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Pyrolysis of Aryl Glycolic Acids. II. The Thermochromic Product Derived from Anisilic Acid[1,2]

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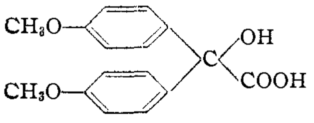
On pyrolysis, anisilic acid is converted first to the lactide, anisilide, which then rearranges to an isocoumaranone derivative. The structure of the latter was established by independent synthesis from resorcinol monomethyl ether and *p*-methoxy mandelonitrile. The observed thermochromism in the pyrolytic products has been associated with the presence of a small amount of bislactone formed by oxidative dimerization of the isocoumaranone. Studies on the free radical dissociation–association equilibrium involving the bislactone are reported.

The thermal decomposition of anisilic acid (I) was first reported by Langenbeck[4] who described

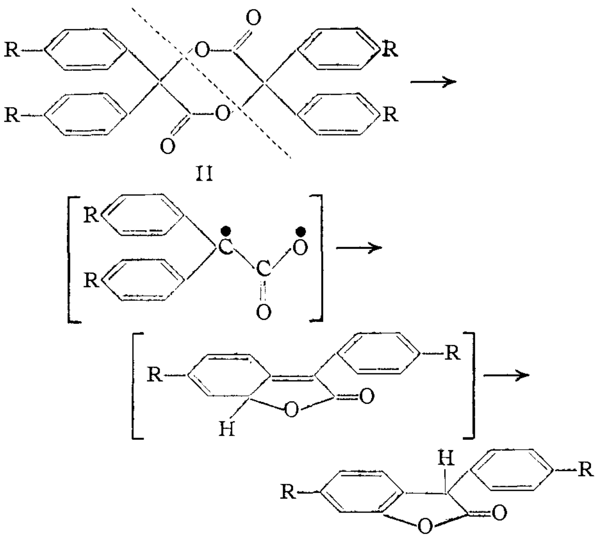


I

the color phenomena exhibited by the crude pyrolytic melt. Although he was unable to isolate any pure material from the reaction mixture, Langenbeck suggested that the thermochromic behavior of the crude melt was due to the presence of free radicals in the products. In the course of studies on the pyrolysis of aryl glycolic acids we have reinvestigated the products formed on heating anisilic acid, and are reporting here our conclusions as to the cause of the thermochromic phenomenon.

Strong heating of anisilic acid in the manner described by Langenbeck led, as was reported, to a blue-green melt containing a mixture of products from which the isolation of pure material was difficult. We therefore employed less vigorous heating conditions so as to carry out the pyrolysis in a more controlled manner which would minimize the drastic break-down. Infrared spectra of the pyrolysis products at various stages of the heat treatment indicated that the decomposition took place in two stages (Fig. 1). The first stage, corresponding to the development of a band at 5.73 μ could be associated with the formation of the lactide, II, as would be expected from the pyrolysis of an α-hydroxy acid. In order to confirm this possibility, anisilide (II, R = OCH_3), previously unreported, was synthesized by refluxing a toluene solution of anisilic acid for several hours in an azeotrope separator. The product was a neutral material $C_{32}H_{28}O_8$ which exhibited a lactide band in the infrared at 5.73 μ, corresponding exactly to the absorption of benzilide in this region.[1]

The second stage of the pyrolysis coincided with the appearance of a new band at 5.51 μ in the carbonyl region of the infrared with accompanying diminution in the intensity of the lactide band. It was possible to isolate the product responsible for this absorption by maintaining anisilide at a temperature slightly above its melting point for about one hour, whereupon it was converted to a new substance, $C_{16}H_{14}O_4$, m.p. 153–154°. This product exhibited a strong 5.51 μ band in the infrared. To account for the above formation of a compound exhibiting this low wave length carbonyl absorption,[5] the possibility was considered that during further heating the anisilide had undergone rearrangement to form an isocoumaranone derivative (III, R = OCH_3), as



III

This view was supported by the observation that a model isocoumaranone (III, R = H) showed carbonyl absorption at precisely the same region of the spectrum, 5.51 μ.

That the isocoumaranone structure was, in fact, correct was established by an independent synthesis of III, R = OCH_3, by condensation of resorcinol monomethyl ether with *p*-methoxymandelonitrile in the presence of sulfuric acid, a method used by Bistrzycki for the preparation of other isocoumaranones.[6] The product, the lactone of *o*-hydroxy-*p*,*p*′-dimethoxydiphenylacetic acid, was identical

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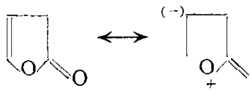
[1] Paper I in this series: H. H. Wasserman and H. E. Zimmerman, This Journal, **72**, 5787 (1950).

[2] Presented at the Meeting of the American Chemical Society in Atlantic City, N. J., September, 1952.

