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# An Abnormal Chapman Rearrangement

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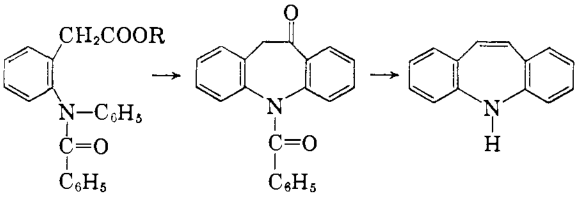
Pyrolysis of the imino-ether V derived from benzanilimino chloride and methyl *o*-hydroxyphenylacetate gave, in addition to the expected Chapman product, 3-benzanilimino-2(3H)-benzofuranone (XVI). The structure of this abnormal product was deduced from hydrolyses and proved by synthesis.

We were interested in developing a general method for the preparation of dihydrodibenzazepinones (III), since these could undoubtedly be converted into various derivatives of dibenzazepine[1] (IV) of potential pharmacological interest. Manske and Ledingham have prepared the oxepinone corresponding to III by ring closure of *o*-phenoxyphenylacetyl chloride; reduction and dehydration then yielded dibenzoxepine.[2] Accordingly, the synthesis of the benzoyl derivative I of *o*-anilinophenylacetic acid was undertaken.

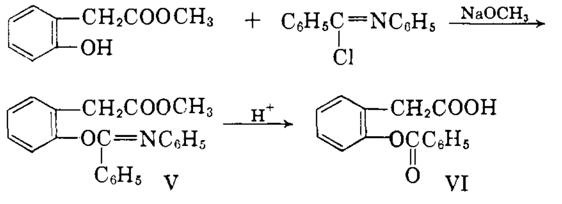


I, R = H
II, R = $CH_3$

III

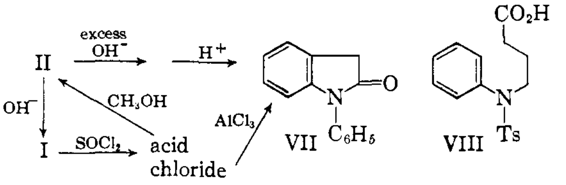
IV

The best route to II, a benzoyldiphenylamine, appeared to be *via* Chapman rearrangement of the appropriate imino-ether.[3] This reaction had proceeded normally, usually in high yield, in all cases found in the literature.[4] The required intermediate V was therefore prepared by the reaction between methyl *o*-hydroxyphenylacetate and benzanilimino chloride. That the product was indeed the desired imino-ether was proved by its hydrogenolysis to N-phenylbenzylamine and its acid-catalyzed hydrolysis to aniline and VI.



Heating the imino-ether V at 268° for 45 minutes yielded a mixture from which three products were isolated. Two of these were obtained in yields of approximately 25%; the third was formed in more variable amounts, a maximum of 7% being obtained. Reasonable analytical values could not be obtained for this minor product and its structure has not been determined.

One of the major products was a colorless substance which, on the basis of analyses and spectra, appeared to be the expected Chapman product II. This structure was confirmed by hydrolysis with excess alkali followed by treatment with acid to give N-phenyloxindole (VII). Partial hydrolysis of II gave the desired N-benzoyl acid I. When this was treated with thionyl chloride, then aluminum chloride, ring closure to III did not occur. Instead, the benzoyl group was displaced and N-phenyloxindole (VII) resulted. This result was not unexpected since Astill and Boekelheide had discovered that treatment of VIII with phosphorus pentachloride, then aluminum chloride in benzene gave high yields of N-phenylpyrrolidinone and phenyl *p*-tolyl sulfone.[5] Later, Proctor and Thomson showed that the acid chloride of VIII could not be prepared, treatment with thionyl chloride, phosphorus oxychloride or phosphorus pentachloride giving directly the pyrrolidinone and *p*-toluenesulfonyl chloride.[6] In contrast, the reaction between I and thionyl chloride did give the desired acid chloride, since treatment with methanol regenerated the ester II. The oxindole formation therefore occurred during the reaction with aluminum chloride. Thus, as we had hoped, the additional benzene ring in I (as compared with VIII) did decrease the ease of displacement on nitrogen, although not sufficiently to permit formation of the seven-membered ring.



