Duryl phenyl ketone gave a viscous yellow oil (approximately 90% yield) which seemed to be impure allyldurylphenylcarbinol. The infrared spectrum has bands assignable to a hydroxyl group (3580 cm.$^{-1}$), as well as to a terminal methylene group (1635, 995, and 915 cm.$^{-1}$) but none in the carbonyl region. Catalytic hydrogenation evidently (infrared spectrum) gave the saturated carbinol which, however, lost water when distilled; the resulting 1-duryl-1-phenyl-1-butene boiled at 157–159° at 0.65 mm. pressure and crystallized when allowed to stand, m.p. 52.5–54°. The n.m.r. spectrum indicated the presence of a trisubstituted olefin. This olefin was made also by treating the carbinol with acetic anhydride, 20% sulfuric acid, or thionyl chloride in pyridine. In all cases the infrared spectrograms were superimposable.

The identification of the olefin was supported by the results of oxidation. The olefin (3.0 g., 0.0113 mole), dissolved in 15 ml. of chloroform, was added to 35 ml. of glacial acetic acid, and a solution of 4.2 g. of chromium trioxide, 3 ml. of water, and 22 ml. of glacial acetic acid was added dropwise. The temperature was maintained at 40–45° during the addition and then at 50° for 20 min. longer. The mixture was cooled and excess chromic acid was destroyed by the addition of 5 ml. of methanol. After the mixture was concentrated by distillation at diminished pressure, water was added and the ketone appeared as a yellow solid. It was washed with acid and then with base and recrystallized from ethanol, m.p. 123–124.5°.

Anal. Calcd. for $C_{23}H_{30}O$: C, 85.8; H, 9.31. Found: C, 85.5; H, 9.62.

The infrared spectrum has a strong carbonyl band at 1710 cm.$^{-1}$, and a propionyl group is indicated by the n.m.r. spectrum.

An olefin, evidently 4-duryl-4-phenyl-1-butene, was obtained by heating allyldurylphenylcarbinol at 225–230° for 6 hr.; the mixture was then treated with boiling 95% ethanol and the ethanol was removed from the solution by evaporation. The red oil, chromatographed on Fluorisil or activated alumina, gave early fractions that separated from ethanol as colorless crystals, m.p. 50–51°.

Anal. Calcd. for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 90.77; H, 9.27.

The infrared spectrum has bands assignable to a terminal methylene group (1635, 995, and 915 cm.$^{-1}$).

A second compound, obtained during the development of the chromatogram, melted at 118–120° after recrystallization from *n*-butyl ether. A mixture melting point with a pure sample of duryl phenyl ketone showed no depression.

An ether solution of 5.57 g. (0.032 mole) of **mesityl vinyl ketone** was added dropwise over a period of 1 hr. to 100 ml. of a solution which contained 0.128 mole of the allyl reagent. The gray slurry that formed was agitated for an additional 1 hr. and poured into an iced, saturated solution of ammonium chloride. The organic portion, when extracted with ether and distilled, gave mesityl 4-pentenyl ketone, b.p. 106.5–108° (0.65 mm.), $n^{24.5}\text{D}$ 1.523. The infrared spectrum has bands that can be assigned to a conjugated carbonyl group (1690 cm.$^{-1}$), a terminal methylene group (1635, 995, and 915 cm.$^{-1}$), and a mesityl group (852 cm.$^{-1}$). Hydrogenation of the pentenyl ketone over platinum oxide gave capromesitylene as an oil that boiled at 100–103° (0.6 mm.), $n^{22}\text{D}$ 1.5048 [lit.[7] b.p. 105–107° (0.8 mm.), $n^{20}\text{D}$ 1.5042]. The dinitro derivative was prepared and found to melt at 121.5–122.5° (lit.[7] m.p. 122.5–123°).

Anal. Calcd. for $C_{15}H_{20}N_2O_5$: N, 9.08. Found: N, 8.89.

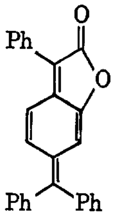
Quinodimethans, Analogs of the Intensely Colored Langenbeck Compound

Raymond D. Kimbrough, Jr.,[1a] Kenneth W. Kraus,[1b]
and John J. Partridge, Jr.[1c]

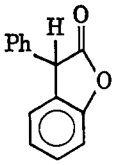
*Nuclear Sciences Division, Engineering Experiment Station
and School of Chemistry,
Georgia Institute of Technology, Atlanta, Georgia 30332*