[3] From the doctoral dissertation of Tien-Chuan Liu, Yale University, 1952.

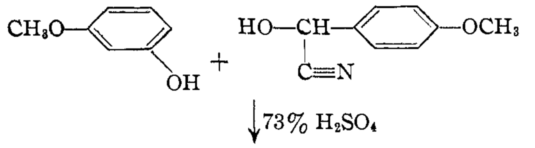
[4] W. Langenbeck, *Ber.*, **62**, 962 (1929).

[5] In III, the polarization of the carbonyl is inhibited by the adjacent positive pole arising through contributions from forms comparable to IIIa. Compared to that in the corresponding saturated lactone, the carbonyl group in III would thus have greater double-bond character and would absorb at a shorter wave length in the infrared.



IIIa

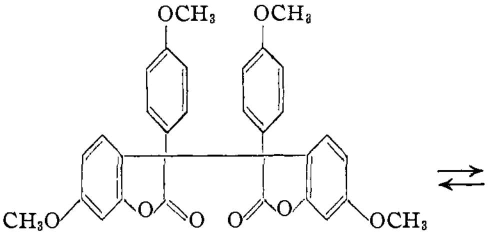
[6] A. Bistrzycki and J. Flatau, *Ber.*, **28**, 989 (1895).



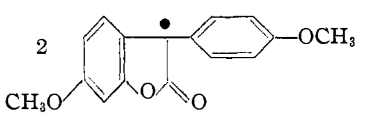
III, R = OCH$_3$

(mixed melting point and infrared spectra) with the product, m.p. 153–154°, derived from the pyrolysis of anisilide.

It was observed that although both the synthetic isocoumaranone (III, R = OCH$_3$), and that derived by pyrolysis, exhibited thermochromic behavior in toluene solution, the intensity of the color development varied from sample to sample. Furthermore, it was found that after repeated recrystallization of the isocoumaranone from benzene–ether mixtures, hot solutions of this compound no longer exhibited the characteristic deep blue coloration. The possibility was accordingly investigated that, in a manner already established[7] for isocoumaranones of this type, some oxidative dimerization had taken place both in the pyrolysis and in the synthesis to yield small amounts of the bislactone, IV. Thus, a dissociation–association equilibrium involving free radicals IV $\rightleftarrows$ IVa, analogous to the hexaarylethane–triphenylmethyl equilibrium, could account for the observed reversible thermochromic changes.



IV



IVa

Evidence indicating that the dissociation of a bislactone (IV) could be responsible for the thermochromism was obtained by the observation that the blue color in hot toluene solutions of "thermochromic" isocoumaranone could be made to disappear by refluxing the solution with benzyl alcohol for two to three hours, or, in a much shorter time, by the addition of phenylhydrazine. These observations are in accord with the recent findings of Schönberg[8] who traced the loss of color in similar systems to the reduction, by benzyl alcohol, of the free radicals produced by dissociation of related bislactones.

Conclusive proof that the bislactone, IV, was responsible for the observed thermochromism was obtained by a synthesis of this product and comparison of its visible spectra with the corresponding spectra of the "thermochromic" isocoumaranone over a range of temperatures. The synthesis of IV was accomplished according to a general procedure used by Löwenbein[9] for the synthesis of analogous bislactones, and involved treating the sodio derivative of III, R = OCH$_3$ with iodine, the product, a white crystalline material melting 170–173°, imparting a pale blue coloration to its solutions in chloroform and toluene at room temperature. This color, which was intensified on heating, disappeared when the solutions were cooled in an ice-bath.

