

solution assumed a reddish-brown color. The mixture was removed from the cone, a small volume of concd. nitric acid was added to complete the solution of the solid, and the solution was boiled for five minutes. The reaction mixture was diluted with water and cooled in an ice-salt mixture, causing the separation of a yellow solid which melted with decomposition at 210–213°. The compound was dissolved in sodium hydroxide solution, treated with Norite, cooled, and reprecipitated with dilute acetic acid. The bright yellow solid obtained, after drying in an oven for ten hours at 105°, melted sharply at 221° (corr.) (dec.).

Anal. Calcd. for $C_{21}H_{14}N_2O_5$: C, 67.38; H, 3.75; N, 7.49. Found: C, 67.39; H, 4.04; N, 7.39.

Two grams of this nitrated product and 15 cc. of concd. hydrochloric acid were heated together in a sealed tube for six hours at 210°. The reaction mixture was filtered and the filtrate poured into 250 cc. of ice water, causing the separation of a light brown solid. The latter was purified by solution in sodium hydroxide solution, treatment with Norite, and reprecipitation with dilute hydrochloric acid. The melting point of the product, which could be shown to be a nitrophenol, was found to be 163° (corr.). A mixed melting point with an authentic sample of 1-hydroxy-4-nitronaphthalene¹⁰ was unchanged.

Anal. Calcd. for $C_{21}H_{14}N_2O_5$: C, 67.37; H, 3.77; N, 7.49. Found: C, 67.39; H, 4.04; N, 7.39.

The hydrochloric acid filtrate, from which the nitronaphthol had separated, was next examined in order to isolate the other cleavage product. Much of the acid present was neutralized with sodium hydroxide and the solution was concentrated to a small volume by evapora-

(10) Andreoni and Biedermann, *Ber.*, **6**, 343 (1873), report m. p. 164°.

tion. A colorless solid, evidently a hydrochloride, separated and was filtered and redissolved in a small volume of water. The addition of sodium hydroxide solution caused the formation of a copious precipitate. The latter was washed, dried, and identified by its melting point behavior and by an unchanged mixed melting point with authentic 3-hydroxyquinaldine.

Since 1-hydroxy-4-nitronaphthalene and 3-hydroxyquinaldine were thus obtained as cleavage products by the action of concd. hydrochloric acid on the product of nitration, the latter may be formulated as 3-(4-nitro-1-naphthoxy)-4-quinaldinecarboxylic acid.

Summary

1. Pfitzinger's method has been extended to include the utilization of aryloxy ketones in the initial synthesis of four examples of a new type of substituted cinchoninic acid. The structure of one of these acids has been elucidated through a study of its degradation products, and the structures of the remaining acids have been formulated on the basis of analogy.

2. These quinaldine carboxylic acids, and the aryloxyquinaldines formed by their decarboxylation, resist reduction by means of concd. hydriodic acid and red phosphorus.

3. The phthalone of 3-(1-naphthoxy)-4-quinaldinecarboxylic acid has been prepared.

4. Nitration of the 1-naphthoxyquinoline derivative occurs in the naphthalene nucleus in the position para to the oxygen linkage.

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Fluorenones and Diphenic Acids. VIII.^{1,2} The Ring Cleavage of Fluorenone-4-carboxylic Acids

BY ERNEST H. HUNTRESS AND MARGARET K. SEIKEL³

The earliest instance of the rearrangement of substituted fluorenones under the influence of concentrated sulfuric acid was that of 1,6-dichlorofluorenone-5-carboxylic acid (I) into the isomeric 1,6-dichlorofluorenone-4-carboxylic acid (III).^{4,5}

(1) For Article VII of this series see Huntress and Seikel, *THIS JOURNAL*, **61**, 1066 (1939).

(2) Presented before the Division of Organic Chemistry, Baltimore Meeting of the American Chemical Society, April, 1939.

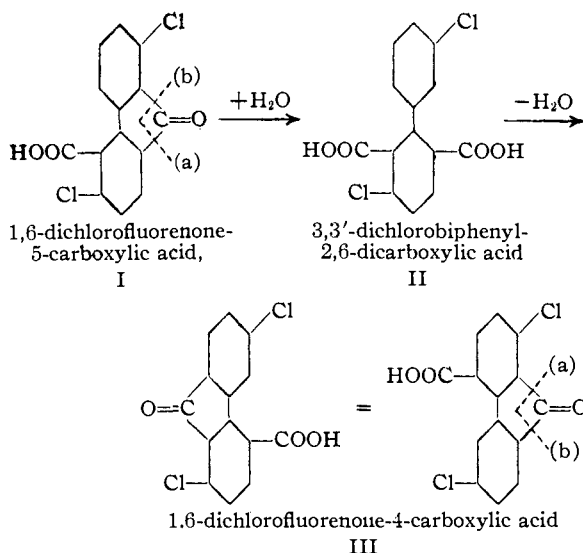
(3) This paper is constructed from part of a dissertation submitted by Miss Seikel to the Faculty of the Massachusetts Institute of Technology in partial fulfillment of the requirements of the degree of Doctor of Philosophy, June, 1938.