Received June 1, 1965

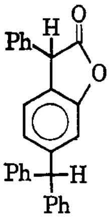
From the pyrolysis of benzilic acid, Langenbeck isolated an intensely purple-black, crystalline compound,[2] whose structure was shown by Wasserman to be the quinodimethan I.[3] Wasserman synthesized I from reaction of the enolate of 3-phenylisocoumaranone, II, with diphenylmethylene chloride and also reduced I with phosphorus and iodine to form III.[3]



I



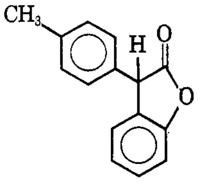
II



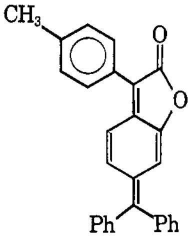
III

The reactions leading to I and III were repeated in the present study. The n.m.r. spectra of I, II, and III were recorded and are consistent with the assigned structures.

p-Tolualdehyde was converted to the cyanohydrin, *p*-methylmandelonitrile, which was not purified but was treated directly with phenol and 73% sulfuric acid for the synthesis of 3-(*p*-tolyl)isocoumaranone (IV). The enol of IV with diphenylmethylene chloride gave the analog, V. The color and spectral properties of V resembled those of I. The infrared spectrum of V had absorption peaks at 5.72 and 5.79 μ, which were also present in I.[3,4]

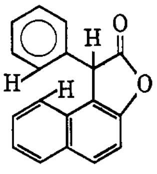


IV

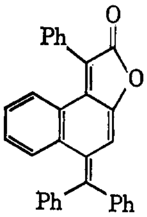


V

The reaction of the enolate of VI with diphenylmethylene chloride produced an intensely red-orange crystalline product. That this material was VII, the expected analog of the Langenbeck compound, was indicated by the analysis and by the infrared and the n.m.r. spectra.



VI



VII

It is unlikely that the diphenylmethylene chloride reacted with the enolate of VI at the phenyl ring rather than the naphthalene ring. The negative charge of the enolate is delocalized onto the naphthalene ring,

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(1) (a) To whom correspondence concerning this paper should be addressed. (b) National Science Foundation College Faculty Research Participant, summer 1963. (c) National Science Foundation Undergraduate Research Participant, summer 1963.

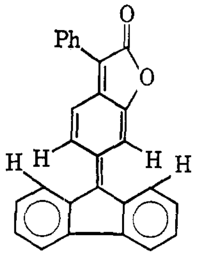
(2) W. Langenbeck and H. Langenbeck, *Ber.*, **B61**, 938 (1928).

(3) H. H. Wasserman, H. W. Ackerman, H. H. Wotiz, and T. C. Liu, *J. Am. Chem. Soc.*, **77**, 973 (1955).

(4) R. S. Armstrong and J. R. W. LeFevre, *Australian J. Chem.*, **10**, 34 (1957).

but similar delocalization onto the benzene ring is impossible, because this ring is crowded out of the plane of the rest of the molecule by interaction of the two hydrogen atoms pictured in VI.[5] The structure of this analog was proven to be VII by the isolation of benzoic acid and benzophenone on chromic acid oxidation.[6] The product resulting from reaction at the benzene ring of the enolate of VI would give benzophenone but no benzoic acid.

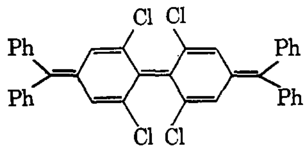
The reaction of the enolate of II with 9,9-dichlorofluorene produced the lavender-black compound, VIII. The characteristic infrared absorption at 5.72 and 5.78 μ was present. VIII decomposed on standing, particularly rapidly in the presence of traces of base or oxygen.



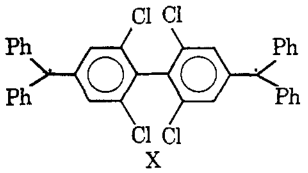
VIII

The decomposition product of VIII was a tan insoluble powder that decomposed without melting above 200°. The lack of intense color indicates that the quinoid chromophore of VIII had been destroyed. The decomposition product did not have the infrared absorption at 5.72 and 5.78 μ, characteristic of the Langenbeck-type compounds, but had an absorption peak of 5.55 μ, characteristic of compounds II, III, IV, and VI.[7]

The instability of VIII may be explained by a consideration of the crowding involved in maintaining the coplanarity of the quinoid and fluorene rings. Models indicate that there is appreciable crowding of the 1- and 8-hydrogen atoms of the fluorene with the adjacent hydrogen atoms on the quinoid ring, shown in VIII. This is the same type of crowding that exists in benzophenone where the two rings are not coplanar.[5] Another example of this type of interaction is IX, which is so twisted that it exists as the paramagnetic diradical X, in which the rings become benzenoid. Diradical X has a tendency to associate to a diamagnetic polymer.[8]