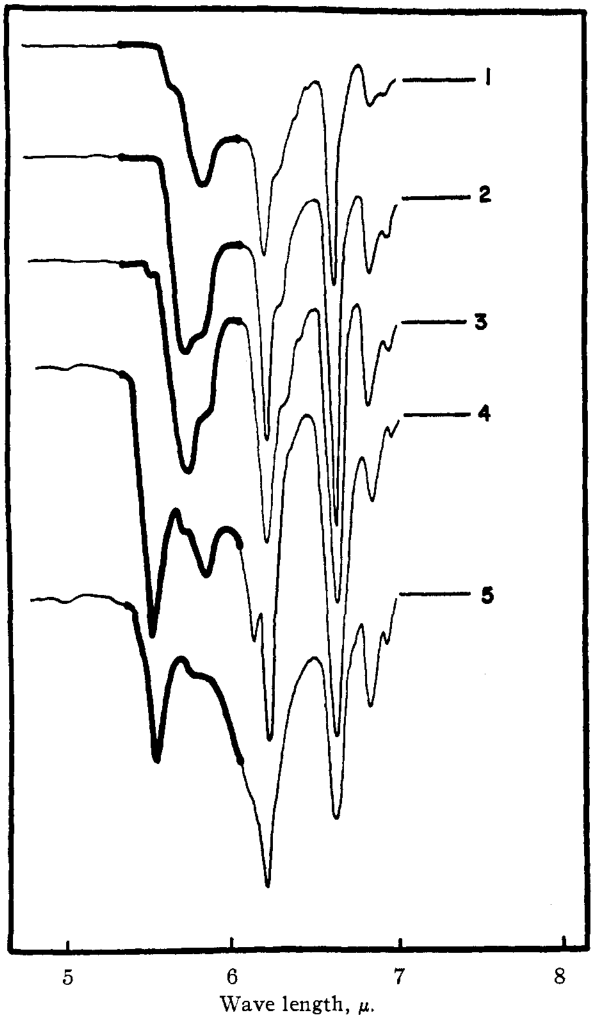


Fig. 1.—Infrared absorption spectra of the crude products formed at various stages in the pyrolysis of anisilic acid: 1, pure anisilic acid; 2, anisilic acid heated just to the melting point, 168°; 3, anisilic acid heated at its melting point till the appearance of the blue color; 4, anisilic acid heated for an additional ten seconds at 170°; 5, anisilic acid heated strongly over a free flame for 30 seconds.

All of the absorption spectra of bislactone samples in the visible region at temperatures ranging from 25 to 100° showed a maximum at 619 mμ in decalin (Table I). The molar extinction coefficients in-

TABLE I

VARIATION OF EXTINCTION COEFFICIENTS WITH TEMPERATURE AT λ = 619 mμ

	Log ε	
Temp., °C.	Bislactone	Isocoumaranone containing bislactone impurity
25	1.165	...
50	1.756	...
75	2.151	...
100	2.327	0.772

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[7] A. Löwenbein and W. Folberth, *Ber.*, **58**, 601 (1925).

[8] A. Schönberg and A. Mustafa, THIS JOURNAL, **73**, 2401 (1951).

[9] A. Löwenbein and H. Simonis, *Ber.*, **57**, 2407 (1924).

creased with temperature, indicating a larger number of absorbing molecules at the higher temperatures consistent with the association–dissociation equilibrium IV ⇄ IVa. *Although there was no trace of the 619 mμ band in the visible spectra of "thermochromic" isocoumaranone samples at temperatures up through 75°, this band did appear in the spectrum (λ 618–620 mμ, log ε 0.772) as the temperature was raised to 100°.*

The amount of bislactone present in the "thermochromic" isocoumaranone was calculated from spectral measurements to be approximately 2–3%. The presence of a free radical in solutions of the bislactone was clearly shown by paramagnetic measurements,[10] and the per cent. dissociation was estimated at 5 and 165° on the basis of molecular weight data, as summarized in Table II.

TABLE II

Molal concn. bislactone	Solvent	Method	Mol. wt.	Temp., °C.	Dissociation, %
0.231	Camphor	Rast	433	165	24.3
.256	Camphor	Rast	447	165	20.4
.038	Benzene	F.p. depres.	514	5	4.3

It is thus clear that the thermochromic behavior of the products derived from the pyrolysis of anisilic acid must be attributed to the dissociation of the bislactone (IV) into free radicals (IVa), small amounts of the bislactone in all probability having been formed from the main pyrolysis product (III, R = OCH_3) by oxidative dimerization.

Acknowledgment.—We gratefully acknowledge the assistance afforded by a Frederick Gardner Cottrell Grant of the Research Corporation.

Experimental[11]

Anisilide.—Anisilic acid (5.9 g.) was dissolved in 300 ml. of freshly distilled, dry toluene and the mixture was refluxed. After 10 minutes, a pale blue color developed. This blue color remained for one to ten hours depending upon the sample of the anisilic acid used. In general, the more impure the anisilic acid, the longer the blue color persisted. After the disappearance of the blue color, the toluene solution was concentrated to about 20 ml. and an equal volume of petroleum ether was added. Upon cooling the solution, well-defined crystals were obtained; yield 5.1 g. (92.3%), m.p. 168–170° (a colorless melt). If the reflux was stopped while the solution was still blue, the anisilide isolated melted at 167–169° with a green color. The anisilide was recrystallized from a toluene–petroleum ether mixture, m.p. 169–170.5°. Highly purified anisilide from any preparation always gave a colorless melt.

Anal. Calcd. for $C_{32}H_{28}O_8$: C, 71.11; H, 5.19. Found: C, 71.08; H, 5.40.

***o*-Hydroxy-*p*,*p*′-dimethoxydiphenylacetic Acid Lactone from the Pyrolysis of Anisilide.**—When a sample of pure anisilide was heated over a free flame for about two minutes, a red melt which exhibited the thermochromic blue color was obtained. The red melt could be recrystallized from a mixture of benzene and ether to yield a product, m.p. 145–148°. After repeated recrystallizations from the same solvent mixture, tiny white needles were obtained, m.p. 153.5–154.5°. This product always melted with an intensely blue color.

