV are listed some of the reactions studied in the present work, and the structures assigned to the products. Lactones A and B, formed by addition of hydrogen, are assigned the isocoumaranone and bislactone structures XIX and XX,[30] respectively; the dipiperidine derivative is pictured as XXI, formed by 1,8-addition of a molecule of piperidine followed by salt formation with a second molecule of piperidine. Other reactions of Langenbeck's compound will be described in a forthcoming publication.

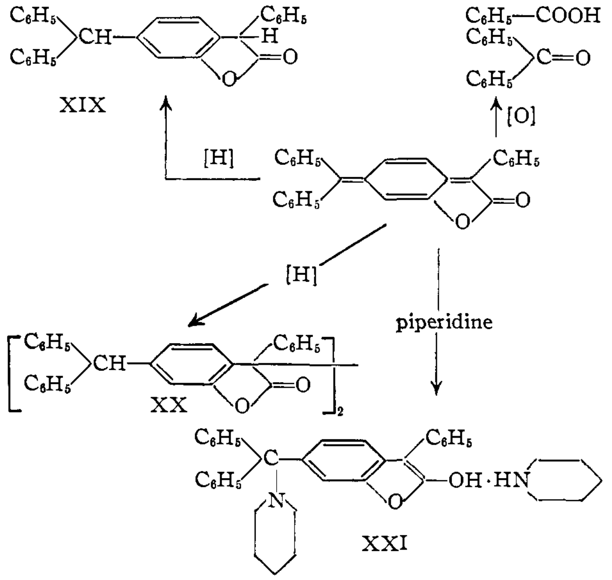


CHART IV

Acknowledgments.—The authors wish to acknowledge support of this work by a Frederick Gardner Cottrell Grant of the Research Corporation. Thanks are expressed to Prof. W. Bergmann

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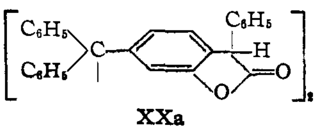
(30) That lactone B may have the alternate bislactone structure XXa is not excluded by any of the evidence although, in view of the greater lability of the hydrogen atom alpha- to the carbonyl group, this is a less likely possibility.



XXa

for his help and encouragement, and to Prof. R. B. Woodward for valuable discussions.

Experimental

Langenbeck's Compound. The Lactone of 1-Carboxybenzilidene-2-hydroxy-4-benzhydrylidene-2,5-cyclohexadiene (VII).—Twenty-five grams of benzilic acid and 0.4 g. of sodium carbonate were mixed in a 250-ml. erlenmeyer flask equipped with a tall air condenser. On heating rapidly with two meker burners, the mixture melted, foamed and turned dark red. Heating was stopped when the mixture had foamed to about three times the melted volume (after about one minute) and, after the reaction had subsided, the mixture was refluxed with 100 ml. of carbon tetrachloride for a few minutes. The solution was then chilled, filtered cold, the filtrate diluted with 2 volumes of ethanol and refrigerated overnight. The resulting precipitate was removed by filtration, washed with ethanol and then recrystallized five times with ethyl acetate. By this process 2.5 g. of dark, red-violet crystals, m.p. 165–166°, was obtained.

Anal. Calcd. for $C_{27}H_{18}O_2$: C, 86.61; H, 4.85. Found: C, 86.59; H, 4.92.

The infrared absorption spectrum of Langenbeck's compound in chloroform solution shows broad absorption at about 5.75 μ which can be resolved into two bands at 5.72 and 5.77 μ.

Oxidation of Langenbeck's Compound with Basic Permanganate.—Langenbeck's compound, 490 mg., was refluxed with 5 g. of KOH in 20 ml. of ethanol until the color of the solution faded to a straw-yellow. Two-hundred ml. of water was added and 50 ml. of solvent was removed by distillation. Five grams of potassium permanganate was added, the solution diluted to 600 ml., heated and 400 ml. of distillate collected. Ether extraction of the distillate gave 142 mg. of benzophenone (0.60 mole per mole of parent compound), identified by mixture melting point and infrared spectrum. The excess oxidant was decomposed with sodium bisulfite, the manganese dioxide removed by filtration, the filtrate acidified, chilled and then extracted with ether. The residue remaining after removal of ether was worked up for benzoic acid, final purification being accomplished by vacuum sublimation. In this way 143 mg. of pure benzoic acid (0.89 mole per mole of oxidized compound) was isolated.

