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OXIDATIVE CYCLISATION OF DIPHENYL-2 CARBOXYLIC ACID

G. W. Kenner, M. A. Murray, and C. M. B. Tylor
University Chemical Laboratory, Cambridge

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Abstract—The dehydrogenation of diphenyl-2 carboxylic acid to the lactone (II; R = H) has been accomplished by oxidation with chromic acid or hydrogen peroxide and its derivatives, by decomposition of the diacyl peroxide derived from this acid, and by electrolysis of its sodium salts. From the effects of several 3′-substituents (R = OMe, $NHCOCH_3$, CN, NO_2) on these reactions it has been concluded that the oxidations with chromic acid and hydrogen peroxide etc. proceed through attachment of the oxidising agent to the carboxylic group and subsequent cationoid substitution in the neighbouring ring. The free radicals (III) are believed to be intermediates in the other two cyclisations.

INTRODUCTION

During another investigation[1] 2-hydroxymethyldiphenyl was crystallised although it had previously only been described as an oil. In order to confirm the structure of these crystals, they were oxidised energetically with chromic acid in acetic acid. However, the product was not diphenyl-2 carboxylic acid but instead the lactone of 2′-hydroxydiphenyl-2 carboxylic acid, 3:4-benzcoumarin (II; R = H). It was then shown that diphenyl-2 carboxylic acid could be dehydrogenated by chromic acid giving more than 50% of this lactone. Being interested in the mechanism of the dehydrogenation, we have studied it qualitatively following two paths of investigation. Firstly, the dehydrogenation has been accomplished in other ways. The carboxylic acid has been treated with hydrogen peroxide under various conditions ("peracid method"). The diacyl peroxide has been prepared from the carboxylic acid and been decomposed by heat. The sodium salt of the carboxylic acid has been electrolysed. Secondly, the behaviour of a series of 3:-substituted diphenyl-2 carboxylic acids (I; R = NO_2, CN, NHAc, OMe, X = H) has been examined; the preparation of these materials and the characterisation of the lactones derived from them are discussed in the last paragraph of this introduction.

Some general comments may be useful before the detailed presentation of our results. Two possible trivial origins of the lactone are obvious. Its precursor might be fluorenone formed by the usual condensation, and indeed the lactone has been obtained from fluorenone by means of Caro's acid.[2] But chromic acid, under our conditions, does not effect this oxidation and it is unlikely that fluorenone would be produced by the other reagents which would probably be more capable of oxidising it. An additional argument against this mechanism is that the lactones produced from substituted acids always have the structure shown in the above diagram, while the isomer (V) should sometimes be produced from a fluorenone.[3] The second possibility is that oxidation at the 2′-position produces 2′-hydroxydiphenyl-2 carboxylic acid,

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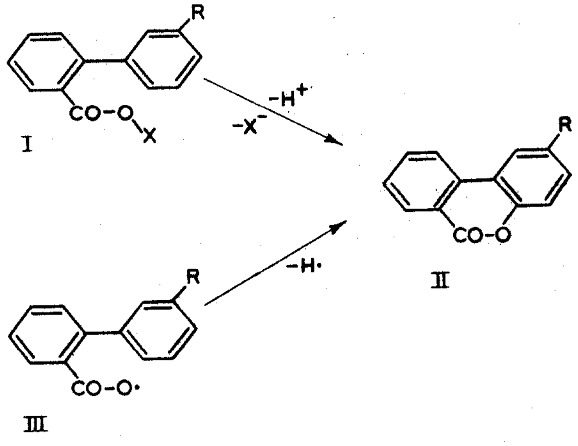
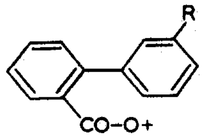
[1] M. A. Murray Ph.D. Thesis, Cambridge (1948).

[2] G. Wittig and G. Pieper *Ber. Dtsch. Chem. Ges.* 73, 295 (1940).