(4) Huntress, Cliff and Atkinson, *THIS JOURNAL*, **55**, 4262-4271 (1933).

(5) Huntress and Atkinson, *ibid.*, **58**, 1514-1518 (1936).

If the mechanism of this rearrangement were to involve the successive addition and subtraction of water, the intermediate product would be an isophthalic acid derivative (II). A sample of this hitherto unreported acid was therefore desired for an examination of its properties, particularly with respect to its behavior in concentrated sulfuric acid. Since the opening of the ketonic ring of the dichlorofluorenones themselves by means of fusion with potassium hydroxide in diphenyl ether had been accomplished successfully⁶ it seemed possible that the same procedure might be applied

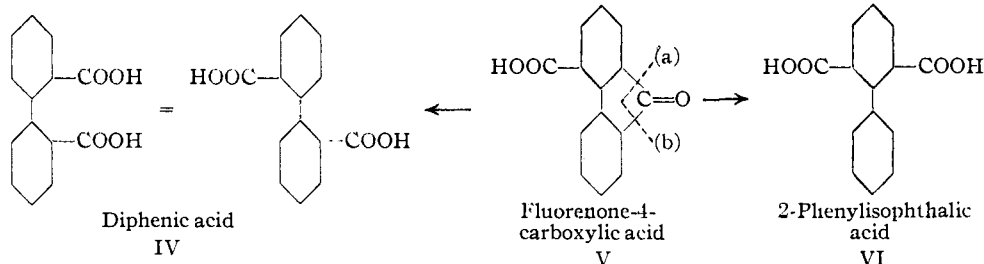
(6) Huntress and Seikel, *THIS JOURNAL*, **61**, 1066 (1939).



to their carboxylic acid derivatives, with similar results, in the preparation of the desired isophthalic acid derivative.

In preparing the way for this main objective we have also studied this method of ring opening upon the halogen-free parent, fluorenone-4-carboxylic acid. In supplementing the results we have also applied the cleavage reaction to 1,6-dichlorofluorenone-4-carboxylic acid.

Ring Cleavage of Fluorenone-4-carboxylic Acid (V).—According to the linkage ruptured, it is evident that fluorenone-4-carboxylic acid could be opened to yield the salts of either diphenic acid (IV) (rupture at a) or the previously unreported⁷ 2-phenylisophthalic acid (VI) (rup-



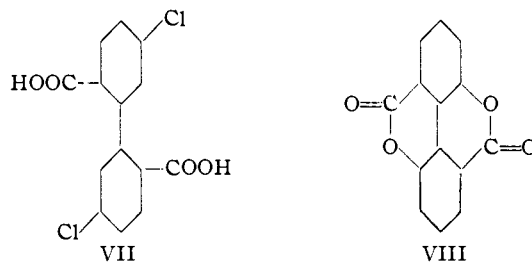
ture at b) or both. Furthermore, in applying the alkali fusion method to substances containing the carboxyl group, there was always present the possibility of ordinary decarboxylation, converting di- to monocarboxylic acids or even degrading the latter to hydrocarbons.

When fluorenone-4-carboxylic acid was sub-

(7) During the writing of this paper this acid was reported by Bell and Briggs, *J. Chem. Soc.*, 1567 (1938), with whose results we are in complete accord.

jected to the action of potassium hydroxide in diphenyl ether in the usual way⁸ both diphenic acid (IV) and 2-phenylisophthalic acid (VI) were formed. Moreover, a portion of the original keto acid always failed to undergo fission and was recovered unchanged; its proportion appeared to be independent of the time of reaction. The separation of these three acids from the fusion mixture was worked out as described in the Experimental Part.

Ring Cleavage of 1,6-Dichlorofluorenone-4-carboxylic Acid (III).—Fission of the ketonic linkage of this acid would yield either or both of two different acids analogous to those of the parent case. Thus breaking at (a) would yield 5,5'-dichlorodiphenic acid (VII); at (b) 3,3'-dichlorobiphenyl-2,6-dicarboxylic acid (II).