The second major product from the pyrolysis of V was a yellow compound which showed strong absorption at 375 mμ, this being characteristic of the $C_6H_5N=$ chromophore. The molecular formula $C_{21}H_{15}NO_2$ suggested that methanol was also formed in the pyrolysis, and this was confirmed in a subsequent run. Basic hydrolysis of this abnormal Chapman product yielded aniline and a somewhat unstable hydroxy-ketone, $C_{14}H_{12}O_2$. Although readily extracted from aqueous sodium hydroxide with ether, this compound was a weakly acidic phenol and therefore probably *o*-substituted. Treatment with acid caused dehydration to a neutral substance possessing neither the hydroxyl nor ketonic functions.

It seemed likely that the hydroxy-ketone was the then unknown 2′-hydroxydesoxybenzoin (IX).

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(1) (a) Australian patent applications 32,722/57 and 32,733/57; (b) P. N. Craig, C. A. Leonard, B. M. Lester and D. H. Tedeschi, Abstracts of Papers, Second Regional Meeting Delaware Valley, Feb. 5, 1958.

(2) R. H. F. Manske and A. E. Ledingham, THIS JOURNAL, **72**, 4797 (1950).

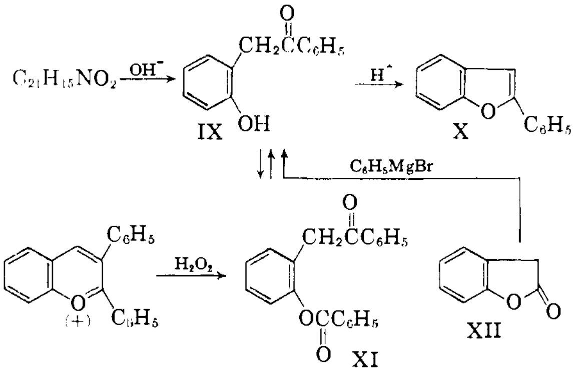
(3) (a) A. W. Chapman, *J. Chem. Soc.*, **127**, 1992 (1925); (b) A. W. Chapman, *ibid.*, 1743 (1927).

(4) F. Möller in "Methoden Der Organische Chemie," Band XI/I, Vierte Auflage, Georg Thieme Verlag, Stuttgart, pp. 910–913.

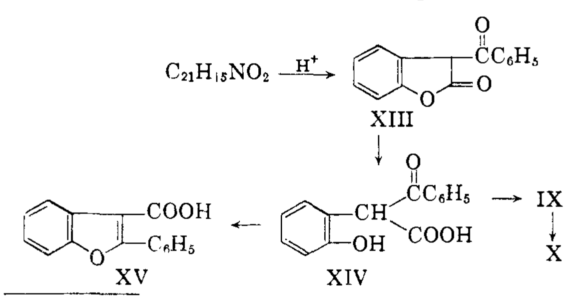
(5) B. D. Astill and V. Boekelheide, THIS JOURNAL, **77**, 4079 (1955).

(6) G. R. Proctor and R. H. Thomson, *J. Chem. Soc.*, 2302 (1957).

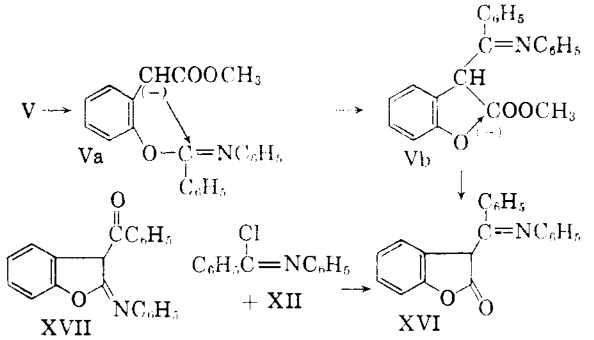
Previous routes which could have given this material had, instead, led to 2-phenylbenzofuran (X).[7,8] Dilthey and Quint have prepared the benzoate XI of IX by cleavage of the pyrylium salt derived from salicylaldehyde and desoxybenzoin.[7] Basic hydrolysis of XI, followed by acidification, then gave X. We repeated Dilthey's preparation and hydrolysis of XI and found that extraction of the basic hydrolysate gave material identical with our hydroxyketone. Furthermore, our dehydration product was found to be identical with authentic 2-phenylbenzofuran (X), while treatment of our hydroxy-ketone with benzoyl chloride yielded material identical with Dilthey's benzoate XI. After our work had been completed, an independent synthesis of IX was reported, the compound being prepared in low yield from isocoumaranone (XII) and phenylmagnesium bromide.[9]



