

acids of these isomers, if the latter are actually present in the fats mentioned, have as yet not been prepared from natural products.

On the other hand, if the ligroin-insoluble bromide of butter fat (m. p. 170° d.) be assumed to characterize one of the isomers of linoleic acid, then the liquid linolelaidic acid is obviously a single substance. The results of the partial oxidation of this fraction are not sufficiently clear cut to permit a definite conclusion at present. While there is no doubt of the homogeneity of the ϵ - and ζ -sativic acids, m. p. 126 and 158°, respectively, the additional crystalline fraction, m. p. 131–135°, obtained from the β -linolelaidic acid, may be an ill-defined η -sativic acid, a mixture of the γ - and δ -sativic acids arising from the residual solid linolelaidic acid, or a mixture of the ϵ - and ζ -isomers, this last finding support in the failure of the doubtful fraction to depress the melting point of the ϵ -isomer, although the data of Nicolet and Cox¹⁵ and Birosel²³ make this criterion appear largely inapplicable. But if this fraction is the η -sativic acid, it should have been accompanied by the remaining possible θ -isomer. Our methods of separation did not reveal the formation of this substance and we may therefore conclude tentatively that the liquid fraction of

(23) Birosel, *Natural and Applied Science Bulletin of the University of the Philippines*, **2**, 103 (1932).

the isomerization is, aside from the by-products, the individual β -linoleic acid. Ordinary linoleic acid thus appears to be elaidinized into only two of its isomers, as would follow from the assumption that the 9,10-double bond may elaidinize alone, but that the 12,13-bond cannot elaidinize without the previous or simultaneous isomerization of the 9,10-bond. The fourth possible member of the linoleic acid group consequently remains to be isolated.

The work on the problem of isomerism in the linoleic acid series is being continued and extended to the linolenic acids.

Summary

Linoleic acid was elaidinized with nitrogen oxides and with selenium.

A crystalline linoleic acid, m. p. 28–29°, a liquid isomer in an impure form, and conjugated by-products were isolated from the reaction mixture.

The crystalline linolelaidic acid yielded equal parts of a liquid and a solid tetrabromide, m. p. 78°. Partial oxidation produced two sativic acids, m. p. 122 and 146°.

The non-crystalline isomer formed only liquid bromides, and two sativic acids, m. p. 126–127° and 156–158°.

The isomerism of the linoleic acids is discussed.
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Fluorenones and Diphenic Acids. VII.^{1,2} Ring Cleavage of 1,8-, 1,6- and 3,6-Dichlorofluorenones with Potassium Hydroxide in Diphenyl Ether

BY ERNEST H. HUNTRESS AND MARGARET K. SEIKEL³

Previous work⁴ in this Laboratory has shown that when 3,3'-dichlorodiphenic acid (I) is heated with concentrated sulfuric acid it first yields 1,6-dichlorofluorenone-5-carboxylic acid (II) but that this material is isomerized on further heating with the sulfuric acid to yield 1,6-dichlorofluorenone-4-carboxylic acid (III).

(1) For Article VI of this series see Huntress and Seikel, *THIS JOURNAL*, **61**, 816 (1939).

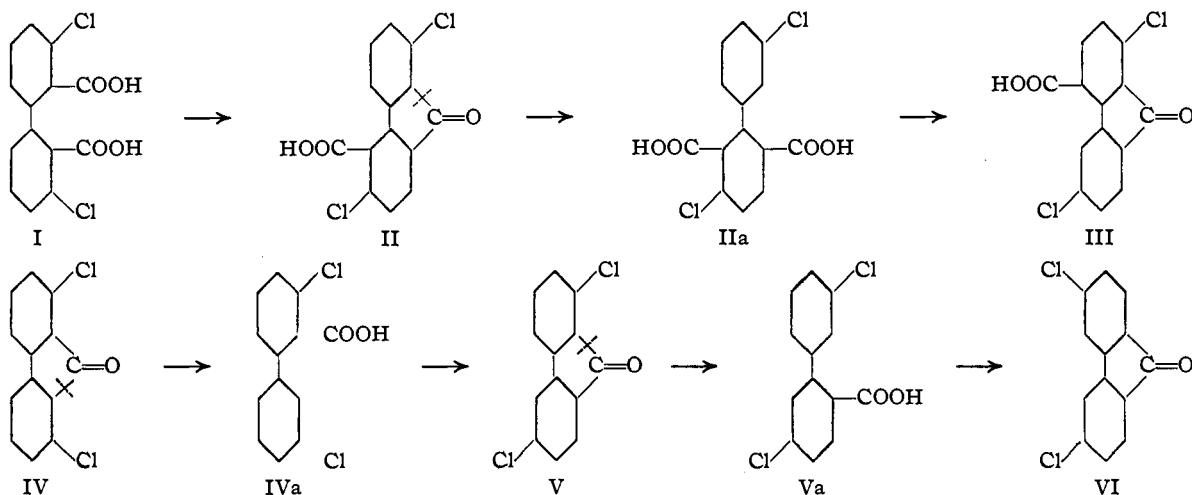
(2) Presented before the Division of Organic Chemistry, Baltimore Meeting of the American Chemical Society, April, 1939.