Ozonolysis of Langenbeck's Compound.—A solution of 1 g. of Langenbeck's compound in 140 ml. of carbon tetrachloride was chilled in ice–water and ozone was bubbled in rapidly until the deep-red color of the solution faded to a pale yellow (after about 7 minutes). The solution was swept free of ozone with nitrogen and 2 g. of zinc dust and 10 ml. of acetic acid were added.

After several minutes of vigorous stirring, the solution gave a negative starch–iodide test. The zinc was removed by filtration, and the solution was washed with water. The carbon tetrachloride was removed from the organic layer by distillation *in vacuo*. The residue was steam distilled, one liter of distillate being collected. Ether extraction of the distillate gave 331 mg. of oily residue which crystallized on inoculation with benzophenone. This product, 249 mg. (equivalent to 0.51 mole of benzophenone per mole of starting material), yielded the 2,4-dinitrophenylhydrazone of benzophenone, m.p. and mixture m.p. 238–240°. No other neutral fragment was isolated from the oily reaction mixture.

Lactone A. 3-Phenyl-6-benzhydrylisocoumaranone (XIX). (a) **By Reduction by Phosphorus and Iodine.**—Ten grams of Langenbeck's compound, 6.8 g. of red phosphorus and 2.7 g. of iodine were refluxed for four hours with 100 ml. of acetic acid and 2 ml. of water. The bright red-violet color of the original solution was discharged within 5 minutes. The mixture was cooled and filtered free of phosphorus. Lactone A (7.7 g.) precipitated directly from the filtrate. After one recrystallization from 95% ethanol, colorless needles were obtained, m.p. 134.5–136.5°. Dilution of the acetic acid mother liquor gave a further quantity of lactone A. After one recrystallization, the total yield was 85%.

(b) **By Catalytic Hydrogenation.**—Langenbeck's compound (426 mg.) was dissolved in 50 ml. of freshly distilled ethyl acetate, and the solution shaken with 10 mg. of palladium in a hydrogenation apparatus. After two hours of shaking, a volume of hydrogen corresponding to one molar equivalent of hydrogen was absorbed. The nearly colorless solution was filtered, diluted with 50 ml. of 50% ethanol and cooled. The crystals which separated were purified by recrystallization from methanol, yielding 344 mg. of material melting at 125–130°.

(c) **By Reduction with Hydriodic Acid.**—A mixture of 0.5 g. of Langenbeck's compound and 10 ml. of hydriodic acid, sp. gr. 1.5, was refluxed for four hours. The suspended solid gradually turned pale orange, and became nearly colorless at the end of this period. The flask was then cooled, the solid broken up, and the mixture poured into 200 ml. of ice-water containing excess sodium bisulfite. The solid product was separated by filtration and, after recrystallization from methanol, 350 mg. of material melting 130° was obtained. Essentially the same results were obtained by the use of hydriodic acid of sp. gr. 1.7.

Anal. Calcd. for $C_{27}H_{20}O_2$: C, 86.14; H, 5.36; mol. wt., 376. Found: C, 86.40; H, 5.51; mol. wt., 365.

The infrared spectrum of lactone A in chloroform solution shows an intense band at 5.51 μ.

Hydrolysis of Lactone A. 2-Hydroxy-4-benzhydryldiphenylacetic Acid.—Three grams of lactone A was heated on a steam-bath with 2 g. of potassium hydroxide in 100 ml. of water for five hours. A small amount of tan precipitate was separated from the solution after cooling, and the filtrate was acidified, giving a pale yellow amorphous precipitate. Recrystallization of this solid from benzene–petroleum ether gave a crystalline product (2.5 g.), m.p. 174–175°. This material rapidly underwent change on standing in solution or in a desiccator, the melting point gradually dropping to 106–110°. When the acid was heated up to 160°, it was converted to lactone A, m.p. and mixture m.p. 130°.

Anal. Calcd. for $C_{27}H_{22}O_3$: C, 82.21; H, 5.62. Found: C, 82.23; H, 6.04.

In another experiment, the initially formed acid was treated with aqueous potassium bicarbonate solution, whereupon a potassium salt was formed which was insoluble in cold water, but which could be recrystallized from methanol, or warm water, m.p. 185°. The neutralization equivalent of this product was found to be 428. The calculated value for $C_{27}H_{21}O_3K$ is 433.

Lactone B. 3,3′-Bis-(3-phenyl-6-benzhydrylisocoumaranone (XX).—By slow evaporation of the ethyl acetate–ethanol mother liquors from which lactone A was separated, as described in (b) above, there was isolated 9 mg. of material, which, on recrystallization from ethyl acetate, melted 214–218°.