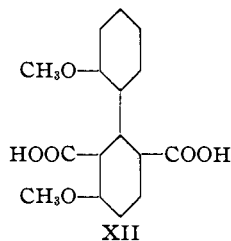
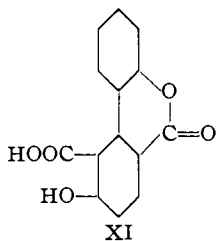
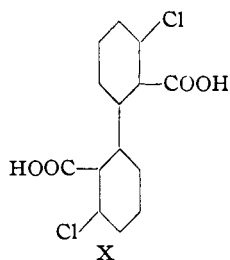
An extensive study of the influence of various factors upon the ring opening of acid III, however, never revealed any trace of an isophthalic acid derivative (II). Apart from the usual original keto acid, the main reaction product was identified as 5,5'-dichlorodiphenic acid (VII) which was obtained readily in 45% yield.

Accompanying this 5,5'-dichlorodiphenic acid in the fission products was another compound which, after separation by virtue of its insolubility in sodium bicarbonate solution, proved to be free from halogen. This substance was characterized as the dilactone (VIII) of 6,6'-dihydroxydiphenic acid. The dilactone was methylated with dimethyl sulfate and alkali and a good yield of the

(8) Huntress and Seikel, *THIS JOURNAL*, 61, 816 (1939).

known dimethyl 6,6'-dimethoxydiphenate obtained. The melting point of this ester and also that of the 6,6'-dimethoxydiphenic acid (IX), which it yielded upon hydrolysis, were in agreement with recorded values. The formation during the alkali-diphenyl ether fusion of the salt of 6,6'-dihydroxydiphenic acid from which acidification precipitates this dilactone (VIII) presumably represents an independent reaction accompanying the main one of ring opening. The yield of dilactone was small but by use of higher fusion temperature (225°) and a very short time (one minute) could be raised to 10-12%. It probably results from the replacement of both halogen atoms by hydroxyl groups, followed by their subsequent migration and opening of the ketonic ring. That the latter does not occur before the replacement is evidenced by the fact that when 5,5'-dichlorodiphenic acid (VII) was subjected to the usual fusion at 175° for thirty minutes or even to direct fusion with potassium hydroxide alone at 170° for ten minutes, only a trace of dilactone could be isolated and the original acid was recovered in excellent purity and in 80% yields.

Ring Cleavage of 1,6-Dichlorofluorenone-5-carboxylic Acid (I).—In a fashion entirely analogous to the preceding case, fission of the ketonic ring of 1,6-dichlorofluorenone-5-carboxylic acid (I) might be expected to yield either 3,3'-dichlorodiphenic acid (X) (from cleavage at a) or 3,3'-dichlorobiphenyl-2,6-dicarboxylic acid (II) (by cleavage at b) or both. An extensive study



of the influence of conditions of the potassium hydroxide-diphenyl ether fusion upon the nature and amount of the products was carried out.

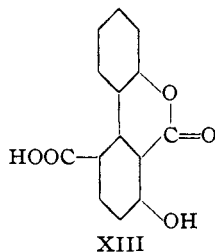
Under all circumstances a certain amount of the original keto acid (I) survived fusion and was recovered unchanged. It always was accompanied by a proportion of "unrecrystallizable gums," which, although they often accounted for as much as half of the original weight of material, could not be separated into identifiable individuals. Apart from these two fractions, however, two definite reaction products were isolated and identified.

The product of most interest was 3,3'-dichlorobiphenyl-2,6-dicarboxylic acid (II) which was obtained in yields of 10-20%. It was characterized by ultimate analysis for chlorine and by its neutralization equivalent. Its melting point (236°) was quite distinct from that of the other well-known isomeric possible cleavage product 3,3'-dichlorodiphenic acid (X) whose melting point is 304-305° dec.

This isophthalic acid derivative (II) was always accompanied by a small proportion of halogen-free by-product. This compound appears to be the hitherto unreported lactone of 2',3-dihydroxybiphenyl-2,6-dicarboxylic acid (5- or 3?-hydroxy-6-carboxybiphenylmethylid) (XI). It was best obtained in a separate series of fusions at higher temperature (220°) and shorter time (one minute) at the expense of and without isolation of the acid. The phenolic carboxy-lactone was characterized by complete absence of halogen, by ultimate analyses for carbon and hydrogen, and by determinations both of its neutralization and saponification equivalents. The absolute values of all these constants were in excellent agreement with the theoretical values for structure (XI) and widely different from those for a dihydroxybiphenyl dicarboxylic acid. The 1:2 ratio of saponification equivalent to neutralization equivalent constitutes valid evidence for the simultaneous presence of one carboxyl group and one lactone linkage in the same molecule. Finally, on treatment with dimethyl sulfate and alkali, compound (XI) yielded a neutral ester which upon alkaline saponification gave in good yield the previously unreported 2',3-dimethoxybiphenyl-2,6-dicarboxylic acid (XII), which gave ultimate analyses and neutralization equivalent in accordance with the theoretical values.