[3] W. von E. Doering and L. Speers *J. Amer. Chem. Soc.* 72, 5515 (1950).

which then condenses to the lactone. In the cases of the peracid and the electrolytic methods of oxidation there is good evidence to the contrary, and this explanation is inherently improbable for the electrolytic oxidation and peroxide decomposition. The chromic acid oxidation may proceed in this way and this could probably be checked by experiments with ^{18}O, but for the present we prefer the more economical hypothesis that its mechanism is analogous to that of the peracid oxidation. We believe that in these oxidations the major, if not the entire, source of the lactone is an activated derivative (I) generated by reaction between the carboxylic acid and the oxidising agent; the cyclisation then follows the usual course of cationoid aromatic substitution with expulsion of a proton from the 2′-position. On the other hand electrolysis of the carboxylic salt or decomposition of the peroxide should produce the radical (III) from which a hydrogen atom could be displaced. These two modes of cyclisation may be regarded as variants of a fundamental process, favoured by oxidising agents of either the two-electron-transfer or one-electron-transfer types.[4] It must be emphasised that the simultaneous operation of several mechanisms, including under some conditions the two discussed at the beginning of this paragraph, cannot be excluded by qualitative experiments such as described here. At this stage it is convenient to think in terms of a single mechanism operating at one time.

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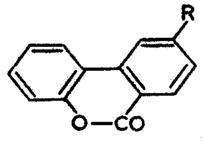
V

The cleanest way of dehydrogenating diphenyl-2 carboxylic acid is to treat it with another carboxylic acid and hydrogen peroxide ("peracid method"). Indeed when account is taken of the recovered starting material the yield may come close to being quantitative. This is strong evidence against the intermediacy of 2′-hydroxydiphenyl-2 carboxylic acid, since some of the 4′-hydroxy isomer should be generated simultaneously and degraded to phthalic acid. It is nevertheless difficult to achieve a very

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[4] R. E. Kirk and A. W. Browne *J. Amer. Chem. Soc.* **50**, 337 (1928).

high conversion of the acid into lactone because the cyclisation is slow and there is gradual destruction of the product. Oxidation in cold trifluoroacetic acid gave 63 % of lactone and 15 % of the starting material was recovered. This reaction was much faster than that in acetic acid and the rate in trichloroacetic acid was intermediate. Hydrogen peroxide gave a slow reaction in water but no lactone was produced in *tert*-butyl alcohol. Obviously cyclisation is promoted by acidic conditions and therefore it is probably an ionic reaction. The fact that the same lactone is produced from diphenic acid with hydrogen peroxide in acetic acid* agrees with this idea because there is a clear analogy with decarboxylation by means of acids or halogens; in each instance carbon dioxide and a proton are expelled by a cationoid reagent. Stronger evidence has been provided by oxidation under standard conditions of diphenyl-2 carboxylic acid and four 3′-substituted derivatives. The yields of lactones with the various substituents (total recovery of material in parenthesis) were: OCH_3 30(71), $NHCOCH_3$ 20(82), H 16(95), CN 7(95), NO_2 2(97). In the first two instances loss of material through destructive oxidation was also apparent in darkening of the solutions; a control experiment, with diphenyl itself showed that the benzene rings were attacked. It might be argued that the effect of a substituent is merely to encourage or hinder hydroxylation of the benzene ring in the position para to itself and that the lactone is then formed from the hydroxy-acid, but the recovery was much better in oxidations of the unsubstituted acid on a larger scale and therefore, as already mentioned, this explanation is unlikely. The probable cause of the graded series of yields is the normal effect of a substituent on cationoid substitution. A consequent deduction is that the cationoid reagent is *not* the particle (IV), although such cations have been postulated as intermediates in oxidations.[7–11] Presumably this cation would be a very energetic molecular species generated slowly from the diphenyl-2 carboxylic acid, and the neighbouring benzene ring would be substituted very efficiently. In this event the substituent would not have much influence on the rate-determining step. The results accord better with the postulate of rate-determining cyclisation of an active species generated by a series of pre-equilibria; this might well be the conjugate acid (I; $X = \overset{+}{O}H_2$) of the peracid (I; $X = OH$).