Acid-catalyzed hydrolysis of the abnormal Chapman product gave, in addition to 2-phenylbenzofuran (X), an acid, $C_{15}H_{10}O_3$. This was found to be identical with an authentic sample of 2-phenylbenzofuran-3-carboxylic acid (XV) sent to us by Dr. J. N. Chatterjea.[10] Although it was conceivable that this acid was a primary hydrolysis product, it seemed more likely that it had resulted from acid-catalyzed rearrangement of 3-benzoylisocoumaranone (XIII). This compound would be expected to give readily the unstable acid XIV which could then either decarboxylate to IX (followed by ring closure to X) or cyclize to XV. Chatterjea, however, has prepared XIII[10] and boiled it with acid; 2-phenylbenzofuran (X) was the only product isolated.[11] In several similar cases, however, Chatterjea was able to effect the rearrangement to benzofurancarboxylic acids.[11] We therefore repeated Chatterjea's synthesis of XIII and subjected the compound to the conditions of our acid hydrolysis. Conversion into XV was readily accomplished.[12]



On the basis of the above hydrolysis products, only two structures, XVI and XVII (or tautomeric forms of these), appeared reasonable for the abnormal pyrolysis product. Both of these would yield 3-benzoylisocoumaranone (XIII) and aniline as primary hydrolysis products. However, while the formation of XVII could be rationalized, the following route to XVI appeared much more reasonable.[13]



The imino-ether V, itself a weak base, could be converted into its anion Va, this then reacting intramolecularly to yield the phenolate anion Vb. Attack at the ester carbonyl with displacement of methoxide ion would then give XVI.

The abnormal Chapman product was then proved to be XVI by direct synthesis. When isocoumaranone (XII) and benzanilimino chloride were heated to 185° without a catalyst, HCl was given off and XVI obtained. This was identical in all respects with the pyrolysis product.

Finally, since a base-catalyzed mechanism has been suggested for the formation of XVI under pyrolysis conditions, it seemed that a strong base should convert V into XVI at a much lower temperature. The imino-ether was therefore heated in benzene with sodium methoxide; XVI was obtained in 56% yield, thus providing strong support for the above mechanism.

After our work had been completed, Chatterjea reported the synthesis of XVI from isocoumaranone and N,N′-diphenylbenzamidine. By mild basic hydrolysis he obtained 2-phenylbenzofuran (X) and 3-benzoylisocoumaranone (XIII), while acid hydrolysis gave X.[14]

## Experimental[14a]

**Methyl *o*-Hydroxyphenylacetate and Isocoumaranone (XII).**—The former was prepared in four steps from *o*-methoxybenzaldehyde essentially according to the literature method.[15] However, our crude *o*-hydroxyphenylacetic acid

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[7] W. Dilthey and F. Quint, *J. prakt. Chem.*, **131**, 1 (1931).

[8] P. Yates, THIS JOURNAL, **74**, 5376 (1952).

[9] A. Spetz, *Acta Chem. Scand.*, **10**, 1422 (1956).

[10] J. N. Chatterjea, *J. Indian Chem. Soc.*, **33**, 175 (1956). We are grateful to Dr. Chatterjea for sending us samples of several benzofuran derivatives.

[11] J. N. Chatterjea, *ibid.*, **34**, 299 (1957).