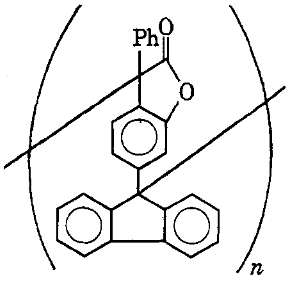


IX

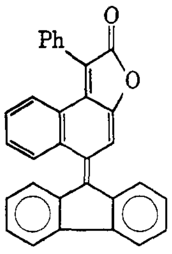


X

A comparable tendency in VIII toward diradical formation and dimerization or polymerization would explain both its instability toward oxygen and its decomposition on standing. Polymerization of VIII would probably produce the repeating unit XI which is consistent with the observed loss of the quinoid chromophore and the regeneration of the lactone ring with absorption at 5.55 μ. The analysis is consistent with the formulation XI. Conversion of the quinoid ring of VIII to a benzenoid ring would provide additional driving force for the polymerization.



XI



XII

Similar results were obtained in efforts to prepare XII from the enolate of VI and 9,9-dichlorofluorene. The product was also intense lavender-black and unstable, particularly with base or oxygen. XII gave the characteristic absorption in the infrared at 5.72 and 5.79 μ. XII is even more twisted than VIII and a similar argument can be advanced for its instability. The decomposition product was also a tan powder which showed absorption in the infrared at 5.55 μ and was probably a polymer whose structure is analogous to XI.

Reaction of the enolate of ethyl diphenylacetate with diphenylmethylene chloride did not produce an intensely colored compound. The product of this reaction was a mixture of tetraphenylethylene and tetraphenylethylene chloride.[9]

Schoenberg recovered I quantitatively from a benzene solution that had been exposed to the sunlight.[10] (Photoreductions, such as ketones to pinacols, which proceed readily in solutions of alcohols or alkanes, go very slowly or not at all in benzene solution.[11] Benzene is used as an inert solvent for photolyses of substances that are reduced in alcohols or alkanes.[12]) In a preliminary experiment, an isopropyl alcohol solution of I was exposed to the sun. The color faded and a tan insoluble material formed. The infrared spectrum of this product showed no absorption in the 5.7–5.8-μ region, characteristic of I, but there was absorption at 5.55 μ, characteristic of the lactone II.[7] The insolubility, the lack of intense color, and the infrared spectrum suggest a polymer of the type XIII.

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[5] For a discussion of such effects, see R. N. Jones, *J. Am. Chem. Soc.*, **67**, 2127 (1945); F. A. Vingiello, S-G. Quo, and P. Polss, *J. Org. Chem.*, **30**, 266 (1965).

[6] R. D. Kimbrough, *Anal. Chim. Acta*, **32**, 95 (1965).

[7] H. H. Wasserman, E. R. Wasserman, and T. C. Liu, *J. Am. Chem. Soc.*, **75**, 2056 (1953).

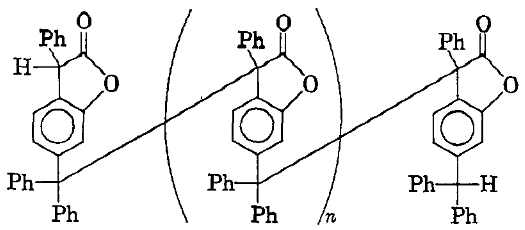
[8] E. Mueller and H. Neuhoff, *Ber.*, **72**, 2063 (1939); E. Mueller and E. Tietz, *ibid.*, **74**, 807 (1941).

[9] An equimolar mixture of tetraphenylethylene and tetraphenylethylene chloride can be recrystallized without changing the composition and seems to be a single substance, melting with decomposition at 185–186°. (The decomposition point of the tetraphenylethylene chloride, 186°, is not changed by addition of tetraphenylethylene.) The equimolar mixture seems to be the "*compound*" $C_{26}H_{19}Cl$, which was obtained together with benzopinacol from treatment of diphenylethylene chloride with acetic acid: J. Schmidlin and R. von Escher, *ibid.*, **43**, 1160 (1910).

[10] A. Schoenberg and A. Sina, *J. Chem. Soc.*, 175 (1947).

[11] R. D. Kimbrough, *Diplomarbeit* (M.S. Thesis), Universitaet Goettingen, 1955.

[12] N. C. Yang and D. H. Yang, *J. Am. Chem. Soc.*, **80**, 2913 (1958).