Anal. Calcd. for $C_{54}H_{38}O_4$: C, 86.38; H, 5.10; mol. wt., 750. Found: C, 86.36; H, 5.12; mol. wt. (benzene, freezing point depression), 670.

In chloroform solution, lactone B shows a carbonyl band in the infrared at 5.55 μ. Its ultraviolet absorption spectrum (peak at 245 mμ, plateau at 265–285 mμ) is similar to that of lactone A. At its melting point it decomposes with the formation of a deep red melt. Solutions of lactone B in hot toluene are pale blue, and gradually become decolorized when cooled.

Conversion of Lactone A to Lactone B by Chromic Acid Oxidation.—To a solution of 1 g. of lactone A in 100 ml. of acetic acid was added 0.19 g. of CrO_3 and 100 ml. of water. The reaction was allowed to stand at room temperature overnight, whereupon a small amount of precipitate separated. This solid, m.p. 208°, was identified as lactone B by comparison of its infrared spectrum with a sample of the pure bislactone. Over a period of several weeks, further solid separated from the reaction mixture, and a total of 0.3 g. of lactone B was obtained in this way.

Synthesis of Langenbeck's Compound from 3-Phenylisocoumaranone.—A mixture of 3-phenylisocoumaranone (2 g.) and 0.24 g. of sodium was refluxed in benzene for one hour and then allowed to stand overnight. The slight amount of unreacted sodium was removed by filtration, and to the solution was added, in an atmosphere of nitrogen, a solution of 1.13 g. of benzophenone dichloride in 15 ml. of dry benzene. An immediate deep red coloration developed, and a solid separated. The solution was refluxed for two hours under nitrogen, then cooled, and the purple-black precipitate collected by filtration. The solid was taken up in benzene and the benzene solution concentrated to yield a crude purple-black product. This material was recrystallized from ethyl acetate, and then from high-boiling petroleum ether to yield 0.57 g. of Langenbeck's compound (32%), m.p. 160°. The infrared spectrum of this product was superimposable upon that of the product m.p. 165° obtained by pyrolysis of benzilic acid. Use of 2-hydroxy-4,4'-dimethoxydiphenylacetic acid lactone (IX, R = OCH_3) in place of 3-phenylisocoumaranone in the above reaction did not lead to any *o*-quinodimethan analog of Langenbeck's compound. The only products recovered were the starting isocoumaranone and other colorless unidentified materials.

The Dipiperidine Derivative (XXI).—Eighty milliliters of freshly distilled piperidine, b.p. 105–107°, was added to 5 g. of Langenbeck's compound, and solution was effected with the aid of gentle warming on a steam-bath. The resulting dark-red solution was stoppered and allowed to remain at room temperature for three days at which time the color of the solution had faded to a straw-yellow. The excess piperidine was removed *in vacuo*, and the resulting red residue was triturated with 20 ml. of ligroin. Continued washing with ligroin resulted in the formation of an almost white product m.p. 208° dec. (reported m.p. 212°).

2-Hydroxy-4-diphenylhydroxymethylbenzophenone (XVII) by the Action of Periodic Acid on the Dipiperidine Derivative.—To a solution of 3.7 g. of piperidine salt (XXI) in 100 ml. of peroxide-free dioxane was added a solution of 1.8 g. of periodic acid in 40 ml. of water. The mixture was refrigerated for one week, then diluted with water and extracted with ether. The ether extract was washed with aqueous bisulfite, dried and concentrated *in vacuo*. The resulting oily residue was dissolved in hot alcohol and reprecipitated with water. Repetition of this process and recrystallization of the amorphous precipitate from *n*-heptane yielded 50 mg. of a crystalline product, m.p. 132–133°.

Anal. Calcd. for $C_{26}H_{20}O_3$: C, 82.08; H, 5.30. Found: C, 82.00; H, 5.49.

This compound shows bands at 2.8 and 6.13 μ in the infrared, is soluble in dilute alkali, and gives a deep brown coloration with ferric chloride.

Methyl 3-Hydroxy-4-formylbenzoate (XV, R = CH_3).—Eight hundred milligrams of 3-hydroxy-4-formylbenzoic acid prepared by the method of Tiemann[24] was dissolved in 100 ml. of absolute methanol, and 0.5 ml. of concentrated sulfuric acid was added. After refluxing this mixture overnight and removal of solvent, a solid residue was obtained which was crystallized from ethyl alcohol yielding needles (30%), m.p. 135–135.5°.