Upon refluxing the above product with toluene, or heating with benzpl alcohol at 110°, the blue color, which appeared at the beginning of the heating, gradually vanished, and a colorless or pale yellow solution was obtained. In boiling xylene this product exhibited an intense blue color which could be discharged almost immediately by the addition of a dilute solution of phenylhydrazine in xylene. From this latter reaction mixture there was isolated a white crystalline product which showed no sign of a blue color when heated in solvents up to 138°. Mixed melting point and infrared absorption spectra did not distinguish between this purified non-thermochromic product and the "thermochromic" material.

***o*-Hydroxy-*p*,*p*′-dimethoxydiphenylacetic Acid Lactone from the Condensation of *p*-Methoxymandelonitrile with Resorcinol Monomethyl Ether.**—Fifteen milliters of 73% sulfuric acid was added to a mixture of 7.75 g. of resorcinol monomethyl ether and 4.1 g. of *p*-methoxymandelonitrile, while cooling the reaction mixture in an ice-bath. The reaction mixture was then heated on a steam-bath for 20 minutes with frequent shaking. The viscous, red mass so obtained was poured into 200 ml. of cold water. The precipitate formed was filtered and washed with water until the washings were no longer acidic; yield 4.85 g. (71.5%). The product was recrystallized from 95% alcohol, m.p. 155.5–156.5°. Mixed melting point with the product isolated from the pyrolysis of anisilide showed no depression.

Infrared and ultraviolet absorption spectra of this synthetic product indicated that it was identical with the product obtained from the pyrolysis of anisilide.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.11; H, 5.19; mol. wt., 270. Found: C, 70.82; H, 5.00; mol. wt. (Rast), 272.

***o*-Hydroxy-*p*,*p*′,*p*″,*p*‴-tetramethoxytetraphenylsuccinic Acid Bislactone.**—Sodium sand was prepared by melting 0.2 g. of sodium in toluene followed by rapid and vigorous stirring with a Hershberg stirrer. The toluene was decanted and the sodium sand washed five times with anhydrous ether. A suspension of 1.8 g. of pure *o*-hydroxy-*p*,*p*′-dimethoxydiphenylacetic acid lactone in 10 ml. of anhydrous ether was then added and the mixture was refluxed over a steam-bath for 2.5 hours. At the end of this time the reaction mixture was filtered, and a dilute solution of 0.82 g. of iodine in anhydrous ether was slowly added to the clear filtrate until no more precipitate of sodium iodide was formed or until the iodine solution was no longer decolorized. The sodium iodide was then filtered and the clear filtrate stored in the refrigerator overnight. The crystals of the bislactone formed were filtered and dried. More of the bislactone was obtained by concentrating the ethereal solution to a small volume followed by the addition of five times its volume of 95% ethanol. The melting point of the crude material was 153–155°. After three recrystallizations from benzene–95% ethanol mixture (1–5), the melting point was raised to 170–173°.[12] The total yield was 0.68 g. (37.9%). The product was very soluble in chloroform, benzene, toluene and xylene forming pale blue solutions, which could be decolorized by cooling in an ice-bath.

Anal. Calcd. for $C_{32}H_{26}O_8$: C, 71.37; H. 4.83; mol. wt., 538. Found: C, 71.24; H, 4.92; mol. wt., 514 (*a* 0.038 molal solution in benzene, cryoscopically); 433 and 447 (0.231 molal and 0.256 molal, respectively, in camphor, Rast method).

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

Ultraviolet Absorption Spectra.—The measurements were made on a Beckman spectrophotometer, model DU. Hot-stages were mounted on both sides of the cell chamber with an efficient water cooling jacket for measurements at elevated temperatures.[13] The temperatures of the hot-stages were regulated by a variac previously calibrated to an accuracy of ± 5°. By using well-fitted cell covers and decalin as a solvent, evaporation during the process of measurement was negligible as shown by the fact that a solution of the bislactone cooled from 100° to room temperature gave the same optical density as that exhibited by the solution before heating.

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[10] We are indebted to Dr. S. I. Weissman of Washington University, St. Louis, Mo., for the paramagnetic studies. The bislactone showed strong paramagnetic resonance absorption in *p*-chlorotoluene solution, the intensity increasing with the color as the temperature was raised.

[11] All melting points are corrected.

[12] Similar unsharp melting points were observed by Löwenbein and Simonis in the preparation of analogous compounds, *Ber.*, **57**, 2047 (1924).

[13] Thanks are expressed to Dr. J. M. Sturtevant and Mr. A. A. Blumberg for their advice and help in setting up the hot-stages for the ultraviolet absorption measurements at elevated temperature.