(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 for the degree of Doctor of Philosophy, June, 1938.

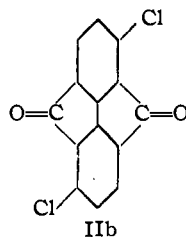
(4) Huntress and Atkinson, *THIS JOURNAL*, **58**, 1514–1518 (1936).

Possible Mechanism.—Since it is extremely unlikely that either the halogen atoms or the carboxyl group migrate as such under these conditions,⁵ and since by similar treatment both 1,8- (IV) and 1,6-dichlorofluorenone (V) also isomerize to 3,6-dichlorofluorenone (VI), it is conceivable that the observed results might be effected by fission of the ketonic linkage followed by subsequent reclosure in the opposite sense to yield the new products. Thus a possible mechanism which would account for all the facts could be represented as follows

(5) Cf. Moyle and Smith, *J. Org. Chem.*, **2**, 128 (1937).



The possibility that in the conversion of II to III there should be formed temporarily a diketone (IIb) which would then undergo fission to yield (III) seems unlikely on several grounds.



For example such a mechanism is inapplicable to the isomerization of either of the ketones (IV and V), and in the absence of any evidence to the contrary the observed isomerizations of both types may be assumed to occur by similar mechanisms. Moreover, attempts to prepare diketones of type IIb have failed⁶ and examples of two five-membered rings condensed in this fashion with two six-membered rings cannot be found.

We desired to ascertain whether substances such as IIa, IVa or Va could be prepared under conditions which would avoid ring closure, or failing their actual isolation to obtain evidence of any tendency of the substituted fluorenone nucleus to undergo fission in the sense indicated.

Discussion of Results

The results obtained by the action of fused potassium hydroxide in diphenyl ether upon 2-chlorofluorenone¹ have led us to extend the study of this reagent to the 1,8- and 1,6-dichlorofluorenone with a view to the determination of the properties of 3,3'-dichlorobiphenyl-2-carboxylic

acid (IVa) and 3',5-dichlorobiphenyl-2-carboxylic acid (Va). For completeness we have also studied the corresponding behavior of 3,6-dichlorofluorenone.

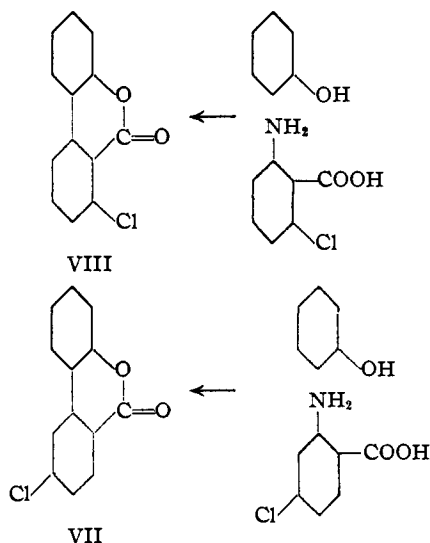
Treatment of these dichlorofluorenone with potassium hydroxide suspended in diphenyl ether caused opening of the fluorenone ring and the corresponding dichlorobiphenyl carboxylic acids were isolated readily in excellent yields. From each of the two symmetrically substituted dichlorofluorenone only one ring cleavage acid would be expected irrespective of which bond was severed and these two acids were both realized. Thus from 1,8-dichlorofluorenone (IV) there was obtained in yields of 50–60% the expected 3,3'-dichlorobiphenyl-2-carboxylic acid (IVa). From 3,6-dichlorofluorenone (VI) in similar fashion even better yields (90–92%) of 3',5-dichlorobiphenyl-2-carboxylic acid (Va) resulted. Ring opening of the unsymmetrically substituted 1,6-dichlorofluorenone, however, which conceivably might yield either or both of the two cleavage acids obtained above from the symmetrical isomers, actually resulted in 50% yield of only one, *viz.*, 3',5-dichlorobiphenyl-2-carboxylic acid (Va).