Chromic acid in hot acetic acid yielded almost 60 % of the lactone from diphenyl-2 carboxylic acid under our best conditions. With the series of 3′-substituted acids under standardised, slightly milder conditions the yields of lactones and, in parenthesis, the total recoveries of material were: OCH_3 15(27), $NHCOCH_3$ 1(21), H 20(73), CN 8(82), NO_2 4(88). During the reactions the first two solutions turned dark green while the others remained orange. Under still milder conditions 40 % of methoxy-lactone and 20 % of the acetamide-lactone could be obtained. The general trend of

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* It is incidentally interesting that the lactone is also a by-product in the oxidation of phenanthraquinone to diphenic acid with hydrogen peroxide in acetic acid because the corresponding lactones have already been reported as by-products in the oxidations of 3:6-dimethoxyphenanthraquinone[5] and retenequinone.[6] The simple explanation that the lactones are formed from the diphenic acids seems probable but it was earlier rejected for the first example since attempts to oxidise the diphenic acid had failed.[5]

[5] L. F. Fieser *J. Amer. Chem. Soc.* **51,** 2471 (1929).

[6] D. E. Adelson, T. Hasselstrom, and M. T. Bogert *J. Amer. Chem. Soc.* **58,** 871 (1936).

[7] J. E. Leffler *Chem. Rev.* **45,** 385 (1949).

[8] J. E. Leffler *J. Amer. Chem. Soc.* **72,** 67 (1950). cf. D. B. Denney *J. Amer. Chem. Soc.* **78,** 590 (1956).

[9] W. A. Mosher and C. L. Kehr *J. Amer. Chem. Soc.* **75,** 3172 (1953).

[10] D. Bryce-Smith *Nature, Lond.* **172,** 863 (1953).

[11] L. S. Levitt *J. Org. Chem.* **20,** 1297 (1955).

these results is similar to that in the peracid experiments, and we conclude that here again the cyclisation is essentially a cationoid substitution in the aromatic ring. Presumably the reactive intermediate is a mixed anhydride of the carboxylic acid and chromic acid, and the reaction is analogous to the well-known oxidation of alcohols through removal of proton from a chromate ester.[12]

The crystalline diacyl peroxide was prepared from diphenyl-2 carboxylic acid. On heating in either acetic acid or carbon tetrachloride at 80° during one hour it yielded 80% and 60% respectively of the lactone.* Under the same conditions 50% and 60% respectively of the nitro-lactone was obtained from the corresponding diacyl peroxide. Some 40% of the cyano-lactone was obtained from decomposition of the crude peroxide in carbon tetrachloride. These few results contrast with those from the peracid method and they suggest the operation of a free-radical mechanism.

As free radicals are usually postulated as intermediates in Kolbe electrolyses, the electrolysis of sodium diphenyl-2 carboxylate was examined. In fact the lactone was formed, and the conversion could be raised to 33% by continual extraction of the product with benzene.† In presence of caustic soda the process was slower and less efficient, but a moderate yield of the lactone was still extracted by the benzene. As sodium 2′-hydroxydiphenyl-2 carboxylate does not, of course, lactonise, the extracted lactone cannot have been produced by hydroxylation of the benzene ring and subsequent lactonisation; it must have been an oxidation product. Comparison of the behaviours of the 3′-substituted compounds was less informative about electrolysis than about the peracid and chromic acid oxidations. The material accounted for as either lactone or starting material amounted to no more than 60% of the theoretical and the experiment with the 3′-acetamido compound was unsuccessful. In this instance the principal reaction appeared to be destructive oxidation by anodic oxygen, and it was shown that *m*-acetamidobenzoic acid suffered the same fate under conditions which scarcely affected benzoic acid itself. The yield of nitro-lactone was very small but this could be explained by its insolubility in benzene and its great susceptibility to alkaline hydrolysis. The yields of methoxy- and cyano-lactones were similar to that of unsubstituted lactone under comparable conditions. While great weight cannot be attached to this evidence, it does conform with the postulate of free-radical substitution and contrasts suitably with the variation in yields from the peracid and chromic acid oxidations of these three diphenyl-2 carboxylic acids.

Evidently the dehydrogenation of diphenyl-2 carboxylic acids, which came to our notice by chance, is quite a common phenomenon occurring by at any rate two types of mechanism. The reaction is doubtless favoured by being a cyclisation, and consequently the analogies are not numerous. As already mentioned, comparable substitution in the napthhalene nucleus during decomposition of peroxides[14] and during electrolysis[15] has been observed. The closest analogy to the peracid and chromic-acid

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* Phenylation of aromatic hydrocarbons through the decomposition in them of dibenzoyl peroxide has been fully studied.[13] Benzoyloxylation may be an important, or even dominating, competitor, for example with naphthalene derivatives.[14]

† Likewise α-naphthyl acetate is a product of the electrolysis of sodium acetate in presence of naphthalene.[15]

[12] F. Holloway, M. Cohen, and F. H. Westheimer *J. Amer. Chem. Soc.* 73, 65 (1951); and literature cited therein.