Evidence for the position of the single uncombined phenolic hydroxyl group is admittedly less satisfying. In view of the demonstrated rearrangement of at least one of the atoms or groups

in the positions originally occupied by halogen atoms, it is possible that similar changes may have occurred during formation of the phenolic carboxylic lactone. The only alternative structure, however, would be that represented by (XIII) and



the dimethoxybiphenyl dicarboxylic acid obtained via methylation and subsequent hydrolysis would be the same from either (XI) or (XIII)

During the study of the alkaline opening of the ketonic ring of 1,6-dichlorofluorenone-5-carboxylic acid (I), the possibility of direct decarboxylation during fusion was examined by measurement of the amount of carbonate produced in the alkali. The results indicated, however, that such reaction was negligible.

Ring closure of 3,3'-dichlorobiphenyl-2,6-dicarboxylic acid (II) by loss of one molecule of water conceivably could yield four different dichlorofluorenone carboxylic acids. Of these possibilities two are well known, *viz.*, 1,6-dichlorofluorenone-5-carboxylic acid (I) and 1,6-dichlorofluorenone-4-carboxylic acid (III). The other two, *viz.*, 1,8-dichlorofluorenone-4-carboxylic acid and 3,6-dichlorofluorenone-4-carboxylic acid are unknown. Experiment showed that 3,3'-dichlorobiphenyl-2,6-dicarboxylic acid (II) readily ring closed with concentrated sulfuric acid, the reaction being complete after forty-five minutes even at room temperature. The product was a mixture of dichlorofluorenone carboxylic acids but its main constituent was 1,6-dichlorofluorenone-4-carboxylic acid (III). This result is in accord with the possible formation of (II) as an intermediate in the sulfuric acid isomerization of (I) to (III) but this fact must not be construed as proof that (II) is such.

The relative ease of ring closure of the several dicarboxylic acids involved in this work deserves comment. The two isophthalic acid derivatives (II and VI) both ring closed with greatest ease as compared with diphenic acid and its derivatives (X and VII). Although in concentrated sulfuric acid at room temperature the latter were ex-

tremely slow to ring close, yet the reaction with 3,3'-dichlorobiphenyl-2,6-dicarboxylic acid (II) was complete in forty-five minutes and that for biphenyl-2,6-dicarboxylic acid (VI) was complete in about two minutes. Under the same conditions, however, ring closure of diphenic acid was still incomplete after four days, that of 3,3'-dichlorodiphenic acid (X) was complete in twenty hours, although that for 5,5'-dichlorodiphenic acid was still incomplete after a month. At steam-bath temperatures, however, ring closure of the diphenic acid series was greatly accelerated. Thus with both diphenic acid and 3,3'-dichlorodiphenic acid (X) ring closure at 100° was complete within a few minutes but 5,5'-dichlorodiphenic acid (VII) required two hours.

Experimental

All melting points reported in this paper were taken by the method described in Mulliken's "Identification of Pure Organic Compounds," Vol. I, page 218, on a 360° rod-form melting point thermometer immersed in sulfuric acid to the 0° point. All melting points are uncorrected.

The three acids I,^{4,5} III^{4,5} and V⁹ were prepared substantially as described in our earlier papers. However, in the preparation of I from 3,3'-dichlorodiphenic acid (X) the use of much milder conditions, *viz.*, concentrated sulfuric acid at room temperature for twenty hours, followed by recrystallization from glacial acetic acid (instead of alcohol) gave a much purer product, m. p. 243–244°. Similarly, ring closure of 5,5'-dichlorodiphenic acid (VII) at 100° (rather than 125°) gave a quantitative yield of III with the much improved melting point of 249°.

Fluorenone-4-carboxylic Acid (V).—Best results were obtained when the fusion mixture was kept at the temperature 170–180° and fusion for a short period (fifteen minutes) gave as good results as when carried on for a much longer time (three hours). The original keto acid was dissolved in hot diphenyl ether and added to the alkali which had already been fused and emulsified with the solvent. The potassium salt of the original keto acid immediately precipitated and subsequently reacted with the alkali. Reaction was never complete, however, and 15–25% of the original keto acid was recovered from the mixture of fusion products.

