2. N-(β-Phenylethyl)-chloroacetamide was dehydrated by the action of phosphorus pentoxide giving 1-chloromethyl-3,4-dihydroisoquinoline.

The Preparation of Certain Disubstituted Fluorenones by the Action of Heat upon the Corresponding Substituted Diphenic Acids or their Derivatives

BY E. H. HUNTRESS AND I. S. CLIFF

The number of substituted fluorenones containing substituents in the positions ortho to the carbonyl linkage is so small as to excite interest. Of the few instances reported in the literature[1] some could not be duplicated in other laboratories and others are obtainable only by tedious processes or from very difficultly accessible sources.[2] In connection with certain studies of the phenanthridone series now in progress in this Laboratory it was desired to obtain from readily accessible sources fluorenones which should contain substituents in the 1- or the 1,8-positions. This result has now been obtained by extending to certain dichlorodiphenic acids the method of preparation used in making fluorenone from diphenic acid.[3]

The two ketones with which we are here mainly concerned are 1,8- and 1,6-dichlorofluorenone. Both substances are obtained by operating upon suitable derivatives of the hitherto unknown 3,3'-dichlorodiphenic acid (I). The 1,8-dichlorofluorenone (III) is smoothly obtained in quantitative yield by the action of heat upon 3,3'-dichlorodiphenic anhydride (II), none of the 1,6-ketone being formed. The 1,6-dichlorofluorenone (V) is obtained in 55% yield by the action of heat upon 1,6-dichlorofluorenone-5-carboxylic acid (IV) (the keto acid corresponding to 3,3'-dichlorodiphenic acid), none of the 1,8-ketone being formed.

(1) Cf. Huntress and Cliff, THIS JOURNAL, 54, 826 (1932). In this earlier note we accidentally omitted mention of fluorenone-1-carboxylic acid, long known, but recently synthesized and studied by Mayer and Freitag, Ber., 54, 347-357 (1921), and by Sieglitz, ibid., 57, 316-7 (1924).

(2) During the progress of this work we have encountered several further cases of ortho substituted fluorenones. Fieser [THIS JOURNAL, 51, 2485 (1929)] has reported 1,4,6-trimethoxyfluorenone from the sulfuric acid ring closure of 2,5,5'-trimethoxy-2'-carboxybiphenyl. The same worker also prepared 1,6-dimethoxyfluorenone-4-carboxylic acid by similar ring closure of 5,5'-dimethoxydiphenic acid but reported no attempt to isolate the corresponding dimethoxy ketone. Finally von Braun and Manz [Ann., 496, 170-196(1932)] have reported an impressive list of 1-substituted fluorenones obtained as degradation products of fluoranthene derivatives: e. g., fluorenone-1-propionic acid and its 2-amino-, 2-acetylamino-, 6-amino- and 6-acetylamino- derivatives; fluorenone-1,6-dicarboxylic acid; fluorenone-1,2-dicarboxylic acid and its anhydride, dimethyl ester, and acid methyl ester; 2-nitrofluorenone-1-carboxylic acid; 2-bromofluorenone-1-carboxylic acid; fluorenonehydrindone; and certain other fluorenone-1-carboxylic acids containing also the anthraquinone nucleus.

(3) Huntress, Hershberg and Cliff, THIS JOURNAL, 53, 2720-2724 (1931).