XIII

Experimental Section

Analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points were taken on a hot-stage apparatus and are not corrected. Infrared spectra were recorded on a Perkin-Elmer Infracord. Ultraviolet–visible spectra were recorded with a Bausch and Lomb Spectronic 505. N.m.r. spectra were measured with a Varian A-60 spectrometer at 60 Mc. using tetramethylsilane as an external standard. Chemical shifts are reported in τ values and relative intensities are given in parentheses.

Preparation of 3-Phenylisocoumaranone (II).—A mixture of 20 g. of mandelic acid, 28 g. of phenol, and 60 ml. of 73% sulfuric acid was heated 20 min. in a steam bath with frequent shaking. The mixture was poured into 200 ml. of cold water. The water was decanted and the sticky mass was washed three times with 200 ml. of water. The product was recrystallized from ethanol, yield 9.0 g. (32%), m.p. 107–111°. An additional recrystallization from ethanol gave m.p. 111–112°, lit.[13] m.p. 113–114°; infrared ($CHCl_3$) 5.53, 6.17, 6.76, 6.83, 7.76, 8.53, 8.92, 9.44, and 11.05 μ; n.m.r. (CS_2) multiplet τ 2.5–2.8 (9), singlet 5.11 (1).

Preparation of 4-Diphenylmethylene-2-hydroxy-α-phenyl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetic Acid, γ-Lactone (the Langenbeck Compound) (I).—A solution of 2.1 g. of II in 15 ml. of dry benzene was stirred under nitrogen at 25° with 1.0 g. of 50% sodium hydride dispersion in oil until no more hydrogen was evolved. A solution of 2.4 g. of IV in 15 ml. of benzene was added and the stirring was continued overnight. The mixture was cooled in ice and the solid was collected on a filter. After recrystallization from ethyl acetate the yield was 0.61 g. (35%), m.p. 163–165°. Two additional recrystallizations from ethyl acetate raised the melting point to 166–167° (lit.[2,3] m.p. 168°); n.m.r. (CCl_4) doublet τ 2.1–2.3 (2), multiplet 2.5–2.8 (15), singlet 3.30 (1).

Reduction of I to 3-Phenyl-6-benzhydrylisocoumaranone (III).—The procedure of Wasserman[3] for the reduction of I with phosphorus and iodine gave a 70% yield of product. It was recrystallized from ethanol to constant melting point, 128–129° (lit.[3] m.p. 134.5–135.5°). The infrared spectrum agreed with that reported[3]: n.m.r. (CS_2) multiplet τ 2.5–3.1 (18), singlet 4.33 (1), singlet 5.17 (1).

Preparation of *p*-Methylmandelonitrile.—To a stirred mixture of 15 g. of sodium cyanide, 50 ml. of water, and 36 g. of *p*-tolualdehyde was added 85 ml. of a saturated solution of sodium bisulfite over a 12-min. period. During the addition of the first half of this solution, 90 g. of cracked ice was added to the reaction mixture. The oily layer of *p*-methylmandelonitrile was separated and filtered. It was used directly in the synthesis of IV.

Preparation of 3-(*p*-Tolyl)isocoumaranone (IV).—The *p*-methylmandelonitrile from above, 56 g. of phenol, and 110 ml. of 73% sulfuric acid were heated on the steam bath for 20 min. with frequent shaking. Two layers formed during the heating. The mixture was poured into 600 ml. of cold water and the oil which formed solidified after repeated washings with water. The solid was dissolved in benzene and dried with calcium chloride and the benzene was evaporated. The residue was placed in a sublimation apparatus at 150° and 2 mm. and the solid that formed on the cold finger was removed periodically. The yellowish solid obtained was recrystallized twice from ethanol to give 6.7 g. (10%) of white crystals: m.p. 90–91°; infrared ($CHCl_3$) 5.51, 6.16, 7.76, 8.94, 9.46, 11.04 μ; n.m.r. (CS_2) multiplet τ 2.6–2.9 (8), singlet 5.24 (1), singlet 7.61 (3).

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.3; H, 5.4. Found: C, 80.4; H, 5.3.

Preparation of 4-Diphenylmethylene-2-hydroxy-α-(*p*-tolyl)-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetic acid, γ-Lactone (V).—A mixture of 2.0 g. of IV, 0.25 g. of sodium, and 15 ml. of dry benzene was refluxed until hydrogen evolution stopped and was kept overnight. The benzene solution was decanted from the unreacted sodium and a solution of 1.13 g. of diphenylmethylene chloride in 15 ml. of benzene was added. A deep purple color formed immediately and the solution was refluxed for 2 hr. It was cooled and the purple-black solid was collected on a filter, yield 1.0 g. (53%). Two recrystallizations from ethyl acetate gave 0.45 g. (24%), m.p. 202–203.5°. Further recrystallizations from ethyl acetate gave m.p. 203.5–204.5°; infrared ($CHCl_3$) 5.72, 5.79, 7.43, 7.68, 10.49 μ; n.m.r. (CS_2) singlet τ 2.15 (1), singlet 2.28 (1), multiplet 2.4–2.9 (14), doublet 3.25 (1), singlet 7.51 (3).