Separation of unchanged monobasic keto acid from the (two) dibasic acids formed in the fusion was based upon the insolubility of the former in hot water as compared with the solubility of the *mixed* dibasic acids in cold water. The aqueous extract of the fusion mixture was therefore acidified (6 *N* sulfuric acid) and heated at 100° until most of the precipitate had dissolved. The residual powdery yellow keto acid was filtered from this hot solution. On cooling the hot aqueous filtrates, the dibasic acids were precipitated in part but to obtain good recovery ether extractions of the salt-saturated water solutions were necessary.

After much experimentation a successful method for

(9) Moore and Huntress, *THIS JOURNAL*, **49**, 1329 (1927).

the separation of the dibasic acids was devised. This was based upon substantial differences in the rate of hydrolysis of their corresponding anhydrides. The crude mixed acids were dissolved in hot acetic anhydride (10 ml. for 3 g.) and the solution rapidly evaporated to dryness (five minutes on hot-plate in rapid air stream). Sodium bicarbonate extraction of the somewhat sticky residue showed complete conversion of the acids to insoluble anhydrides. Extraction of the mixed anhydrides with cold 3-6 *N* sodium hydroxide, however, hydrolyzed the anhydride obtained from 2-phenylisophthalic acid without affecting the diphenic anhydride. The latter is known to be monomolecular but the molecular weight of the anhydride yielded by 2-phenylisophthalic acid under these circumstances was not investigated further for, whatever its type, we were here concerned only with its rate of hydrolysis as a means of separation from diphenic anhydride.

The residue of the latter melted at 215-218° but one recrystallization from benzene raised this value to 220-221.5°. Acidification of the alkaline extract yielded the previously unreported 2-phenylisophthalic acid which in this crude form melted at 270-277°. The ratio in which the two acids were formed by the cleavage of fluorenone-4-carboxylic acid was calculated from one experiment to be approximately 3 phenylisophthalic to 4 diphenic. That is, a 37.5% yield of 2-phenylisophthalic acid and a 51.5% yield of diphenic anhydride were actually isolated from the crude mixed dibasic acids. Since this crude mixture itself represented a 75% yield from the original keto acid, the over-all yields of 2-phenylisophthalic acid and of diphenic acid were 28 and 39%, respectively. The lower melting of the above two acids from the alkaline fusion of fluorenone-4-carboxylic acid and the corresponding anhydride unaffected by cold 6 *N* sodium hydroxide were identified as diphenic acid and diphenic anhydride, respectively.

2-Phenylisophthalic Acid (VI).—The crude acid melting 270-277° from hydrolysis of the anhydride was purified by two recrystallizations from boiling water (0.5 g. in 100 ml.) from which it was obtained in 19-20 mm. long feathery white needles, m. p. 281-282°.

Anal. Calcd. for $C_{14}H_{10}O_4$: C, 69.40; H, 4.16; neut. equiv., 121. Found: C, 69.18, 69.53; H, 3.97, 3.93; neut. equiv., 121, 122.

On treatment with cold concentrated sulfuric acid this product dissolved immediately, yielding a red solution which upon dilution with water precipitated fluorenone-4-carboxylic acid, m. p. 221-222°, which did not depress the melting point of an authentic sample. This ring closure is far more rapid than with diphenic acid itself.

1,6-Dichlorofluorenone-4-carboxylic Acid (III).—Cleavage of this compound with potassium hydroxide in diphenyl ether by the usual general procedure was studied in a long series of experiments. In addition to a certain amount of unchanged original material inevitably recovered in all experiments, two other main reaction products were obtained in proportions which depended upon experimental conditions; one proved to be a dibasic acid, the other a lactone.

The yields of the dibasic acid were highest when fusion was carried out at 170-175° for one to five minutes. Higher temperatures or longer fusion periods lowered the

yield of mixed original acid and cleavage acid and increased the proportion of gums. The yields of lactone, however, were greatest at a temperature of 220-225° and a fusion time of one minute.

Isolation of the several fusion products was effected as follows: after acidification of the usual alkaline extract of the diphenyl ether reaction mixture, the resultant precipitate was either allowed to settle overnight or was heated in solution on the steam-bath for half an hour with subsequent chilling. Both procedures were designed to allow for or to hasten the lactonization of the by-product in the acid solution.