[13] D. H. Hey *J. Chem. Soc.* 1974 (1952).

[14] R. L. Dannley and M. Gippin *J. Amer. Chem. Soc.* 74, 332 (1952).

[15] R. P. Linstead, B. R. Shephard, and B. C. L. Weedon *J. Chem. Soc.* 3624 (1952).

cyclisations is apparently the reaction between silver bromide dibenzoate and aromatic compounds;[16] benzoic esters are among the products and this mode of reaction has been classified as an electrophilic substitution, largely on account of the orientation phenomena for example the formation of *m*-nitrophenyl benzoate from nitrobenzene. Aryl benzoates are also produced by the action of halogens on silver benzoate in presence of aromatic compounds.[17, 18] It has incidentally been reported that the action of bromine on silver diphenate does not give 2:2′-dibromodiphenyl.[19] Another set of reactions, which may be connected with our chromic acid oxidations although less directly, is that leading to γ-lactones from branched-chain aliphatic acids through the action of permanganate or manganate.[20] As the reaction conditions are alkaline, the actual product is the γ-hydroxy acid, but it is likely that the lactone is the primary product in at least some instances. It has been shown[21] that there is probably more than one mechanism operating and it is unlikely that cationoid substitution, such as we postulate to explain our results, would occur at an aliphatic carbon atom. Nevertheless lactonisation in the aliphatic series may be connected with that in the aromatic to the extent that the oxidising agent is attached to the carboxyl group instead of attacking the hydrogen atom on the tertiary carbon atom, as previously suggested.[21]

The main source of our starting materials, apart from diphenyl-2 carboxylic acid itself, was the Gomberg reaction between *m*-nitrobenzene diazoacetate and methyl benzoate, which gave a mixture, separable by chromatography, of the methyl 3′-nitrodiphenyl-2 and -4 carboxylates. The preparation of the other 3′-substituted diphenyl-2 carboxylic acids from the nitro compound followed standard methods. An attempted unambiguous synthesis of this nitro compound was based on the reaction between *m*-nitrobenzylidene malonic ester and butadiene;[22] it failed at the final step of dehydrogenation.

During the foregoing discussion it has been assumed throughout that structure (II) represents all the lactones, although in principle oxidation could also have occurred *ortho* to the substituent R. In fact each oxidation seemed to produce an overwhelming proportion of one lactone and these products, with the exception of the cyano-lactone, could be correlated with the phenylazo-lactone (II; $R = N_2C_6H_5$). The structure of this substance rests on its preparation by azocoupling of the disodium salt of 2′-hydroxydiphenyl-2 carboxylic acid and on its behaviour as a normal lactone. 2′-Hydroxy-3′-phenylazodiphenyl-2 carboxylic acid should be hindered from lactonisation by hydrogen-bonding between the hydroxy and azo groups, and indeed this was found to be true of the 3′:5′-bis compound formed by coupling with excess diazonium salt.

EXPERIMENTAL*

Gomberg Reaction between m-Nitrobenzene Diazoacetate and Methyl Benzoate

A solution of *m*-nitroaniline (50 g) in concentrated hydrochloric acid (140 c.c.) and water (75 c.c.) was cooled in ice and diazotised with sodium nitrite (30 g) in water

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* All m.p.s. are corrected.

[16] D. Bryce-Smith and P. Clarke *J. Chem. Soc.* 2264 (1956).

[17] L. Birkenbach and K. Meisenheimer *Ber.* **69**, 723 (1936).

[18] C. Prévost and J. Wiemann *Compt. Rend.* **204**, 989 (1937).

[19] F. Bell and I. F. B. Smyth *J. Chem. Soc.* 2372 (1949).

[20] J. Kenyon and M. C. R. Symons *J. Chem. Soc.* 2129 (1953); and literature cited therein.

[21] J. Kenyon and M. C. R. Symons *J. Chem. Soc.* 3580 (1953).

[22] K. Alder and H. F. Rickert *Ber. Dtsch. Chem. Ges.* **72**, 1983 (1939).