[12] For examples of this type of rearrangement in other heterocycles see F. Korte, *Angew. Chem.*, **71**, 135 (1959).

[13] The mechanism of the normal Chapman rearrangement has been studied by K. B. Wiberg and B. I. Rowland, THIS JOURNAL, **77**, 2205 (1955).

[14] J. N. Chatterjea, *J. Indian Chem. Soc.*, **36**, 69 (1959).

[14a] Analyses were carried out under the supervision of Mr. K. D. Fleischer. Spectra were run under Dr. F. C. Nachod's supervision. Ultraviolet spectra were determined in 95% ethanol, infrared spectra in potassium bromide.

[15] J. Levine, T. E. Eble and H. Fischbach, THIS JOURNAL, **70**, 1930 (1948).

was esterified directly and the product distilled, b.p. 90–94° (0.1 mm.).

Isocoumaranone was obtained by heating the crude *o*-hydroxyphenylacetic acid at atmospheric pressure until the evolution of water ceased; the residue was then vacuum distilled. From 2 moles of *o*-methoxybenzaldehyde, 152 g. (57%) of isocoumaranone, b.p. 131–134° (22 mm.), was obtained. Recrystallization from ether–hexane gave white prisms, m.p. 47.5–49.5°.

Methyl *o*-hydroxyphenylacetate could also be prepared *via* isocoumaranone, 20.1 g. (0.15 mole) of the lactone being refluxed for 5 hours with 200 ml. of methanolic HCl. Solvent removal and recrystallization from ether–pentane gave 20.8 g. (84%) of white solid, m.p. 71–73°.

**Benzanilimino Chloride.**[16]—A mixture of 296 g. of benzanilide and 312 g. of phosphorus pentachloride was slowly heated. After the initial, vigorous reaction had ended, the dark liquid was refluxed for 2 hours, then distilled, 305 g. (94%) of light yellow product, b.p. 115–120° (0.3 mm.), m.p. 38–40°, being obtained.

**N-Phenylbenzimino *o*-(Carbomethoxymethyl)-phenyl Ether (V).**—The reaction was run with stirring in a nitrogen atmosphere. To a cold solution of 27 g. (0.5 mole) of sodium methoxide in 600 ml. of methanol was added 83 g. (0.5 mole) of methyl *o*-hydroxyphenylacetate. As soon as the phenol had dissolved, a solution of 108 g. (0.5 mole) of benzanilimino chloride in 150 ml. of anhydrous ether was added quickly and the mixture stirred at room temperature overnight. After most of the solvent had been removed on the water-pump, the residue was poured into water. The resulting solid was air-dried, then recrystallized from isopropyl alcohol to give 128.4 g. (74%) of white prisms, m.p. 102.5–104.5°. An additional recrystallization from the same solvent gave the analytical sample, m.p. 103–105°. The infrared spectrum had bands at 5.80 and 5.98 μ while the ultraviolet spectrum showed $\lambda_{max}$ 275 mμ ($\epsilon$ 5,170) and 295 mμ ($\epsilon$ 3,700).

*Anal.* Calcd. for $C_{22}H_{19}NO_3$: C, 76.50; H, 5.55; N, 4.06. Found: C, 76.93; H, 5.66; N, 3.81.

Hydrogenation of the imino-ether was carried out in absolute ethanol with a 10% palladium-on-charcoal catalyst. The reduction was stopped shortly after 2 moles of hydrogen was absorbed. Removal of catalyst and solvent left an oil which yielded, with ethanol hydrogen chloride, N-phenylbenzylamine hydrochloride, m.p. 212–215° (lit. m.p. 214–216°).

***o*-Benzoyloxyphenylacetic Acid (VI).**—A portion of the imino-ether V was boiled for 10 minutes with concentrated aqueous HCl. A gummy solid resulted which was recrystallized twice from chloroform–hexane to give fine, white needles, m.p. 141–143° (lit.[17] 142°). The infrared spectrum showed bands at 5.76 and 5.88 μ.

*Anal.* Calcd. for $C_{15}H_{12}O_4$: C, 70.30; H, 4.72. Found: C, 70.05; H, 4.62.