The character of these two acidic products was fully supported by satisfying analyses for chlorine and for neutralization equivalents. Although the melting points of the two isomers have nearly the same absolute values, 157–158° and 154–155°, respectively, yet the melting point of a mixture of the two was sharply depressed. The structures assigned to the two cleavage acids were confirmed by reclosure of the fluorenone ring on treatment with concentrated sulfuric acid. Under these circumstances 3,3'-dichlorobiphenyl-2-car-

(6) (a) Bell and Robinson, *J. Chem. Soc.*, 2236 (1927); (b) Meyer, Meyer and Taeger, *Ber.*, 53, 2035 (1920).

boxylic acid (IVa) after fifteen minutes at room temperature gave a quantitative yield of dichlorofluorenones which, by fractional sublimation under reduced pressure, was separated into approximately 25–35% of 1,8-dichlorofluorenene (IV) and 65–75% of 1,6-dichlorofluorenene (V). The formation of 1,8-dichlorofluorenene (which could not occur from structure Va) constitutes adequate evidence for the structure of 3,3'-dichlorobiphenyl-2-carboxylic acid (IVa). Similar sulfuric acid treatment of the isomeric cleavage acid (Va) gave a quantitative yield of dichlorofluorenones which, by fractional sublimation under reduced pressure, was separated into approximately 30–40% of 1,6-dichlorofluorenene (V) and 60–70% of 3,6-dichlorofluorenene (VI). The formation of 3,6-dichlorofluorenene (which could not occur from structure IVa) constitutes adequate evidence for the structure of 3',5'-dichlorobiphenyl-2-carboxylic acid (Va).

In addition to the desired dichlorobiphenyl carboxylic acids which thus constituted the principal cleavage products, there was also obtained from the two dichlorofluorenones with one (or two) halogen atoms in the ortho relationship to the carbonyl group, a smaller proportion of compounds which have been shown to be lactones. That from 1,8-dichlorofluorenene (IV) was characterized as 3-chlorobiphenylmethylolide (VIII)



or the lactone of 2'-hydroxy-3-chlorobiphenyl-2-carboxylic acid; that from 1,6-dichlorofluorenene (V) as 5-chlorobiphenylmethylolide (VII) or the lactone of 2'-hydroxy-5-chlorobiphenyl-2-carboxylic acid. No corresponding lactone was ob-

tained from 3,6-dichlorofluorenene (VI) which has neither of its halogen atoms adjacent to the carbonyl group.

The position of the chlorine atom in each of the two lactones was demonstrated by synthesis, 3-chlorobiphenylmethylolide (VIII) being isolated from the several reaction products of diazotized 6-chloroanthranilic acid with phenol and 5-chlorobiphenylmethylolide (VII) from the reaction products of diazotized 4-chloroanthranilic acid with phenol. Melting points of mixtures of the corresponding lactones from the dichlorofluorenones and from synthesis were not depressed.

The formation, during the alkali-diphenyl ether fusion, of the salts of hydroxychlorobiphenyl carboxylic acids from which acidification precipitates these lactones presumably represents two other independent reactions (replacement of halogen by hydroxyl and rearrangement) accompanying the main one of ring opening. It appears to be significant that with these dichlorofluorenones, these independent reactions occur only with a halogen atom in ortho relation to the carbonyl group.

Experimental

All melting points reported in this paper were taken by the method described by Mulliken,⁷ on a 360° rod form melting point thermometer immersed in sulfuric acid to the 0° point. All melting points are uncorrected.

Products Obtained by the Potassium Hydroxide-Diphenyl Ether Fusion.—The three dichlorofluorenones (IV, V and VI) were prepared as in previous work.⁸

During the coupling of diazotized 4-chloroanthranilic acid to obtain 5,5'-dichlorodiphenic acid we obtained a small quantity of the new compound 5,5'-dichlorodiphenyl ether 2,2'-dicarboxylic acid, separable from the main product by its difficult solubility in hot alcohol. The white solid melted variously at 336° dec., 318° dec., 310° dec.