The Action of Heat upon 3,3'-Dichlorodiphenic Acid Itself.—With these results available we have examined the action of heat upon 3,3'-dichlorodiphenic acid itself. Quantitative elimination of carbon dioxide occurs and approximately equal amounts of both 1,8- and 1,6-dichloro-fluorenones are obtained. This fact at first suggests that intermediate formation of both anhydride and keto acid had occurred, each subsequently suffering loss of carbon dioxide independently. Furthermore, although the pyrolysis of the keto acid could clearly yield only the 1,6-ketone, elimination of carbon dioxide from the anhydride might conceivably be accompanied by intermediate rotation of one nucleus prior to final · ring closure and thus also be a source of 1,6-dichloro ketone. That this latter intermediate rotation is improbable, however, is supported by our results with 5,5'-dichlorodiphenic anhydride which on pyrolysis gave only 3,6-dichlorofluorenone and none of the 1,6-dichlorofluorenone which would have resulted if transient ring rotation had been involved.
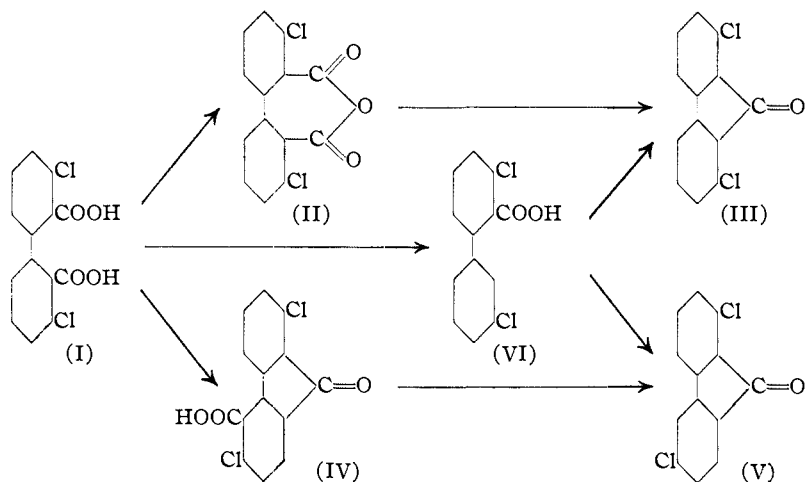
It is also evident, however, that if the original substituted diphenic acid were to lose carbon dioxide before it lost water, there would result an intermediate 3,3'-dichloro-2-carboxybiphenyl (VI) which might then undergo ring closure in two senses to yield both the observed dichloro-fluorenones. As a matter of fact we once actually isolated this intermediate monocarboxylic acid, but its amount was so small that its mode of ring closure on heating could not be examined. No formation of 3,3'-dichlorobiphenyl (loss of two moles of carbon dioxide) was ever observed.

These experimental results therefore permit the following conclusions regarding the action of heat upon 3,3'-dichlorodiphenic acid. (1) The action of heat may follow *either* or *both* of the following courses: (a) both the anhydride and the keto acid may be formed and each lose water to

yield the 1,8- and 1,6-dichlorofluorenone, respectively; (b) the intermediate monocarboxylic acid may form and subsequently lose water in two ways, one to yield the 1,8-ketone, the other after ring rotation to give the 1,6-ketone. (2) The action of heat cannot involve the anhydride alone or the keto acid alone but may involve the monocarboxylic acid alone.

During the course of our work we have had occasion to operate in a similar manner upon the anhydride obtained[4] from 5,5'-dichlorodiphenic acid. Under the conditions at which the 3,3'-dichlorodiphenic anhydride readily lost carbon dioxide, the 5,5'-isomer was stable and sublimed unchanged, but on raising the temperature to 400° carbon dioxide was evolved smoothly and a good yield of a dichloro ketone was isolated. Since upon the usual assumption of ortho ring closure after loss of carbon dioxide the only two possible pyrolytic products would be 3,6- or 1,6-dichlorofluorenone, and the product here obtained is isomeric with, but definitely different from, the known 1,6-isomer, its characterization as 3,6-dichlorofluorenone appears to be adequate. The good yield of this ketone which was obtained indicates that during pyrolysis there is slight probability that rotation of one of the rings occurs to any great extent.