(60 c.c.). The diazonium solution was stirred with methyl benzoate (1 l.) at 0° while a solution of hydrated sodium acetate (140 g) in water (350 c.c.) was added. Stirring was continued for 2 days (at room temperature after the first 3 hr). The organic layer was then evaporated, finally at 100°/1 mm, to a brown tar (80 g) ,which was taken up in dry benzene and percolated through a column of active alumina (1 kg). The column was washed with benzene. Some methyl benzoate, which had remained in the tar, was soon followed in the eluate by *methyl 3′-nitrodiphenyl-2 carboxylate* (14 g, 15%), which had m.p. 94–95° after recrystallisation from methanol (Found: C, 65·8; H, 4·2; N, 5·6. $C_{14}H_{11}O_4N$ requires C, 65·4; H, 4·3; N, 5·4%). Later fractions contained *methyl 3′-nitrodiphenyl-4 carboxylate* (12 g, 13%), which had m.p. 147–148° after recrystallisation from methanol (Found: C, 65·2; H, 4·3; N, 5·5%).

Alkaline hydrolysis of the latter ester yielded the relatively insoluble *3′-nitrodiphenyl-4 carboxylic acid*, having m.p. 311–313° (decomp.) after recrystallisation from ethanol or acetic acid (Found: C, 63·8; H, 3·6; N, 5·6. $C_{13}H_9O_4N$ requires C, 64·2; H, 3·7; N, 5·8%). For structural determination this nitro-acid was reduced by adding its solution in hot dilute ammonia to warm ammoniacal ferrous sulphate solution. The hydrochloride of the amino-acid crystallised in needles when the filtered reduction solution was acidified with concentrated hydrochloric acid and cooled. One portion of the hydrochloride was oxidised with potassium permanganate in boiling sodium carbonate solution during 40 minutes; dimethyl terephthalate, m.p. 138–140°, was obtained by esterification of the acidic product with methanol and sulphuric acid. Another portion of the amino-acid hydrochloride was suspended in dilute hydrochloric acid and diazotised. The diazonium solution was kept overnight with excess hypophosphorous acid. The insoluble product was purified through recrystallisation of its sodium salt from water; it was diphenyl-4 carboxylic acid, m.p. 224–226°.

Derivatives of Diphenyl-2 Carboxylic Acid

Hydrolysis of the methyl ester with boiling 10% sodium hydroxide solution afforded *3′nitrodiphenyl-2 carboxylic acid*, m.p. 155–157°, recrystallised from aqueous acetic acid (Found: C, 64·1; H, 3·4; N, 5·7. $C_{13}H_9O_4N$ requires C, 64·2; H, 3·7; N, 5·8%). This acid had partition coefficient 1·50 between ethyl acetate and potassium phosphate solution (0·7M K_2HPO_4, 0·3M KH_2PO_4) while benzoic acid had coefficient 0·25. Consequently counter-current distribution in this system after saponification of the crude ester was an alternative method for isolating the nitro-acid from the Gomberg reaction.

Hydrogenation of the nitro-acid in ethanol with Adams platinum catalyst at room temperature and pressure furnished 3′-aminodiphenyl-2 carboxylic acid, which crystallised from alcohol and had m.p. 174–176°. The amino-acid was used directly for further experiments. Acetylation with a hot mixture of equal parts of acetic anhydride and acetic acid yielded *3′-acetamidodiphenyl-2 carboxylic acid*, m.p. 185–187°, recrystallised from water (Found: C, 70·5; H, 5·2; N, 5·7. $C_{15}H_{13}O_3N$ requires C, 70·6; H, 5·1; N, 5·5%). The amino-acid was diazotised in dilute mineral acid and then treated in three ways. Reduction for 20 hours at 5° with 10 moles of hypophosphorous acid gave diphenyl-2 carboxylic acid, purified by dissolution in alkali and reprecipitation; identification of this acid by m.p. 109–111°, mixed m.p., and conversion by concentrated sulphuric acid into fluorenone proved the orientation of substituents in the series of derivatives. Sandmeyer treatment of the diazonium salt with cuprous cyanide gave *3′-cyanodiphenyl-2 carboxylic acid*, m.p. 156–157° after recrystallisation from water (Found: C, 75·6; H, 4·3; N, 6·4. $C_{14}H_9O_2N$ requires C, 75·3; H, 4·1; N, 6·3%). When the diazonium salt was kept at 60° for 15 minutes, a tarry solid was precipitated. This solid was dissolved in sodium hydroxide solution and treated with dimethyl sulphate at room temperature. Isolation of the acidic product and its recrystallisation from water gave *3′-methoxydiphenyl-2 carboxylic acid*, m.p. 88–90° (Found: C, 73·9; H, 5·6. $C_{14}H_{12}O_3$ requires C, 73·7; H, 5·3%).