This precipitate was extracted with warm sodium bicarbonate solution and the insoluble finely divided suspension filtered off on a Celite (silica) mat. From the orange colored bicarbonate filtrate the mixture of keto and dibasic acids was thrown down upon acidification. The material insoluble in sodium bicarbonate was dissolved from the Celite filter with warm 1 *N* sodium hydroxide, giving an orange solution whose color could be diminished slightly by filtering through Norite-Celite mixture. Upon acidification of this solution, slow precipitation of the white lactone began and could be hastened by warming.

The acidic material (soluble in sodium bicarbonate) was separated by fractional crystallization into two components. From 75% acetic acid two crops of crystals deposited overnight and were separated by hand; one consisted of heavy white crystals, m. p. 292.0-292.5°; the other of fluffy yellow puffs, m. p. 235-240°. Further dilution of the mother liquor to 50% acetic content and later to 33% acetic content precipitated additional material; the first being a mixture of the two products, the second comprising more of the high melting white acid. After one further recrystallization from acetic acid the lower melting yellow compound was identified as the original 1,6-dichlorofluorenone-4-carboxylic acid by its appearance, properties, and failure to depress the melting point of an authentic sample, m. p. 248-249°.

The heavy white high melting crystals obtained above were identified by their failure to depress the melting point of an authentic sample of 5,5'-dichlorodiphenic acid, m. p. 292-292.5°. Furthermore, treatment with warm concentrated sulfuric acid at 100° for three quarters of an hour converted this product into the original 1,6-dichlorofluorenone-4-carboxylic acid (III) which after one recrystallization from glacial acetic acid did not lower the melting point of authentic material.

Dilactone of 6,6'-Dihydroxydiphenic Acid (VIII).—The crude lactone, separated from the acidic fission products by virtue of its insolubility in sodium bicarbonate and slightly purified by reprecipitation from 1 *N* sodium hydroxide solution, was obtained in almost colorless needles which did not melt below 350°. Above 330°, however, the substance sublimed rapidly and was so purified by fractional sublimation at 15-20 mm. and bath temperature of 270-280°. It was then recrystallized from a large proportion of glacial acetic acid (0.1 g. required 50 ml. of solvent).

Anal. Calcd. for $C_{14}H_8O_4$: C, 70.57; H, 2.54; sap. equiv., 119. Found: C, 70.39, 70.25; H, 2.68, 2.59; sap. equiv., 117, 125. Calcd. for $C_{14}H_{10}O_6$: C, 61.30; H, 3.68; sap. equiv., 137.

The substance gave negative tests for chlorine (both Beilstein and sodium fusion methods). It gave no evidence of any coloration either with aqueous or alcoholic ferric chloride (no phenolic groups). Although insoluble in sodium bicarbonate solution, it dissolved readily in warm 1 *N* alkali and was reprecipitated by acidification (evidence of lactone character). It dissolved in cold concentrated sulfuric acid yielding a solution with *strong* violet fluorescence of exactly the same shade as that produced by biphenylmethylolid.

A sample of this dilactone was methylated by dissolving in alkali and shaking with dimethyl sulfate according to the method used for biphenylmethylolid.¹⁰ From the strongly alkaline solution there separated a white solid out of which hot methyl alcohol extracted a good yield (64%) of dimethyl 6,6'-dimethoxydiphenate. On cooling and concentrating the methyl alcohol solution two fractions were obtained with melting points of 136–136.5° and 136.5–137°, respectively (recorded, 137°).¹¹ After hydrolysis of this ester with dilute alkali, acidification precipitated 6,6'-dimethoxydiphenic acid which after one recrystallization from acetic acid melted at 290–291.5°; recorded, 288–290°,^{11a,11c} 293–294°.^{11b}

1,6-Dichlorofluorenone-5-carboxylic Acid (I).—This compound was fused with potassium hydroxide in diphenyl ether according to the usual procedure. When the hot (180°) solution of the keto acid in diphenyl ether was poured onto the emulsified alkali, its yellow potassium salt immediately precipitated. Within three to four minutes, however, a pink color developed which deepened rapidly to vermilion. This color remained unchanged (even after one and one-half hours) but the suspended precipitate in this time gradually formed a gummy ball. After aqueous extraction the diphenyl ether was practically, if not completely, colorless and the water solution was yellow.

Both the fusion conditions and the technique of isolation of the several reaction products were very extensively studied. Fusion temperature of 160–170° and fusion time of fifteen minutes gave best general results. By working up the fusion mixture, four materials were obtained: (1) unchanged recovered keto acid; (2) a lactone, probably 5-hydroxy-6-carboxybiphenylmethylolid (XI); (3) 3,3'-dichlorobiphenyl-2,6-dicarboxylic acid (II); and (4) uncrystallizable gums.