Experimental Part

3,3'-Dichlorodiphenic Acid (I).—A search of the literature indicated that of the four possible symmetrically substituted dichlorodiphenic acids only two had been reported, viz., 5,5'-dichlorodiphenic acid, m. p. 297° uncorr.,[5] and dl-6,6'-dichlorodiphenic acid, m. p. 288°,[6] together with both its optically active forms. In preparing our new 3,3'-dichlorodiphenic acid we have taken advantage of the fact that 3-chloro-o-toluidine (6-chloro-2-aminotoluene) is now commercially available in the form of its hydrochloride under the name "Fast Scarlet TR Base."[7] The sequence of simple stages by which this product was converted to 3,3'-dichlorodiphenic acid is indicated below.
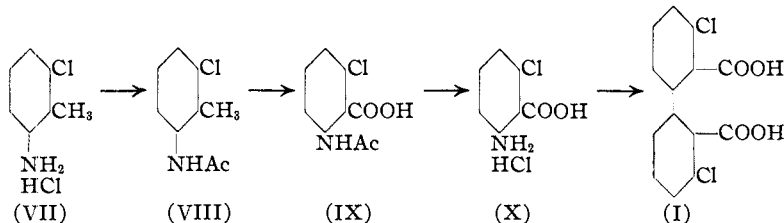
6-Chloro-2-acetylaminotoluene (VIII).—Fifty-one grams (0.286 mole) of commercial 6-chloro-2-aminotoluene hydrochloride was dissolved in about 600 ml. of cold water, 42 g. (0.309 mole) of crystallized sodium acetate was added and dissolved, and the re-

(4) Hunn, This Journal, **45**, 1024–1030 (1923).

(5) Ref. 4, p. 1028.

(6) Christie, James and Kenner, J. Chem. Soc., **123**, 1948–1951 (1923).

(7) In addition to the above 6-chloro-2-aminotoluene two other isomeric monochloro-o-toluidine hydrochlorides are also commercially available. 5-Chloro-2-aminotoluene hydrochloride (sold as "Fast Red TR Base") and 4-chloro-2-aminotoluene hydrochloride (sold as "Fast Red KB Base") also constitute important components in the preparation of certain colors of the Naphthol AS group. Since the commercial hydrochlorides are of high purity and their synthesis on the laboratory scale is laborious, attention is called to this useful source of materials for organic syntheses. Our products were obtained from the General Dyestuffs Corporation.

sultant solution then vigorously shaken with 36 g. (0.354 mole) of redistilled acetic anhydride. The resultant large gray precipitate of crude acetylation product was filtered with suction and washed with water; weight of dry crude, 40 g. (77%). The melting point of this crude was 154–155° and experience soon showed that it was thus sufficiently pure for immediate oxidation to the corresponding acid. If recrystallized from 400 ml. of boiling 50% alcohol, however, the melting point rose to 155–156° (156° recorded) while the final yield fell to 56–58%.

6-Chloro-2-acetylaminobenzoic Acid (IX).—For the preparation of this acid, the preceding product (VIII) was oxidized with potassium permanganate in aqueous magnesium sulfate solution according to the proportions of Cohn.[8]

Ten grams of 6-chloro-2-acetylaminotoluene (0.055 mole) was dissolved in 1250 ml. of hot water and to this solution 21 g. (0.086 mole) of magnesium sulfate crystals and 30.0 g. (0.19 mole) of powdered potassium permanganate were added at once. The resultant mixture was vigorously stirred with a motor and kept at 80–85° for two hours. The large brown precipitate of oxides of manganese was then filtered from the hot solution with suction and washed with hot water. A stream of sulfur dioxide was then passed through the solution until the color disappeared and a white precipitate of acetylated acid was thrown down. After filtering, washing with cold water, and drying at 100° the product consisted of 6.5 g. (56%) of white acid, m. p. 215° (recorded m. p. 215°).

Later preparations of this material were carried out on the unrecrystallized "crude" acetylation product from the original "Fast Scarlet TR Base," often using as much as 200 g. of the latter compound. The melting points of the products so obtained were as good as those from the purified acetyl derivative while the over-all yield for the acetylation–oxidation sequence was from 35–45% when operating on the large scale.

6-Chloro-2-aminobenzoic Acid Hydrochloride (6-Chloroanthranilic Acid Hydrochloride).—Hydrolysis of the preceding acetyl derivative with a large excess of hot concentrated hydrochloric acid at 100° (not higher) gave on cooling excellent yields of pure 6-chloroanthranilic acid hydrochloride. Even as much as 88 g. of acetylated acid heated with 440 ml. of concentrated hydrochloric acid for two hours in an oil-bath at 100° gave 81% of the acid hydrochloride, white crystals on cooling, m. p. 195° dec. as recorded.[9]