Anal. Calcd. for C₁₄H₈Cl₂O₃: Cl, 21.71; neut. equiv., 163.5. Found: Cl, 21.83; neut. equiv., 166–169, 156–158.

Cold concentrated sulfuric acid solutions of this product showed a brilliant green fluorescence and on dilution yielded a yellow acidic compound, m. p. 346–347° dec. This was probably the corresponding dichloroxanthone carboxylic acid but because of lack of material the matter was not investigated further.

The fusion with potassium hydroxide in diphenyl ether was carried out in a manner analogous to that described in the preceding paper.¹

1,8-Dichlorofluorenene (IV).—The fusion mixture with this isomer differed from that with the 3,6-derivative, a buff colored ball of gum precipitating at once. Careful tests on small portions of the reaction mixture showed that

(7) Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, Vol. I, p. 218.

(8) Huntress and Cliff, *This Journal*, **55**, 2564–2566 (1933).

the diphenyl ether became colorless within four minutes. Acidification of the fusion mixture precipitated a crude gummy material which by means of hot aqueous sodium bicarbonate solution was divided into a soluble and insoluble fraction. Acidification of the bicarbonate extract precipitated an acid; the bicarbonate insoluble material proved to be a lactone.

3,3'-Dichlorobiphenyl-2-carboxylic Acid (IVa).—The acidic fusion product as reprecipitated from the sodium bicarbonate solution was obtained in yields of 50–60% and melted at 150–152°. After several recrystallizations from dilute acetic acid (33%) it formed yellow transparent ferns; from dilute alcohol it separated as clear yellow,⁹ flat parallelograms, m. p. 157–158°.

Anal. Calcd. for $C_{12}H_8Cl_2O_2$: Cl, 26.56; neut. equiv., 267. Found: Cl, 26.49, 26.73; neut. equiv., 269, 266, 264.

For ring closure a sample of this acid (0.125 g.) was dissolved in concentrated sulfuric acid (4 ml.) and allowed to stand for fifteen minutes before diluting with water. The cold sulfuric acid solution was brown-red and had none of the purple tinge characteristic of the presence of 3,6-dichlorofluorenone. The precipitated ketones (98% yield) after extraction with hot sodium bicarbonate solution were washed, dried and separated by fractional sublimation, carried on first at ordinary pressure, later at 14–20 mm. with the bath temperature reading from 150–220°. The crude mixture sublimed without residue and was recovered quantitatively. Of ten fractions obtained, the first seven melted at 200–206° and represented 76% of the whole; the melting point of the eighth rose to 200–223° (4%); the material in the last two melted at 247–250° and 253–253.5° (20%). The lowest melting product was further purified by one recrystallization from benzene and three extractions with boiling 70% alcohol after which it melted sharply at 218–219° and was conclusively characterized as 1,6-dichlorofluorenone (V) by its failure to depress the melting point of an authentic sample. The high melting sublimate (last fraction) was recognized as 1,8-dichlorofluorenone (IV) by its failure to depress the melting point of authentic material.

The acid (IVa) on heating to 410–420° began to evolve carbon dioxide. The ketones simultaneously formed were separated from the accompanying black tar by extraction with hot alcohol and subsequent recrystallization from benzene. This yielded a somewhat impure sample of 1,6-dichlorofluorenone, m. p. 217–220°.

3-Chlorobiphenylmethylolid (VIII).—The portion of potassium hydroxide–diphenyl ether fusion product which after precipitation was insoluble in sodium bicarbonate solution constituted a 20–30% yield of the lactone, 3-chlorobiphenylmethylolid and in crude form melted from 125–135°. On recrystallization from alcohol it separated in colorless transparent hair-like needles, m. p. 135–135.5°.

Anal. Calcd. for $C_{13}H_7ClO_2$: Cl, 15.38; sap. equiv., 230.5; mol. wt., 230.5. Found: Cl, 15.57; sap. equiv., 229; mol. wt. (Rast), 221.

(9) This acid previously had been reported⁸ as obtained from decarboxylation of 3,3'-dichlorodiphenic acid in the form of pure white needles, m. p. 152.5°. As obtained in the present work its melting point was 5° higher but it could never be freed from a persistent yellow color for which we have no explanation.