Separation of these products was finally achieved as follows. Acidification of the hot fusion solution immediately precipitated any unchanged keto acid. The filtrate clouded immediately and upon standing overnight deposited a yellow (often gummy) precipitate which was shown to be an acidic lactone. The yellow filtrate (which gave a lavender ferric chloride reaction) was saturated with salt and extracted with ether; after being washed free from salt the ether was evaporated, leaving a brown glassy residue. On treatment with very limited amounts of water most of it dissolved, leaving a white difficultly soluble powder which ultimately proved to be the dichlorodiphenic acid. The difference between the weight of the glassy ether extract and the dichlorodiphenic acid was

designated as "uncrystallizable gum." Although this fraction represented in most cases almost half the weight of the original material, it proved impossible to isolate from it any definite compound.

3,3'-Dichlorobiphenyl-2,6-dicarboxylic Acid (II).—This acid was obtained in yields of only 10–20%. It was somewhat difficult to recrystallize but very slowly separated from dilute alcohol in rosetts of white heavy opaque irregular needles, m. p. 236.0–236.5°.

Anal. Calcd. for C₁₄H₈Cl₂O₄: Cl, 22.80; neut. equiv., 155.5. Found: Cl, 22.67, 22.77; neut. equiv., 155, 156.

Careful study of the behavior of this acid toward cold concentrated sulfuric acid showed that reaction was completed in forty-five minutes as shown by the melting range of samples taken at intervals from two minutes to twenty hours. The product was a mixture of the corresponding dichlorofluorenone carboxylic acids as evidenced by its neutralization equivalent of 290 and 291 (theoretical: 293).¹²

That the expected 1,6-dichlorofluorenone-4-carboxylic acid was the main constituent of the reaction mixture was evidenced by the method of mixed melting points. *viz.*

	M. p., °C.
A. 1,6-Dichlorofluorenone-5-carboxylic acid (I)	243–244
B. Mixture of A and C	200–220
C. The mixture of keto acids from the H ₂ SO ₄ reaction	233.5–234.5
D. Mixture of C and E	243–247
E. 1,6-Dichlorofluorenone-4-carboxylic acid (III)	248.5–249

All attempts to separate the sulfuric acid product into constituents, however, were unsuccessful. The melting points of the first and second crops of crystals from dilute acetone or glacial acetic acid differed only by 3 and 5°, respectively. Vacuum sublimation at 15–20 mm. and bath temperature of 200–210° yielded three fractions all melting between 231.5–233.5°.

5 - Hydroxy - 6 - carboxybiphenylmethylolid (XI).—The purification of this carboxy-lactone required very extensive study. The crude material was often gummy, always yellow (due to the presence of unchanged keto acid), and melted over a broad range. After trying many combinations of extraction with hot water, application of the "anhydride" procedure used above in the purification of 2-phenylisophthalic acid, sodium bicarbonate extractions, etc., none of which gave a product with satisfactory analyses, a separate set of potassium hydroxide-diphenyl ether fusions was carried out on 1,6-dichlorofluorenone-5-carboxylic acid. Conditions were then employed which from previous experience had been observed to favor the formation of the carboxy-lactone at the expense of, and without isolation of, the well-defined 3,3'-dichlorobiphenyl-2,6-dicarboxylic acid. In these special fusions the reaction temperature was raised to 220° (instead of 170°) and the time reduced to one minute (from fifteen minutes). The carboxy-lactone from these fusions was purified successfully by several recrystallizations from

(10) Rule and Bretscher, *J. Chem. Soc.*, 926 (1927).

(11) (a) Kenner and Turner, *ibid.*, 2341 (1928); (b) Stanley, McMahon and Adams, *This Journal*, **55**, 709 (1933); (c) Wittig and Petri, *Ann.*, **505**, 37 (1933).

(12) The acid used for these determinations was dried in a vacuum oven at 110° for six hours since 1,6-dichlorofluorenone-4-carboxylic acid had been shown by Huntress and Atkinson³ to be hydrated.

glacial acetic acid (using Norite). The compound was thus obtained in almost colorless needles, m. p. 299–301° dec. This melting point was accompanied by some sublimation and possibly some decarboxylation, but the pure product showed no preliminary darkening.

Anal. Calcd. for $C_{14}H_8O_5$: C, 65.61; H, 3.15; neut. equiv., 256; sap. equiv., 128. Found: C, 65.66, 65.77; H, 3.30, 3.25; neut. equiv.,¹³ 253, 254, 255; sap. equiv.,¹³ 129, 129. Calcd. for $C_{14}H_{10}O_6$: C, 61.30; H, 3.68; neut. equiv., 137.