In one experiment there was obtained in place of the expected product a 95% yield of m-chloroaniline hydrochloride. On this occasion the crude hydrolytic product had melted at about 220° dec. instead of 195° dec. as in a normal run. The identity of the product was confirmed by its conversion to acetyl-m-chloroaniline, m. p. 71–72° (recorded 72°); and by its conversion through the diazonium salt to m-chlorophenol, b. p. 213–214° (214° recorded); p-nitrobenzoate, m. p. 98–99° (99° recorded), 3,5-dinitrobenzoate, m. p. 156° (156° recorded). Critical examination of our procedure in this run disclosed that in this particular case heating of the hydrochloric acid saponification had been carried out over a free flame. Since the resultant local overheating evidently caused loss of carbon dioxide, this difficulty was subsequently avoided by using a 100° heating bath. The excellent melting points of the usual crude products showed that if any traces of m-chloroaniline were formed, they remained in the acid mother liquor on cooling.

3,3′-Dichlorodiphenic Acid (3,3′-Dichloro-2,2′-dicarboxybiphenyl) (I).—Following preliminary experiments to fix conditions, the desired acid was prepared by coupling two molecules of diazotized 6-chloroanthranilic acid hydrochloride in the presence of ammoniacal cuprous ammonium sulfite. The yield of crude product varied from 61–94%. The procedure for a typical experiment was as follows.

(8) Cohn, *Monatsh.*, **22**, 487 (1901).

(9) Cohn, Ref. 8. With runs of smaller size the yield was often higher.

To a solution of 28.0 g. (0.135 mole) of 6-chloroanthranilic acid hydrochloride in a mixture of 56 ml. of concentrated hydrochloric acid with 280 ml. of ice water was slowly added 9.3 g. (0.135 mole) of sodium nitrite in 186 ml. of water. The disappearance of free nitrous acid was followed by means of iodo-starch paper and when diazotization was complete any undissolved solid (6-chloro-2-acetylaminobenzoic acid IX from imperfect hydrolysis) was removed by filtration. Meanwhile an ammoniacal cuprous sulfite solution was prepared as follows: 90 g. (0.36 mole) of copper sulfate crystals was dissolved in 380 ml. of water plus 210 ml. of concentrated ammonium hydroxide (sp. gr. 0.90), saturated with sulfur dioxide without cooling, then treated with 165 ml. more of ammonium hydroxide, and sulfur dioxide again passed until white crystals precipitated on cooling. After decanting most of the liquid this solid was then redissolved by addition of 255 ml. of water and 230 ml. of ammonium hydroxide. When both the diazotized solution and the ammoniacal cuprous sulfite solution were ready, the former was allowed to run slowly into the latter at 20°, mixing taking place beneath the surface and being promoted by rapid motor stirring. During this process a large amount of nitrogen gas was evolved and considerable frothing occurred. After completion of the reaction the solution was strongly acidified with 400 ml. of concentrated hydrochloric acid and a stream of air passed through for half an hour to oxidize any cuprous copper. In some runs a little solid ferric chloride also was added to facilitate this effect. On standing this strongly acid solution deposited a heavy precipitate of crude dichlorodiphenic acid which was filtered with suction, washed with cold water and dried. The melting point of the yellowish-gray crude was generally 293–298°. After two recrystallizations from hot 50% alcohol the melting point rose to 304–305° uncorr. dec., was not changed by a further recrystallization and the color was pure white. For crude products possessing high melting points and but little color, simple solution in sodium carbonate, filtration, and slow reacidification of the hot clear solution often sufficed to yield pure material. In other cases solution in boiling alcohol, refluxing with Norite decolorizing carbon, filtration, and reprecipitation by gradual dilution with hot water was employed.

Anal.[10]   Calcd. for $C_{14}H_8Cl_2O_4$: Cl, 22.80.   Found: Cl, 22.50, 22.66.   *Neut. Equiv.*   Calcd.: 155.5.   Found: 155.9, 156.3.