Anal. Calcd. for $C_9H_8O_4$: C, 60.00; H, 4.48. Found: C, 59.70; H, 4.41.

2-Hydroxy-4-diphenylhydroxymethylbenzhydrol (XVI).—Phenylmagnesium bromide was prepared from 0.882 g. of magnesium turnings in 20 ml. of anhydrous ether and 5.7 g. of bromobenzene in 10 ml. of ether. To the suspension was added 1.08 g. of methyl 3-hydroxy-4-formylbenzoate in 50 ml. of ether. The mixture was refluxed for 30 minutes, and then allowed to stand overnight. A mixture of 30 ml. of water and 30 ml. of acetic acid was then added. The yellow ether layer was separated, washed with aqueous bicarbonate solution and then evaporated to dryness, yielding a yellow oil. The oil was further purified by chromatography on an alumina column using 50% ether–petroleum ether as an eluant. Recrystallization of the amorphous solid thus obtained from *n*-heptane yielded 0.57 g. (25%) of solid, which melted unsharply at 68–70°. The infrared absorption spectrum of this product shows no bands in the carbonyl region and is identical with the spectrum of the alcohol derived by lithium aluminum hydride reduction of the ketone XVII.

Anal. Calcd. for $C_{26}H_{22}O_3$: C, 81.65; H, 5.80. Found: C, 81.17; H, 6.13.

Reduction of the Ketone XVII by Lithium Aluminum Hydride.—Fifty milligrams of lithium aluminum hydride was suspended in 50 ml. of anhydrous ether, and to the mixture was added 89 mg. of 2-hydroxy-4-diphenylhydroxymethylbenzophenone dissolved in 15 ml. of anhydrous ether. The reaction mixture was stirred for 1 hr., and then allowed to stand overnight. The excess lithium aluminum hydride and lithium salt were decomposed by the addition of aqueous acetic acid, and the ether layer separated. The ether solution was washed with aqueous bicarbonate, dried over sodium sulfate and the dried solution was concentrated to an oil. By chromatography on an alumina column using ether–petroleum ether as eluant, a product was obtained (15 mg.) which was identical (comparison of infrared spectra) with the product XVI obtained by the action of excess phenylmagnesium bromide on methyl 3-hydroxy-4-formylbenzoate.

2-Hydroxy-4-diphenylhydroxymethylbenzophenone (XVII) by Synthesis.—To a solution of 0.159 g. of 2-hydroxy-4-diphenylhydroxymethylbenzhydrol (XVI) in 35 ml. of dry acetone and 50 ml. of dry benzene, was added 0.5 g. of freshly prepared aluminum isopropoxide. The reaction mixture was refluxed for 22 hours and then allowed to stand overnight at room temperature. The resulting solution was evaporated to dryness *in vacuo*, the residue acidified with 6 *N* sulfuric acid and then extracted with ether. Evaporation of the dried ether solution yielded a brown oil which was converted to a crystalline solid (90 mg.) m.p. 130° by crystallization from *n*-heptane. The infrared spectrum of this product was identical with that of the ketone XVII, m.p. 130–132°, obtained by periodic acid oxidation of the dipiperidene derivative XXI.

Infrared Absorption Spectra.—All infrared absorption spectra were determined on a Perkin–Elmer recording spectrophotometer, model 21.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Steric Effect of Methylene Groups. VII

BY STUART W. FENTON, ARTHUR E. DEWALD[1] AND R. T. ARNOLD

RECEIVED AUGUST 12, 1954

In previous papers of this series chemical and physical evidence has been presented to show that the steric effect of a methylene group in a five-membered ring is smaller than that in a corresponding six-membered ring. Rates of saponification of esters derived from hydrindene-4-carboxylic acid, 5,6,7,8-tetrahydro-1-naphthoic acid, and the 7- and 4-dimethylamino derivatives of these two acids, respectively, have now been determined and completely support the conclusions drawn from our earlier work.

It has been assumed tacitly during the development of classical stereochemistry that the steric effect of a particular substituent (such as methyl, nitro, etc.) exhibits a reasonably constant steric influence. Considerable success has been achieved in correlating the experimental steric effectiveness of groups with their calculated sizes.[2]

Earlier publications from this Laboratory[3] dealing with comparative studies in the hydrindene and tetralin series have shown that the methylene groups in these substances exert different steric influences on *ortho* substituents attached to the benzenoid ring, and that the methylene group in the five-membered ring has the smaller effect. With re-

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