**Pyrolysis of the Imino-ether V.**—The reaction was carried out in a vessel suspended over a bath of boiling bibenzyl, the temperature of the reaction mixture thus being maintained at 268°. With stirring and a slow stream of nitrogen, 25 g. (0.073 mole) of imino-ether was heated for 45 minutes. The resulting very dark oil was diluted with 75 ml. of absolute ethanol, cooled to room temperature, and the product filtered and washed with ethanol. A 29% yield (6.5 g.) of yellow solid, m.p. 202–210°, resulted; this was **3-benzanilimino-2(3H)-benzofuranone**, the abnormal Chapman product XVI. Recrystallization from chloroform–ethyl acetate gave an 88% recovery of material melting at 209–212°. Two more recrystallizations, one from absolute ethanol and the other from ethyl acetate, gave the analytical sample as slightly greenish-yellow needles, m.p. 210–213°. The ultraviolet spectrum had $\lambda_{max}$ 253 mμ ($\epsilon$ 15,900) and 375 mμ ($\epsilon$ 21,800). The infrared spectrum showed a single carbonyl peak at 5.89 μ.

*Anal.* Calcd. for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.83; N, 4.47; O, 10.21; mol. wt., 313. Found: C, 80.27; H, 5.03; N, 4.50; O, 10.20; mol. wt., 299.

Attempts to reduce the abnormal Chapman product with hydrogen and palladium or platinum or with sodium borohydride were not successful. An oxime could not be prepared even under forcing conditions.

The normal Chapman product **methyl *o*-(N-benzoylanilino)-phenylacetate (II)** was obtained by cooling the ethanolic mother liquors to give 6.4 g. (29%) of tan solid, m.p. 126–131°. Three recrystallizations from absolute ethanol gave the analytical sample as white prisms, m.p. 132.5–134.5°. The ultraviolet spectrum had $\lambda_{max}$ 234 mμ ($\epsilon$ 15,500) and 271 mμ ($\epsilon$ 7,900). Infrared bands were present at 5.78 and 6.04 μ.

*Anal.* Calcd. for $C_{22}H_{19}NO_3$: C, 76.50; H, 5.55; N, 4.06. Found: C, 76.14; H, 5.65; N, 4.05.

When the pyrolysis was carried out at 282° for 20 minutes, much lower yields of both products were obtained, but at 250° for 3 hours approximately the same yields as above resulted.

In one run, the gaseous product was condensed and characterized as methanol by its reaction with *p*-nitrobenzoyl chloride, the resulting ester being compared by m.p. and mixed m.p. with an authentic sample.

The separation of products was complicated by a third material which was always present in the crude abnormal Chapman product. In one run, this minor product could be partially separated by hand, since it crystallized as red-brown prisms while the major component came down as a greenish powder. However, it was best obtained by basic hydrolysis of the mixture, the abnormal Chapman product being completely destroyed (see below) while the minor product remained unchanged. In this way, it was determined that the amount of this material varied from less than 10 to about 25% of the initial ethanol-insoluble material. Three recrystallizations from ethyl acetate gave fine, yellow, needles, m.p. 223.5–225.0°. Strong ultraviolet absorption occurred at 243 and at 374 mμ, while the infrared spectrum showed bands at 5.84 and 5.75 μ (both weak), and at 6.07 and 6.12 μ. No hydroxyl band was present.

*Anal.* Found: C, 82.32, 82.37, 82.41; H, 5.21, 5.06, 5.02; N, 6.98, 6.86; 0, 5.55; mol. wt., 345.

In contrast to XVI, this material gave a positive test with ferric chloride in chloroform and this test was used to determine the presence of this minor product in XVI. Acid hydroysis gave aniline, but the other products were not determined. It is possible that this product is actually a mixture; however, neither recrystallizations nor chromatography on alumina affected either the m.p. or the analytical values.