Oxidation of Diphenyl-2 Carboxylic Acid and its 3′ Derivatives

(*a*) *Isolation of the products*

The lactone and the un-oxidised acid were brought into either benzene or ether and then separated by extraction with sodium carbonate solution. The acid was recovered by acidification and the usual extraction with ether or benzene. The lactone left by evaporation of the original solvent was always dissolved in warm sodium hydroxide solution, which was filtered before being acidified. The lactone was then either collected directly or extracted into ether and washed with sodium carbonate solution. The substituted lactones produced by the various oxidations were identified by mixed m.p.s. with the reference samples prepared as described below.

(*b*) *Oxidations with hydrogen peroxide and its derivatives*

(*i*) *In acetic acid.* A series of comparative experiments, with the results mentioned in the Introduction, was conducted as follows. The acids (0·25 g) were dissolved in acetic acid (20 c.c.) which was kept at 90° during 5 hr. At the beginning of each hour 1 c.c. of 30% hydrogen peroxide was added. The reaction mixtures were concentrated under reduced pressure before isolation of the products. Diphenyl-2 carboxylic acid itself gave 16% of the lactone and 79% was recovered under these conditions. On a preparative scale more material was accounted for. For example, when 5·45 g of acid was oxidised similarly with only 30 c.c. of hydrogen peroxide the yield of lactone, m.p. 86–88°, was 14% and the recovery of acid, m.p. 109–110°, was 86%. Under similar conditions, diphenic acid gave 3% of the same lactone while 95% was recovered, and 1% of lactone and 77% of diphenic acid were obtained from phenanthraquinone.

(*ii*) *In trifluoroacetic acid.* Hydrogen peroxide (0·18 c.c. of 86%) was added to a solution of diphenyl-2 carboxylic acid (1·06 g) in trifluoroacetic acid (5 c.c.), and the mixture was kept at room temperature overnight. The yield of lactone was 0·67 g (63%), while 0·16 g (15%) of the acid was recovered. Lower yields were obtained under a variety of conditions. Although the lactone was not rapidly destroyed at room temperature, it was preferable to avoid a large excess of hydrogen peroxide. When 30% hydrogen peroxide was used the reaction was slower. Experiments in which the acid was dissolved in methylene chloride and treated with trifluoroacetic anhydride and 86% hydrogen peroxide, were much less successful and dark coloured by-products were formed.

(*iii*) *In trichloroacetic acid.* Hydrogen peroxide (2·5 c.c. of 30%) was added to a solution of diphenyl-2 carboxylic acid (0·15 g) in trichloroacetic acid (10 c.c.). When the solution had been heated at 95° for 2 hr, 33% of lactone could be isolated.

(*iv*) *In water.* A suspension of diphenyl-2 carboxylic acid (0·15 g) in hydrogen peroxide (10 c.c. of 30%) was kept at 95° for 2 hr. The yield of lactone was 5% and 90% of the acid was recovered.

(*v*) *In* tert-*butanol.* Diphenyl-2 carboxylic acid was 92% recovered after its solution in *tert*-butanol had been boiled for 5 hr with 30% hydrogen peroxide, and no lactone could be detected.

(*c*) *Oxidation with chromic acid*

A series of comparative experiments, with the results mentioned in the Introduction, was conducted as follows. Chromic anhydride (0·3 g) was dissolved in water (1 c.c.) and added to a solution of the acid (0·1 g) in acetic acid (2 c.c.). The mixture was kept at 100° during 30 min and then it was poured into water. A better yield (50%) of the unsubstituted lactone was obtained by heating together at 100° for 45 min solutions of diphenyl-2 carboxylic acid (10 g) in acetic acid (150 c.c.) and of chromic anhydride (40 g) in water (75 c.c.); 20% of the acid was recovered.