The compound was insoluble in either cold or hot sodium bicarbonate solutions and also in cold 6 *N* sodium hydroxide, but in hot alkali it dissolved yielding a yellow solution from which acidification precipitated the original material (evidence of lactone character). It dissolved in cold concentrated sulfuric acid yielding a colorless solution which only became yellow on warming (indicates no fluorenone formation). It failed to give any trace of coloration either with aqueous or alcoholic ferric chloride and could be recovered unchanged from treatment with acetic anhydride (absence of phenolic group).

The melting point of a mixture of this lactone from the fusion mixture with that synthesized from 6-chloroanthranilic acid and phenol (see below) was not depressed (evidence for position of chlorine atom).

Synthesis of 3-Chlorobiphenylmethylolid (VIII).—The method used was based on that recorded¹⁰ for the parent compound. 6-Chloroanthranilic acid hydrochloride⁸ (p. 2562) (10 g. or 0.048 mol) suspended in alcohol (20 ml.) was treated with concentrated hydrochloric acid (10 ml.) and the cold mixture diazotized by addition of sodium nitrite (3.3 g., or 0.048 mol) dissolved in water (5 ml.). To prevent evolution of nitrogen from this very reactive diazonium salt in the presence of alcohol it was necessary to cool the mixture with solid carbon dioxide. Sodium chloride was removed by filtration and any adhering solid diazonium salt removed from it by several extractions with alcohol. The pure diazonium salt was then precipitated easily from the several alcoholic solutions by addition of excess ether, the total yield amounting to 7 g. (67%). Coupling of this material with phenol (10 g.) and isolation of the resultant lactone was carried out exactly as described in the parent case. The great reactivity of this diazonium salt was again evidenced by its speed of coupling with phenol, the evolution of nitrogen being complete after five minutes of heating as compared with twenty to thirty minutes required for diazotized anthranilic acid in the parent case. A crude yield of 0.34 g. (3.1%) of the bicarbonate insoluble lactone was separated from the numerous other reaction products. It was grayish-tan in color and melted at 129.5°. After sublimation at 15 mm. and 180–190° (bath temperature) it was obtained in the usual white needles, m. p. 135.0–135.5°.

Anal. Calcd. for $C_{13}H_7ClO_2$: Cl, 15.38; sap. equiv., 230.5. Found: Cl, 15.36, 15.25; sap. equiv., 228, 224.

1,6-Dichlorofluorenone (V).—Fusion of 1,6-dichlorofluorenone (V) with potassium hydroxide in diphenyl ether was carried out in the usual way.¹ The reaction mixture immediately assumed a brick-red color characteristically different from either the buff colored gummy ball formed from the 1,8-isomer or the pink tinge produced with the 3,6-isomer. Since unlike these other cases completion of the reaction was impossible to detect with certainty (as water extracts of the diphenyl ether were very yellow) about thirty minutes was allowed. Separation of the various products was effected most advantageously by extraction of the acidified water layer (including some solid) with ether, and subsequently extracting this ether solution with aqueous sodium bicarbonate. Acidification of the bicarbonate extract gave the crude acidic fission

(10) Graebe and Schestakow, *Ann.*, **264**, 306–324 (1895).

product in a yield of about 50% and with a melting point of 151–153°. Evaporation of the ether layer yielded a precipitate of crude lactone, m. p. 164–166°; yield 32%. As so obtained this crude was yellow but this color could be removed by recrystallization from alcohol (using Norite) or even by extracting the yellow ether solution with 1 *N* sodium hydroxide before evaporation.

3',5-Dichlorobiphenyl-2-carboxylic Acid (Va).—After one or two recrystallizations from dilute acetic acid (33%) the acidic fission product was obtained as long transparent colorless needles, m. p. 154–155°.

Anal. Calcd. for $C_{18}H_8Cl_2O_2$: Cl, 26.56. Found: Cl, 26.60, 26.67.

The melting point of a mixture of this material with authentic 3',5-dichlorobiphenyl-2-carboxylic acid (see below) was not depressed but that of a mixture with an authentic sample of the isomeric 3,3'-dichlorobiphenyl-2-carboxylic acid (m. p. 157–158°) was lowered to 128–143°. Furthermore, upon the usual treatment with cold concentrated sulfuric acid followed by dilution with water, a crude mixture of neutral ketones was obtained, from which one recrystallization with benzene yielded 3,6-dichlorofluorenone, m. p. 299–300°, which did not depress the melting point of an authentic sample.