This compound contains no chlorine (Beilstein and sodium fusion tests) and gives no color with ferric chloride reagent. It dissolves in concentrated sulfuric acid giving a yellow solution from which the original material can be recovered unchanged even after standing for seventeen hours at room temperature or after heating for half an hour on the steam-bath. It sublimes at 270–80° but appears to be simultaneously decomposed with evolution of carbon dioxide into a sublimable compound, insoluble in sodium bicarbonate but soluble in 0.1 *N* alkali and melting at 256° after one recrystallization from alcohol. This sublimation product also fails to give any color with ferric chloride, but its solution in concentrated sulfuric acid fluoresces *light blue*, reminiscent of the violet fluorescence of biphenylmethylolid and the corresponding dilactone (VIII). This sublimation product is believed to be 5-hydroxybiphenylmethylolid. Methylation of the carboxy-lactone with dimethyl sulfate and alkali followed by hydrolysis of the intermediate ester yields 2',3-dimethoxybiphenyl-2,6-dicarboxylic acid (XII).

2',3-Dimethoxybiphenyl-2,6-dicarboxylic Acid (XII).—The crude methylation product was hydrolyzed with alkali and the corresponding acid obtained in a 75% yield. After two recrystallizations from dilute acetic acid (5%), the opaque white fronds melted only one degree higher, *viz.*, m. p. 249–249.5°.

Anal. Calcd. for $C_{18}H_{14}O_8$: C, 63.55; H, 4.67; neut. equiv., 151. Found: C, 63.60, 63.48, 63.42; H, 4.36, 4.69, 4.82; neut. equiv., 151, 153, 154.

Summary

1. Heating of fluorenone-4-carboxylic acid (V), 1,6-dichlorofluorenone-4-carboxylic acid (III)

(13) The determination of neutralization and saponification equivalents was accomplished successfully only after much study of conditions. The practically colorless solution of the carboxy-lactone in alcohol remained unchanged until one equivalent of 0.1 *N* alkali had been added. A sharp, easily distinguishable change to yellow then occurred. With further addition of alkali, this yellow color deepened and gradually assumed the pinkish tinge due to the phenolphthalein indicator, but the exact beginning of this change was impossible to detect with precision. To determine the saponification equivalent, therefore, excess alkali was added, the clear red solution heated on the steam-bath for half an hour (to assure complete opening of the lactone ring), cooled and titrated back with acid. The resultant neutral end-point was *colorless* (not yellow) and the solution, although unchanged on standing at room temperature for 15–30 minutes, turned pink on warming (indicating reclosure of the lactone ring even in neutral solution).

and 1,6-dichlorofluorenone-5-carboxylic acid (I) with potassium hydroxide in diphenyl ether causes opening of the ketonic ring and the formation of various biphenyl dicarboxylic acids.

2. With the halogen-free fluorenone-4-carboxylic acid (V) opening of the fluorenone ring occurred in both senses and diphenic acid as well as 2-phenylisophthalic acid were obtained, the former slightly predominating.

3. With the two dichlorofluorenone carboxylic acids, however, only the compounds from a single type of fission could be isolated. Moreover, the types differed for the two isomers. Thus, from 1,6-dichlorofluorenone-4-carboxylic acid (III) the cleavage product was 5,5'-dichlorodiphenic acid (VII); from the isomeric 1,6-dichlorofluorenone-5-carboxylic acid (I) ring opening product was, on the other hand, the hitherto unreported 3,3'-dichlorobiphenyl-2,6-dicarboxylic acid (II). It is thus evident that a chlorine atom in the position ortho to the ketonic linkage has more effect upon its loosening than does the same substituent in para relationship.

4. With the two dichlorofluorenone carboxylic acids there also occurred side reactions involving, in addition to opening of the fluorenone ring, replacement of halogen by hydroxyl, subsequent rearrangement and lactonization.

5. Although all three of our initial materials were acids, no evidence for any substantial amount of decarboxylation under the conditions of alkaline fusion was observed.

6. Comparison of the several biphenylcarboxylic acids involved in this work showed that the isophthalic acid derivatives readily ring closed at room temperature; those of the diphenic acid series, however, required heating and even then were markedly influenced by the relative position of substituents. This circumstance has so far prevented the apprehension of 3,3'-dichlorobiphenyl-2,6-dicarboxylic acid (II) during the sulfuric acid isomerization of 1,6-dichlorofluorenone-5-carboxylic acid (I) to 1,6-dichlorofluorenone-4-carboxylic acid (III), although the products of its ring closure agree with its formation as an intermediate.

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