3,3'-Dichlorodiphenic Anhydride (II).—One gram of pure acid was dissolved in 2.5 ml. of boiling acetic anhydride and refluxed for fifteen minutes. The solution was then cooled and the pale yellow crystals filtered off, later being combined with a small amount of similar product from the evaporation of the filtrate. The quantitative yield of crude of m. p. 257–258° was dissolved in 60 ml. of hot benzene, filtered and reprecipitated by addition of three volumes of ligroin. The 0.45 g. of white anhydride so obtained possessed the same melting point as before. In larger runs the crude anhydride was filtered, washed with cold 1 N sodium bicarbonate for five minutes, then with water, and dried in the air. The yield was invariably almost quantitative and the melting point 257–258° uncorr.

Anal.   Calcd. for $C_{14}H_6Cl_2O_3$: Cl, 24.20.   Found: 24.30, 24.25.   Mol. wt. (Rast method in camphor).   Calcd.: 293.   Found: 294, 294, 286.

Attempts to determine the saponification equivalent of this anhydride were unsuccessful. On boiling with excess standard 0.1 N aqueous sodium hydroxide, solution was still incomplete after five hours. The residual solid melted 257–258° and was unchanged anhydride: acidification of the alkaline filtrate precipitated a little 3,3'-dichlorodiphenic acid, m. p. 299–300°, which failed to depress the melting point of an authentic sample, m. p. 304–305° dec. With stronger alkali, *e. g.*, 1 N sodium hydroxide, the anhydride did not dissolve on boiling for one hour.

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(10) Most of the Carius analyses reported in this paper were carried out in the usual way but on the semi-micro scale using samples of from 42–100 mg.

1,6-Dichlorofluorenone-5-carboxylic Acid (IV).—This is the keto acid corresponding to 3,3'-dichlorodiphenic acid. Five grams of the latter was dissolved in 12.5 ml. of pure concentrated sulfuric acid and the flask placed in an oil-bath previously brought to 125 ± 1°. Heating was continued at this temperature for one hour, the solution turning reddish-brown but no escape of gas being observed. The colored solution was then poured onto 200 g. of chopped ice, the precipitated pale yellow solid filtered with suction, washed with cold water until free from sulfate, and dried at 110°. The quantitative yield (4.75 g.) of crude keto acid thus obtained melted at 228–230°. This crude was then recrystallized three times: first from 60 ml. of boiling glacial acetic acid, second, by dissolving in 100 ml. boiling alcohol, filtering and precipitating with 300 ml. of hot water followed by cooling, and third, by repeating the second process using 80 ml. of alcohol and 150 ml. of water, three grams of pure keto acid being thus obtained. The deep yellow solid melted at 242.5° uncorr. In some later runs the washed crude was redissolved in 1 N sodium bicarbonate solution, filtered, reprecipitated with acid and then reprecipitated with water from its alcohol solution. Attempts to measure the neutralization equivalent in water invariably yielded low results, but by using alcohol as solvent the theoretical values were obtained readily by direct titration.

Anal. Calcd. for $C_{14}H_6Cl_2O_3$: Cl, 24.20. Found: Cl, 24.56, 24.46. *Neut. Equiv.* Calcd.: 293.0. Found: 293.6, 292.7.

1,6-Dichlorofluorenone-5-carboxylic Acid Chloride.—Six-tenths gram of the above keto acid (IV) was refluxed for two hours with 2.2 g. of pure thionyl chloride. The excess reagent was then distilled off at ordinary pressure, leaving 0.6 g. (95%) of crude acid chloride. This was twice precipitated from benzene by appropriate addition of ligroin. The pure product formed clear yellow crystals, m. p. 180–181° uncorr.

Anal. Calcd. for $C_{14}H_5Cl_3O_2$: Cl, 34.19. Found: Cl, 34.11, 34.10.

1,6-Dichlorofluorenone-5-carboxylic Acid Amide.—Eight-tenths gram of the above keto acid chloride was shaken with 10 ml. of concentrated ammonium hydroxide, then boiled for two minutes, cooled and the precipitated solid filtered and washed with water. This resultant crude weighed 0.7 g. (92%) and melted at 230–235°. After one recrystallization from 80% alcohol a yellow product remained from which hot benzene removed a deep yellow material melting at 150–160°. The residue after one recrystallization from 50% alcohol and a second from 90% alcohol yielded pale yellow crystals, m. p. 281° uncorr.