5-Chlorobiphenylmethylolid (VII).—The crude ether-soluble, sodium bicarbonate insoluble lactone was further purified by several recrystallizations from alcohol from which the pure product separated in long white hair-like needles, m. p. 173.5°.

Anal. Calcd. for $C_{18}H_7ClO_2$: Cl, 15.38; sap. equiv., 230.5; mol. wt., 230.5. Found: Cl, 15.34, 15.63; sap. equiv., 207, 218; mol. wt. (Rast), 170, 191.

Like its isomer this lactone was insoluble in either cold or hot sodium bicarbonate or in cold 6 *N* sodium hydroxide, but dissolved in boiling 6 *N* sodium hydroxide yielding a (yellow) solution from which acid reprecipitated the original compound (evidence for lactone character). It was also recovered unchanged even after standing dissolved overnight in cold concentrated sulfuric acid (indicates no fluorenone formation). The melting point of a mixture of this lactone with synthetic 5-chlorobiphenylmethylolid (see below) was not depressed (evidence for position of halogen).

Synthesis of 5-Chlorobiphenylmethylolid (VII).—This substance was synthesized by coupling diazotized 4-chloroanthranilic acid¹¹ with phenol in a manner entirely analogous to that described above for the 3-chloro isomer. The only differences in this reaction arose from the markedly lower reactivity of the 4-chloroanthranilic acid and its diazonium salt. During the diazotization of 4-chloroanthranilic acid hydrochloride the clear diazotized solution was in some runs contaminated by a red precipitate; since this is insoluble in the alcoholic medium it was easily removed by filtration. Its structure was not further investigated. After addition of the phenol approximately thirty minutes were required for complete evolution of nitrogen (difference from case of diazotized 6-chloroanthranilic acid above). After removal of the bicarbonate soluble acids from the crude gummy coupling product, the residue was no longer gummy in character

(difference from biphenylmethylolid and its 3-chloro derivative) but was almost pure 5-chlorobiphenylmethylolid, obtained as a tan powder, m. p. 168–170°, yield 10% (as compared with 5% for the parent and 3.1% for the 3-chloro isomer). Although recrystallization from alcohol raised the melting point at once, two Norite treatments failed to remove the last traces of color and the material was, therefore, sublimed at 15 mm. and 170–180° (bath temperature). The pure white sublimate then melted sharply at 174–174.5°.

Anal. Calcd. for $C_{18}H_7ClO_2$: Cl, 15.38; sap. equiv., 230.5. Found: Cl, 15.16, 15.52; sap. equiv.,¹² 223, 226.

3,6-Dichlorofluorenone (VI).—Fusion of this ketone with potassium hydroxide in diphenyl ether was carried out in the usual manner.¹ Immediate formation of a persistent pink tinge throughout the mixture undoubtedly evidenced the presence of small traces of hydroxyfluorenones. Removal of test portions of the fusion mixture and their extraction with water showed the gradual disappearance of the original yellow color of the ketone from the solvent. In contrast to the short periods required for the 1,8- and the 1,6-isomers (five and thirty minutes, respectively), this 3,6-dichlorofluorenone was run for one to two hours in various experiments. The yield of crude cleavage acid was very high (90–92%) and showed a m. p. of 152–155°. No trace of any phenolic compounds could be found despite the constant testing of all precipitates and neutralized samples of all filtrates with ferric chloride reagent. The excellent yields and high melting points of the crude fission products constitute excellent evidence for the (expected) homogeneity of the product from this isomer.

3',5-Dichlorobiphenyl-2-carboxylic Acid (Va).—The crude acid was purified by solution in sodium bicarbonate (no residue) and reprecipitation with acid, followed by extraction with hot water and finally by recrystallization from dilute acetic acid (33%) from which the pure compound separated in clusters of colorless transparent needles 6–7 mm. long, m. p. 155.0–155.5°.

Although the structure of this acid is evidenced by its mode of formation and by its failure to depress the melting point of a mixture with the corresponding material from the alkaline fission of 1,6-dichlorofluorenone (which had already been analyzed), its neutralization equivalent was determined and found to be 267 (theoretical 267).