**N-Phenyloxindole (VII).**—Complete hydrolysis of the normal Chapman product II was accomplished by refluxing a solution of 500 mg. of II and 3 g. of potassium hydroxide in 7 ml. of water and 20 ml. of methanol for 3 hours. The solution was then diluted with water and acidified with hydrochloric acid followed by brief heating on the steam-bath to cyclize the resulting *o*-anilinophenylacetic acid. The mixture was then made alkaline with excess sodium hydroxide and cooled to give leaflets of VII. Recrystallization from aqueous ethanol gave material melting at 115–118°. This did not depress the m.p. of authentic N-phenyloxindole.[18]

***o*-(N-Benzoylanilino)-phenylacetic Acid (I).**—A solution of 6.9 g. (0.02 mole) of II and 1.08 g. (0.02 mole) of sodium methoxide in 50 ml. of methanol and 20 ml. of water was refluxed for 2 hours. After cooling, the solution was diluted with water, washed with ether and acidified. A gum resulted which was induced to crystallize, then recrystallized from ethyl acetate–hexane to give 3.8 g. (58%) of white acid, m.p. 154.5–156.5°. A second recrystallization from the same solvent pair gave the analytical sample, m.p. 155.5–157°. The ultraviolet spectrum showed $\lambda_{max}$ 236 mμ ($\epsilon$ 14,500) and 271 mμ ($\epsilon$ 7,650). The product absorbed in the infrared at 5.75, 6.05 and 6.15 μ.

*Anal.* Calcd. for $C_{21}H_{17}NO_3$: C, 76.12; H, 5.17; N, 4.23; neut. equiv., 331. Found: C, 76.13; H, 5.22; N, 4.22; neut. equiv., 334.

**Attempted Cyclization to III.**—To a solution of 1.66 g. (0.005 mole) of I in 5 ml. of chloroform was added 5 ml. of thionyl chloride. After 3 hours of refluxing, the solvent and excess reagent were removed and the red, gummy, residue dissolved in 10 ml. of nitrobenzene. This solution was cooled and added in portions to a cold mixture of 2 g. of aluminum chloride and 5 ml. of nitrobenzene. After standing at room temperature, the mixture was decomposed with ice, then hydrochloric acid, and the organic material was

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(16) O. Wallach, *Ann.*, **184**, 79 (1877).

(17) W. Dilthey and W. Höschen, *J. prakt. Chem.*, **138**, 42 (1933).

(18) R. Stollé, *Chem. Ber.*, **47**, 2120 (1914).

extracted into chloroform. The extracts were washed with aqueous hydrochloric acid, sodium bicarbonate and water, then dried and the solvent removed to leave a red gum which could not be crystallized. This was therefore chromatographed on silica gel to give, by ether elution, N-phenyloxindole (VII) as the only crystalline product. This material had m.p. 118–121.5° and did not depress the m.p. of authentic VII prepared *via* the Stollé procedure.[18]

**Re-esterification of I to II.**—A solution of 662 mg. of I, 5 ml. of chloroform and 3 ml. of thionyl chloride was refluxed for 30 minutes. The resulting gummy acid chloride was then boiled with 15 ml. of methanol for 30 minutes. Dilution with water then gave 450 mg. (65%) of almost white solid, m.p. 129–132°. This material strongly depressed the m.p. of N-phenyloxindole but did not depress that of the normal Chapman product II.

**Basic Hydrolysis of XVI; 2′-Hydroxydesoxybenzoin (IX).**—A mixture of 3 g. of crude XVI, 4 g. of potassium hydroxide, 15 ml. of water and 45 ml. of methanol was refluxed for one hour, most of the solid soon dissolving. The major abnormal Chapman product XVI was thus hydrolyzed leaving the minor Chapman product untouched. This was filtered from the cooled solution and the filtrate extracted several times with ether. The ether solution was then extracted with aqueous hydrochloric acid to yield the basic fraction from which aniline was obtained and characterized as its hydrochloride, m.p. 197–199°. The non-basic fraction was dried and the ether removed to leave a solid which could be recrystallized from ethyl acetate–hexane. Almost white hydroxy-ketone IX resulted. Due to the instability of this compound, the m.p. was sometimes raised, sometimes lowered on recrystallization. The highest m.p. we obtained was 127.5–131.5°. The highest yield of material melting over 120° was about 50%. Higher yields could be obtained by acidifying the reaction mixture and immediately extracting with ether, but the product was less pure than that obtained directly from the basic solution. When the acidified solution was allowed to stand overnight, only 2-phenylbenzofuran (X) was obtained. The product was soluble in 10% aqueous sodium hydroxide, but not in carbonate solution. It gave a positive ferric chloride test. The ultraviolet spectrum exhibited two maxima, at 242 m$\mu$ ($\epsilon$ 13,000) and at 275 m$\mu$ ($\epsilon$ 3,500). These data are in good agreement with those of Spetz, who has prepared IX *via* alternate routes.[9] The infrared spectrum had bands at 2.95 and 5.97 $\mu$.