Anal. Calcd. for $C_{14}H_7Cl_2NO_2$: Cl, 24.29. Found: Cl, 23.97, 24.11.

The Preparation of the Dichlorofluorenones

1,8-Dichlorofluorenone (III).—Six and five-tenths grams of pure 3,3'-dichlorodiphenic anhydride (m. p. 257°) was placed in a small Pyrex flask and heated in a Wood's metal bath at 310° for forty-five minutes. Carbon dioxide was evolved as shown by tests of the effluent gas with barium hydroxide solution, and the heating was discontinued when no further gas was given off. A water-cooled tube condenser was then inserted into the neck of the flask, the temperature reduced to 180°, and the flask evacuated to a pressure of 2 mm. The product gradually sublimed onto the surface of the condenser, yielding 5.2 g. (97%) of brilliant yellow crystals, m. p. 240–242°. After recrystallization from 400 ml. of hot benzene, 4.0 g. of pure 1,8-dichlorofluorenone was obtained, m. p. 254° uncorr.

Anal. Calcd. for $C_{13}H_6Cl_2O$: Cl, 28.48. Found: Cl, 28.09, 28.30.

In another run the crude sublimate was washed with sodium bicarbonate solution before recrystallization but no acidic substance was found. From the benzene filtrate of the recrystallization mother liquor a very small amount of yellow substance of m. p.

218–219° was obtained but this depressed the melting point of authentic 1,6-dichlorofluorenone.

1,8-Dichlorofluorenone Oxime.—Two grams (0.008 mole) of pure 1,8-dichlorofluorenone and 1.1 g. (0.016 mole) of powdered hydroxylamine hydrochloride were suspended in 200 ml. of 95% alcohol and refluxed for eight hours. After cooling and filtering there remained a residue of 1.7 g. of unchanged 1,8-dichlorofluorenone, the substance being identified by its melting point (254°) and by its failure to depress the melting point when mixed with an authentic sample of the ketone. The alcohol filtrate was heated to boiling and diluted with 200 ml. of hot water. On cooling the clouded liquid, there crystallized out 0.4 g. (19%) of 1,8-dichlorofluorenone oxime. Reprecipitation from boiling alcohol raised the melting point of this pale yellow product to a maximum of 217° uncorr. dec.

Anal. Calcd. for $C_{13}H_7Cl_2NO$: Cl, 26.86. Found: Cl, 27.05, 26.92.

Increasing the time of reaction to twenty-six hours and the proportion of hydroxylamine hydrochloride to three moles gave but 25% yield of oxime, while with forty-three hours of refluxing and seven moles of hydroxylamine salt the yield fell off to 21.5%. Since the original ketone is difficultly soluble in alcohol, an attempt was made to effect oximation in boiling ethyl acetate but no action occurred in twenty-seven hours and the ketone was recovered unchanged. With seven moles of hydroxylamine hydrochloride for twelve hours a yield of 28% was obtained. It is very evident that as compared with the isomeric ketone described below, the 1,8-dichlorofluorenone oximates with great difficulty and this fact constitutes evidence for the position of its substituents.

1,6-Dichlorofluorenone (V).—This ketone was obtained by heating 1,6-dichlorofluorenone-5-carboxylic acid until all carbon dioxide was evolved and only ketone remained. In the earlier runs the acid was merely heated in a flask over a free flame until no more gas bubbled through the barium hydroxide trap. In later experiments the flask was heated in a Wood's metal bath at 350° for an hour. In order to ensure the absence of any unchanged keto acid, the crude product was treated with sodium bicarbonate solution but no acid was ever observed. After drying further purification was effected either by recrystallization from 70% alcohol, or from benzene, or by reprecipitation with ligroin from hot benzene solution. More generally, however, the crude was sublimed directly onto the surface of a water-cooled condenser hung in the neck of the original reaction flask, the operation being conducted under reduced pressure, *e. g.*, 2–15 mm. The yield of pure ketone varied but the largest run (on 8.6 g. of keto acid) gave 4.0 g. (55%) after sublimation. The pure medium yellow ketone melts at 218–219° uncorr.