(*d*) *Anodic oxidations*

These were carried out in a cylindrical vessel (capacity 150 c.c.), fitted with a pair of smooth platinum electrodes (surface area 0·8 cm^2; 0·2 cm apart) surrounded by a glass cooling coil. The solution was continually stirred and extracted with benzene supplied from a boiler and drawn off through a side-arm into the boiler. For comparative experiments the acids (0·3 g) were dissolved in water (100 c.c.) containing sufficient sodium carbonate for the cell to conduct 0·6 A with 60 V applied. Electrolysis was continued for 1 hr at 18°, the current being maintained at 0·6 A by steady reduction of the voltage to about 35 V. The lactone was isolated from the benzene extract while the aqueous solution was worked up for unchanged acid. The yields of lactones and acids from the 3′-substituted-diphenyl-2 carboxylic acids were: OCH_3 21 and 37, $NHCOCH_3$ 0 and 16, H 19 and 35, CN 15 and 46, NO_2 2 and 44. When *m*-acetamidobenzoic acid and benzoic acid were electrolysed under similar conditions the recoveries of them were 25% and 95% respectively. When diphenyl-2 carboxylic acid (0·645 g) was dissolved in 0·5 N sodium hydroxide only 5 V were applied in order to pass 0·6 A. During 2 hr 0·014 g (2·2%) of lactone was extracted by the benzene while 0·570 g (88·5%) of the acid was recovered. Electrolysis of a similar solution of the lactone itself in sodium hydroxide yielded no lactone in the benzene extract although 30% was recovered on acidification of the aqueous solution. Electrolysis of diphenyl-2 carboxylic acid in sodium carbonate on this scale during 2 hr gave 33% of lactone and 12% of the acid was recovered.

Decomposition of the Diacyl Peroxides

(*a*) *Diphenyl-*2 *carboxylic acid* (5 g) and thionyl chloride (7 c.c.) were warmed for 1 hour. The brown residue from evaporation of the thionyl chloride was dissolved in *cyclo*hexane (20 c.c.) and added to a solution of sodium peroxide (1·2 g) in water (20 c.c.) at 0°. The mixture was stirred for 30 min and then kept overnight. Colourless *bis*(*diphenyl-2-carbonyl*) *peroxide* separated and was recrystallised from aqueous acetone in plates, m.p. 107–108° (slight explosion) (Found: C, 79·4; H, 5·0. $C_{26}H_{18}O_4$ requires C, 79·2; H, 4·6%). A solution of the peroxide 0·34 g) in acetic acid (10 c.c.) was kept at 80° during 1 hr and then evaporated. The residue yielded 0·14 g of lactone and 0·09 g of acid. A solution of the peroxide (0·45 g) in carbon tetrachloride (20 c.c.) was boiled for 1 hr and yielded 0·11 g of lactone and 0·07 g of acid.

(*b*) 3′-*Nitrodiphenyl-*2 *carboxylic acid* was likewise converted into the *peroxide*, which was recrystallised from aqueous acetone in needles, m.p. 123° (explosion) (Found N, 5·4. $C_{26}H_{16}O_8N_2$ requires N, 5·8%). Decomposition of this peroxide (0·29 g) in acetic acid gave 0·07 g of lactone, while decomposition of it (0·5 g) in carbon tetrachloride gave 0·15 g of lactone.

(*c*) 3′-*Cyanodiphenyl*-2 *carboxylic acid* was treated with thionyl chloride and then sodium peroxide in the same fashion. A small amount of peroxide, m.p. 126° (explosion), separated but the majority, m.p. 118–120°, was recovered by evaporation of the solvent (toluene instead of *cyclo*hexane). Decomposition of the crude peroxide (0·5 g) in carbon tetrachloride furnished 0·1 g of lactone.

Lactone of 2′-Hydroxy-5′-phenylazodiphenyl-2 Carboxylic Acid

Diazotised aniline (2·3 g) in dilute hydrochloric acid was added slowly with stirring to an ice-cooled solution of the lactone of 2′-hydroxydiphenyl-2 carboxylic acid (4·5 g) and sodium hydroxide (4·6 g) in water (25 c.c.). Acidification of the dark red solution yielded the *phenylazo-lactone* (6 g), which was recrystallised from ethanol in long orange needles, m.p. 174–175° (Found: C, 75·8; H, 4·0; N, 9·4. $C_{19}H_{12}O_2N_2$ requires C, 76·0; H, 4·0; N, 9·3%). This substance was soluble in boiling sodium hydroxide solution, but it was insoluble in sodium carbonate solution.