*Anal.* Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70; O, 15.08. Found: C, 79.14; H, 5.93; O, 15.25.

A **2,4-dinitrophenylhydrazone** was prepared in methanol and recrystallized twice from absolute ethanol to yield thick, orange-red needles, m.p. 197–198.5°.

*Anal.* Calcd. for $C_{20}H_{16}N_4O_5$: C, 61.22; H, 4.11; N, 14.28. Found: C, 61.11; H, 4.19; N, 14.15.

The hydroxydesoxybenzoin IX was converted into its methyl ether by refluxing one hour with methyl iodide and sodium methoxide in ethanol. After phenolic material had been removed with sodium hydroxide, the gummy ether was converted into its 2,4-dinitrophenylhydrazone and this recrystallized twice from absolute ethanol to give a dark orange solid, m.p. 177.5–179°.

*Anal.* Calcd. for $C_{21}H_{18}N_4O_5$: C, 62.06; H, 4.46. Found: C, 61.70; H, 4.62.

Authentic hydroxy-ketone IX was synthesized by refluxing a solution of 1 g. of its benzoate (XI),[7] 1 g. of potassium hydroxide, 3 ml. of water and 10 ml. methanol for 3 hours. The solution was cooled, diluted with water and extracted with ether. The extracts were washed with water, dried and the solvent removed to leave a gummy solid which was recrystallized from ethyl acetate–hexane. Tan prisms, m.p. 122–127°, resulted. This product strongly depressed the m.p. of 2-phenylbenzofuran, but did not depress that of hydroxy-ketone obtained by basic hydrolysis of the abnormal Chapman product. Its ultraviolet and infrared spectra were virtually identical with those of the hydrolysis product, confirming their identity.

**2′-Benzoyloxydesoxybenzoin (XI).**—To a mixture of 212 mg. of 2′-hydroxydesoxybenzoin (IX) (from basic hydrolysis of XVI) and 5 ml. of 10% aqueous sodium hydroxide was added 0.15 ml. of benzoyl chloride. Shaking soon produced a solid which was recrystallized from absolute ethanol. This product, which had m.p. 103–105°, was found to be identical, by mixed m.p., ultraviolet and infrared spectra, with authentic XI prepared *via* Dilthey's route.[7] The ultraviolet spectrum had $\lambda_{max}$ 236 m$\mu$ ($\epsilon$ 24,800), 275 m$\mu$ ($\epsilon$ 3,300) and 281 m$\mu$ ($\epsilon$ 2,700).

**2-Phenylbenzofuran (X).**—A few drops of hydrochloric acid was added to a solution of 100 mg. of IX (from hydrolysis of XVI) and 5 ml. of acetic acid. The solution was heated 10 minutes on the steam-bath, then diluted with water to yield a white solid. This was recrystallized from 95% ethanol to give product of m.p. 119.5–121°. This was identical, by mixed m.p. determination, with authentic X prepared by hydrolyzing Dilthey's benzoate and allowing the acidified solution to sit overnight at room temperature.[7] The ultraviolet spectrum of our material exhibited the maxima reported by Yates for 2-phenylbenzofuran.[8]