Anal. Calcd. for $C_{13}H_6Cl_2O$: Cl, 28.48. Found: Cl, 28.19, 28.14.

1,6-Dichlorofluorenone Oxime.—Four grams (0.016 mole) of 1,6-dichlorofluorenone was suspended in 300 ml. of alcohol and refluxed for eleven hours with 2.2 g. (0.032 mole) of hydroxylamine hydrochloride. The solid dissolved at the end of thirty minutes. To the clear hot solution 700 ml. of boiling water was added and the mixture cooled. The yield of crude oxime was 3.5 g. (83%), m. p. 225° uncorr. dec. After two recrystallizations from alcohol the melting point rose to 230° uncorr. dec. and the oxime was almost white.

Anal. Calcd. for $C_{13}H_7Cl_2NO$: Cl, 26.86. Found: Cl, 26.75, 26.91.

The Action of Heat upon 3,3'-Dichlorodiphenic Acid.—Several different materials have been isolated from the crude product resulting when 3,3'-dichlorodiphenic acid is heated above its melting point until carbon dioxide escapes freely. The end-product of the decarboxylation is a mixture of 1,8- and 1,6-dichlorofluorenone in 60–75% of the theoretical yield for ketone. In one experiment when five grams of acid was heated for twenty minutes at a temperature of 360 ± 1°, the weight of carbon dioxide given off

exactly corresponded to one mole; and when the residue was sublimed at 190–250° under a pressure of 3 mm. the yield of mixed ketones (insoluble in sodium bicarbonate solution) was 75%. This mixture melted 218–220° and after two recrystallizations from 200 ml. and 150 ml. of benzene, respectively, yielded 1.2 g. (30%) of 1,8-dichlorofluorenone. The melting point of this product was 253° and it did not depress the melting point of an authentic sample. The mother liquor from the first recrystallization was evaporated and the 1.3 g. of crude (m. p. 195–198°) was boiled for four hours with an alcoholic solution of hydroxylamine hydrochloride. On working up the reaction product 1,6-dichlorofluorenone oxime was obtained; its identity was certified by its failure to depress the melting point of an authentic sample and by the fact that it did markedly depress the melting point of a sample of the 1,8-dichlorofluorenone oxime.

In addition to the mixture of dichlorofluorenones which constitutes the largest portion of the product obtained by pyrolysis of the diphenic acid, certain other products were noted in some experiments which had been carried out at lower temperatures. Thus in a run in which 5.0 g. of 3,3′-dichlorodiphenic acid was heated at 320° for fifteen minutes and then sublimed at 180–250° at 2 mm., the sublimate (4.0 g.) was partially soluble in sodium bicarbonate solution. On filtration from the residue and acidification there was precipitated 1.5 g. of light yellow solid. After two recrystallizations from alcohol there was isolated 0.8 g. of 1,6-dichlorofluorenone-5-carboxylic acid, m. p. 241°. The identity of this substance was assured by its failure to depress the melting point when mixed with an authentic sample. The residual acid material from the alcohol mother liquors was proved to be unchanged 3,3′-dichlorodiphenic acid in a similar fashion.

In still another experiment similarly conducted but carried out merely by heating over a free flame without temperature measurement, the sublimed crude again contained in addition to the usual mixture of neutral ketones a small amount of acidic substance which dissolved out with sodium bicarbonate solution. Upon purification of the reprecipitated material from dilute alcohol there was obtained pure white needles of 3,3′-dichlorobiphenyl-2-carboxylic acid, m. p. 152.5° uncorr. This previously unreported acid was identified by its analysis and by its neutralization equivalent. The weight obtained corresponded to 14% of the theoretical on the assumption that it was the only product.

Anal. Calcd. for $C_{13}H_8Cl_2O_2$: Cl, 26.55. Found: Cl, 26.48, 26.40. *Neut. Equiv.* Calcd.: 267.0. Found: 267.4.