Coupling with three times as much diazonium salt gave a brown solid, which was soluble in both ether and sodium carbonate solution. Presumably this was 2′-hydroxy-3′:5′-bis(phenylazo)-diphenyl-2 carboxylic acid. As it could not be crystallised, it was reduced with sodium dithionite to an amino-compound, m.p. 235–240°, which yielded, with hot acetic anhydride and acetic acid, the *lactone* of *2′-hydroxy-3′:5′-bisacetamidodiphenyl-2 carboxylic acid*, having m.p. 350–353° after recrystallisation from acetic acid (Found: C, 65·5; H, 4·6; N, 8·9. $C_{17}H_{14}O_4N_2$ requires C, 65·8; H, 4·6; N, 9·0%).

Lactone of 2′-Hydroxy-5′-aminodiphenyl-2 Carboxylic Acid.

Sodium dithionite was added to a boiling aqueous solution of the 5′-phenylazo-lactone and sodium hydroxide until the red colour disappeared. The solution was cooled, washed with ether, heated, and acidified with sulphuric acid. Without delay it was poured into excess sodium carbonate solution. The *amino-lactone* which separated was recrystallised from ethanol and had m.p. 188–189° (Found: C, 73·7; H, 4·5; N, 6·6. $C_{13}H_9O_2N$ requires C, 73·9; H, 4·3; N, 6·6%). Its hydrochloride was scarcely soluble in water, but the sulphate was soluble in hot water.

Lactone of 2′-Hydroxy-5′-acetamidodiphenyl-2 Carboxylic Acid

The foregoing amino-lactone was acetylated with a hot mixture of equal parts of acetic anhydride and acetic acid. The 5′-acetamido-lactone was recrystallised from aqueous acetic acid and had m.p. 231–232° (Found: C, 70·9; H, 4·7; N, 5·6. $C_{15}H_{11}O_3N$ requires C, 71·1; H, 4·4; N, 5·5%).

Lactone of 2′-Hydroxy-5′-cyanodiphenyl-2 Carboxylic Acid

An attempt to prepare this compound from the amino-lactone by the Sandmeyer reaction failed. Recrystallisation of the material produced by decomposition of the peroxide gave 5′-*cyano-lactone* with m.p. 203–204° (Found: C, 75·6; H, 3·1; N, 6·2. $C_{14}H_7O_2N$ requires C, 76·0; H, 3·2; N, 6·3%). The structure assigned to this substance rests purely on analogy with those of the other oxidation products.

Lactone of 2′-Hydroxy-5′-methoxydiphenyl-2 Carboxylic Acid.

The amino-lactone was diazotised by warming a suspension of its sulphate in dilute sulphuric acid with sodium nitrite. The solution was boiled during several hours and the light brown solid which separated was then methylated in chloroform solution with diazomethane. A small yield was obtained of the 5′-*methoxy-lactone*, which was recrystallised from petroleum ether (b.p. 80–100°), m.p. 121–123° (Found: C, 74·6; H, 4·8. $C_{14}H_{10}O_3$ requires C, 74·3; H, 4·5%).

Lactone of 2′-Hydroxy-5′-nitrodiphenyl-2 Carboxylic Acid

The lactone of 2′-hydroxydiphenyl-2 carboxylic acid was warmed for 1 minute with excess concentrated nitric acid. The sparingly soluble 5′-*nitro-lactone* separated and completely precipitated with water; it was recrystallised from acetic acid and had m.p. 259–261° (Found: C, 64·4; H, 3·0; N, 5·7. $C_{13}H_7O_4N$ requires C, 64·7; H, 2·9; N, 5·8%). Its structure was proved by reduction with tin and hydrochloric acid, followed by acetylation with acetic anhydride and acetic acid. The resulting 5′-acetamido-lactone had m.p. 230–232° undepressed by an authentic specimen. Previously[23] the nitration had been described as yielding a nitro-lactone with m.p. 224°.

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[23] R. Richter *J. Prakt. Chem.* (2) **28**, 301 (1883).