Anal. Calcd. for $C_{28}H_{20}O_2$: C, 86.6; H, 5.2. Found: C, 86.5; H, 5.1.

Preparation of α-Phenyl-2-hydroxy-1-naphthaleneacetic Acid Lactone (VI).—The procedure of Guss[14] was followed and the product was recrystallized from ethanol: m.p. 183–185° (lit.[14] m.p. 186–187°); infrared ($CHCl_3$) 5.53, 6.32, 6.88, 8.97, 9.56, 10.31, 11.22 μ; n.m.r. (CS_2) multiplet τ 1.8–2.8 (11), singlet 4.80 (1).

Preparation of 5,6-Benzo-4-diphenylmethylene-2-hydroxy-α-phenyl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetic Acid, γ-Lactone (VII).—A solution of 2.6 g. of VI in 30 ml. of tetrahydrofuran was refluxed for 30 min. with 0.30 g. of sodium under nitrogen. The solution was decanted from unreacted sodium and refluxed with 1.2 g. of diphenylmethylene chloride for 2 hr. The deep red solution was filtered and evaporated. The residue was recrystallized once from ethyl acetate and twice from ethanol. The yield was 0.23 g. (12%): m.p. 208.5–209.5°; infrared ($CHCl_3$) 5.73, 5.77 (shoulder), 7.45, 7.55, 10.57 μ; n.m.r. (CS_2) doublet τ 2.00 (1), multiplet 2.1–2.2 (1), multiplet 2.3–2.8 (15), singlet 2.97 (1), singlet 3.11 (2); ultraviolet (ethanol) 264 mμ (ϵ 11,000), 447 mμ (ϵ 29,000).

Anal. Calcd. for $C_{31}H_{20}O_2$: C, 87.7; H, 4.8. Found: C, 87.9; H, 4.8.

Oxidation of VII.—Chromic acid oxidation of 46 mg. of VII and steam distillation of the products[6] produced 10 mg. (77%) of benzoic acid and 11 mg. (55%) of benzophenone.

Preparation of 4-Fluorenylidene-2-hydroxy-α-phenyl-2,5-cyclohexadiene-$\Delta^{1,\alpha}$-acetic Acid, γ-Lactone (VIII).—All the operations were carried out under nitrogen and all the solvents were distilled and stored under nitrogen prior to use. A solution of 1.05 g. of II in 15 ml. of benzene was stirred for 1 hr. with 0.48 g. of 50% sodium hydride emulsion in oil. A solution of 1.18 g. of 9,9-dichlorofluorene[15] in 15 ml. of benzene was added and the lavender-black mixture was stirred for an additional hour. The reaction mixture was poured onto a column of 75 ml. of silica gel and most of the colored material stuck in the top third of the column. Benzene, 300 ml., was poured through the column and the colored material did not move. The colored material was eluted with 100 ml. of acetone. The acetone was evaporated and the residue was triturated with 20 ml. of ethanol. The material thus obtained weighed 0.2 g. (11%), m.p. 177–181°. The infrared spectrum showed absorption at 5.73 μ and a shoulder at 5.78 μ and only a slight absorption at 5.55 μ: ultraviolet (ethanol) 258 mμ (ϵ 13,000), 516 mμ (ϵ 10,000).

Decomposition Product of VIII.—The reaction mixture from above, that was poured onto the silica gel column, was instead evaporated and exposed to the air overnight. The tan product was triturated twice with 10 ml. of water and twice with 10 ml. of ethyl acetate. The yield was 1.2 g. (67%), m.p. 200 dec.

Anal. Calcd. for $C_{27}H_{16}O_2$: C, 86.7; H, 4.4. Found: C, 85.5; H, 4.1.

Photoreduction of I.—A finely powdered sample of 50 mg. of I was dissolved in 125 ml. of isopropyl alcohol, and the solution in a Pyrex container was exposed to the sun. After 2 months the mixture was decolored and contained a finely divided tan precipitate. The mixture was evaporated and the infrared spectrum of the residue, discussed above, was recorded.

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(14) C. O. Guss and R. W. Lerner, *J. Am. Chem. Soc.*, **72**, 3465 (1950).

(15) I. Smedley, *J. Chem. Soc.*, **87**, 125 (1905).