3,6-Dichlorofluorenone.—When 5,5′-dichlorodiphenic anhydride was heated at 310° and atmospheric pressure for forty-five minutes, no gas was evolved but the anhydride sublimed without change. On raising the temperature to 400° for twenty-five minutes, however, carbon dioxide escaped and a ketone remained. Thus when 1.17 g. of 5,5′-dichlorodiphenic anhydride (m. p. 201°) was heated at 400° for twenty-five minutes, then sublimed at 250° under a pressure of 2 mm., 0.9 g. of bright yellow sublimate (m. p. 260–270°) was obtained. This yielded a small amount of acid to sodium bicarbonate solution, but left an insoluble residue which on recrystallization from hot benzene gave 0.6 g. (66%) of bright yellow glistening needles of 3,6-dichlorofluorenone, m. p. 301° uncorr.

Anal. Calcd. for $C_{13}H_6Cl_2O$: Cl, 28.48. Found: Cl, 28.80, 28.65.

3,6-Dichlorofluorenone Oxime.—Forty-five one-hundredths gram (0.0018 mole) of 3,6-dichlorofluorenone was suspended in 30 ml. of alcohol and refluxed for fifteen minutes with 0.3 g. (0.0043 mole) of hydroxylamine hydrochloride. The clear solution was then diluted with three volumes of water, cooled, and the precipitate filtered. The yield (0.48 g.) of crude oxime (m. p. 237° dec.) was raised to a constant maximum of 243.5° uncorr. dec. after one recrystallization from alcohol.

Anal. Calcd. for $C_{13}H_7Cl_2NO$: Cl, 26.86. Found: Cl, 26.69, 26.81.

Summary

1. 3,3'-Dichlorodiphenic acid (believed to be the first 3,3'-disubstituted diphenic acid) has been prepared by a short synthesis from commercial intermediates.

2. On heating at 360° this acid loses one mole of carbon dioxide and yields approximately equal amounts of 1,8- and 1,6-dichlorofluorenones.

3. However, on heating 3,3'-dichlorodiphenic *anhydride* at 310° a quantitative yield of 1,8-dichlorofluorenone is obtained; on heating 1,6-dichlorofluorenone-5-carboxylic acid (from the action of concentrated sulfuric acid at 125° upon 3,3'-dichlorodiphenic acid) at 350° there is obtained less smoothly only 1,6-dichlorofluorenone.

4. 3,6-Dichlorofluorenone is obtained by heating 5,5'-dichlorodiphenic anhydride at 400°.

5. In the course of this work the following new compounds have been prepared and characterized: 3,3'-dichlorodiphenic acid and its anhydride; 1,6-dichlorofluorenone-5-carboxylic acid and its acid chloride and amide; 3,3'-dichlorobiphenyl-2-carboxylic acid; 1,8-dichlorofluorenone and its oxime; 1,6-dichlorofluorenone and its oxime; 3,6-dichlorofluorenone and its oxime.

CAMBRIDGE, MASSACHUSETTS

The Action of Phosphorus Pentachloride on 1,3-Dioxoindane[1]

BY W. H. HUNTER AND ROSCOE E. JACKMAN

This paper describes the separation and characterization of 1,1,3-trichloroindene, and the previously unreported 1,1,3,3-tetrachloroindane, and 1,1-dichloro-3-oxoindane isolated from the products of the reaction between phosphorus pentachloride and 1,3-dioxoindane. 1,1,3,3-Tetrachloroindane (II) results in moderate yields from the normal interaction of the 1,3 diketone (I) with phosphorus pentachloride.[2] In addition, 1,1,3-trichloroindene (III) is formed in only slightly smaller amounts, together with a small proportion of 1,1-dichloro-3-oxoindane (IV). At least two other chlorine containing condensation products and a lachrymatory oil also result, but these were not identified.

The 1,1,3-trichloroindene (III) may result from either (a) the action of phosphorus pentachloride on the enol form of (I) or (IV) or (b) by the loss of hydrogen chloride from (II). The formation of 1,1-dichloro-3-oxoindane

(1) This paper was prepared from a portion of the thesis of Roscoe E. Jackman presented to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy, July, 1929. The manuscript was written by the junior author after the death of Dr. Hunter in 1931.—L. I. SMITH.

(2) Wislicenus, *Ann.*, **252**, 72 (1889).