**Acid Hydrolysis of the Abnormal Chapman Product XVI.**—One gram of XVI was refluxed for 5 hours with a solution of 25 ml. of 48% hydrobromic acid and 25 ml. of ethanol. That the gas evolved was carbon dioxide was proved by its conversion into barium carbonate. Almost all the original solid dissolved during the reflux period, at the end of which the remaining insoluble material was filtered off and the filtrate cooled to yield a white solid. This was recrystallized three times from heptane to give a product melting at 194.5–197°. A mixed m.p. determination with authentic 2-phenylbenzofuran-3-carboxylic acid[10] (XV) showed that the two materials were identical. Their infrared spectra were identical, both absorbing at 6.02 $\mu$ with a shoulder at 5.95 $\mu$. The ultraviolet spectrum had $\lambda_{max}$ 222 m$\mu$ ($\epsilon$ 24,000) and 303 m$\mu$ ($\epsilon$ 25,000).

In a second run, XVI was hydrolyzed by refluxing 2.5 hours with a solution of 25 ml. of concentrated hydrochloric acid and 25 ml. of ethanol. The resulting mixture was diluted with water, extracted with ether and the above carboxylic acid XV extracted into aqueous sodium bicarbonate. 2-Phenylbenzofuran (X), identical with that obtained *via* basic hydrolysis of XVI and subsequent acidification and *via* the benzoate XI was then obtained from the ethereal solution.

**Rearrangement of XIII to XV.**—3-Benzoyl-2(3H)-benzofuranone (XIII) was prepared by Chatterjea's method.[10] The ultraviolet spectrum had $\lambda_{max}$ 232 m$\mu$ ($\epsilon$ 11,600), 252 m$\mu$ ($\epsilon$ 13,200), and 339 m$\mu$ ($\epsilon$ 11,000). The infrared spectrum showed bands at 5.92 and at 6.16 $\mu$. When 1 g. of XIII was refluxed for 1 hour with 35 ml. of ethanol and 25 ml. of concentrated hydrochloric acid a cloudy mixture resulted from which a solid crystallized on cooling. One recrystallization from heptane gave XV, m.p. 193–195°, identical by mixed m.p. and infrared analysis with the acid obtained by hydrolysis of XVI and with the authentic 2-phenylbenzofuran-3-carboxylic acid of Chatterjea.[10]

**3-Benzanilimino-2(3H)-benzofuranone (XVI).**—A mixture of 20.1 g. (0.15 mole) of isocoumaranone (XII) and 32.4 g. (0.15 mole) of benzanilimino chloride was heated slowly with stirring under nitrogen. At 185°, the evolution of hydrogen chloride began. The mixture was slowly heated to 240°, then cooled to a solid black mass. This was dissolved in boiling chloroform and the solution diluted with absolute ethanol to give 28.0 g. (60%) of crude, brown XVI, m.p. 204–208°. Several recrystallizations from ethanol, one with charcoal, gave a poor recovery of orange-yellow XVI, m.p. 209–212°. This was identical, by ultraviolet and infrared spectra and by mixed m.p., with the abnormal Chapman product. The analytical figures were satisfactory. Found: C, 80.22; H, 4.75; N, 4.43.

In similar runs with added potassium carbonate, none of the desired product was obtained, presumably due to self-condensation of the isocoumaranone.

Our alternate preparation of XVI was carried out by dissolving 3.45 g. (0.01 mole) of the imino-ether V in 50 ml. of dry benzene, flushing the system with nitrogen and adding, with stirring, 1 g. of sodium methoxide. The mixture was then refluxed, with stirring and nitrogen, for 1.5 hours, during which period solvent was continually distilled off and replaced from time to time with fresh, dry, benzene. The mixture was then cooled, diluted with water, acidified and the aqueous layer extracted with benzene. The yellow benzene solution was dried and the solvent removed. One recrystallization from absolute ethanol gave 1.75 g. (56%) of bright yellow solid, m.p. 211–212°. This material was identical, by mixed m.p. and ultraviolet spectra, with XVI prepared from isocoumaranone (above) and with that prepared by pyrolysis of the imino-ether.

RENSSELAER, N. Y.