For ring closure the pure acid (0.15 g., m. p. 155°) was dissolved in cold concentrated sulfuric acid (5 ml.) and allowed to stand for fifteen minutes before dilution with water. The sulfuric acid solution showed the purple-red color characteristic of the presence of the 3,6-ketone.⁴ The mixed ketones obtained in quantitative yield on dilution melted around 260–280° and neither the weight nor the melting range was changed by extraction with hot

(12) For the determination of the saponification equivalent the lactone was dissolved in an excess of hot standard (0.1 *N*) sodium hydroxide and the excess titrated back with standard acid. With this isomer it was observed that as the pH of the solution approached the neutral point, a white cloud of the lactone began to precipitate. After decolorization of the phenolphthalein indicator by a slight excess of acid, the colorless solution again turned pink accompanied by further precipitation of lactone. For this reason rapid titration was required to attain any end-point at all and great accuracy was impossible. The behavior of this isomer is in sharp contrast with that of the 3-chloro derivative which does not lactonize in alkaline (nor even in neutral) solution.

(11) Huntress, Cliff and Atkinson, *This Journal*, **55**, 4269 (1933).

sodium bicarbonate solution (15 ml.). The two ketones were separated by fractional sublimation, run first at atmospheric pressure and then at 14–20 mm. with the bath temperature rising from 150–240°. The first six of nine sublimates (each representing a half-hour period) melted around 208–220°, and constituted 35% of the total weight. After purification by recrystallization from benzene, 70% alcohol and finally again from benzene, the melting point became 212–214° and the substance was identified as 1,6-dichlorofluorenone. The next two fractions (15%) showed rapidly rising melting points while the ninth and last fraction (50%) melted quite sharply at 298–299°. After one recrystallization from benzene it was readily identified as 3,6-dichlorofluorenone by its failure to depress the melting point of an authentic sample.

A sample of pure 3',5-dichlorobiphenyl-2-carboxylic acid (0.15 g.) was refluxed for six hours with absolute methyl alcohol (5 ml.) and concentrated sulfuric acid (1 ml.). Concentration of the solution and addition of water precipitated an oil which even after extraction with sodium bicarbonate could not be induced to crystallize. When the purified oil was dissolved in cold concentrated sulfuric acid the clear yellow solution changed within five minutes to the deep purple color indicative of the formation of ketones. After standing for an hour and diluting with water a yellow crystalline precipitate insoluble in sodium bicarbonate and melting 240–260° indicated the formation of a mixture of ketones and the experiment was discontinued.

Summary

1. Opening of the ketonic linkage of para substituted chlorofluorenones by treatment with potassium hydroxide in diphenyl ether can be effected in excellent yields without any traceable replacement of halogen by hydroxyl.

2. Despite some tendency of ortho chlorinated fluorenones to yield products formed by replacement of halogen by hydroxyl followed (or possibly preceded) by rearrangement to lactones, opening of the ketonic linkage of such dichloro-

fluorenones gave 50–60% yields of the corresponding dichlorobiphenylcarboxylic acids.

3. With unsymmetrically substituted dichlorofluorenones (*e. g.*, 1,6-dichlorofluorenone) the halogen ortho to the ketonic linkage labilizes the latter to such a degree that only one dichlorobiphenylcarboxylic acid results.

4. The rate of cleavage appears to bear a relationship to the position of the halogen atoms.

5. From fluorenones containing an ortho chlorine atom there were obtained, in addition to the cleavage acids, products which were definitely identified as lactones (chlorobiphenylmethylolids), suggesting that the ortho halogen was more sensitive to alkali than the para and was in part replaced by hydroxyl, followed by rearrangement to the salts of the corresponding chlorohydroxybiphenylcarboxylic acid whose lactone was obtained upon acidification.

6. Upon treatment with cold concentrated sulfuric acid both 3',5- and 3,3'-dichlorobiphenyl-2-carboxylic acids ring close within five minutes yielding both possible dichlorofluorenones in ratios indicative of their respective tendency for formation and in accord with those expected from the hydration–dehydration mechanism of the rearrangement of 1,8-dichlorofluorenone and 1,6-dichlorofluorenone to 3,6-dichlorofluorenone.

7. The easy ring closure of 3',5-dichlorobiphenyl-2-carboxylic acid (or its methyl ester) effectively demonstrates the impracticability of its isolation from the hot sulfuric acid solution used for the rearrangement of 1,6-dichlorofluorenone to 3,6-dichlorofluorenone even if it should form as the intermediate.

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