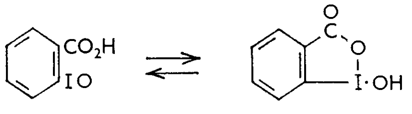
681. *The Structure of* o-*Iodosobenzoic Acid and of Certain Derivatives*

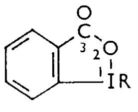
By G. P. Baker, Frederick G. Mann, N. Sheppard, and A. J. Tetlow

The properties and reactions of *o*-iodosobenzoic acid differ markedly from those of its *m*- and *p*-isomers; for example, its simple esters have not previously been prepared. A study of the reactions of *o*-iodosobenzoic acid and various derivatives, and of their infrared spectra, provide strong evidence that these compounds contain the 1-substituted 1,2-benziodoxolin-3-one ring system. The stability of this system is apparently associated with the size of the 5-membered ring: other compounds in which iodine is apparently part of larger rings are less stable.

Meyer and Wachter [1] briefly described the oxidation of *o*-iodobenzoic acid to *o*-iodosobenzoic acid (I), and suggested that the acid (I) could exist in tautomeric equilibrium with the cyclic structure (II), now termed 1-hydroxy-1,2-benziodoxolin-3-one (III; R = OH). Askenasy and Meyer [2] improved the preparation of the acid (I), isolated the sodium and calcium salts, and prepared an acetyl derivative formulated (incorrectly) as o-$C_6H_4(IO)\cdot CO\cdot OAc$ by analogy with the acetyl derivative of *p*-dimethylaminobenzoic acid, p-$C_6H_4(NMe_2)\cdot CO\cdot OAc$. They favoured the structure (II) however for the acid because *m*- and *p*-iodosobenzoic acid had entirely different properties. They failed to prepare the methyl and ethyl ester of the *o*-acid, in the form (I) or (II): thus hydrogen chloride when passed into an ethanolic suspension of the acid gave chlorine and ethyl *o*-iodobenzoate, and the silver salt underwent extensive decomposition with boiling methyl iodide. Hartmann and Meyer [3] showed that the *o*-iodoso- and the *o*-iodoxy-benzoic acids, when treated in cold methanol with hydrogen chloride gave the anhydride (IV) of the 1-hydroxy-iodoxolin-3-one (III; R = OH). The 1-chloroiodoxolin-3-one (III; R = Cl) was prepared by Willgerodt [4] by the action of chlorine on *o*-iodobenzoic acid.



(I) (II)



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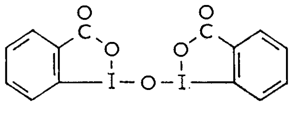

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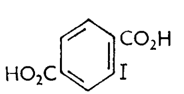

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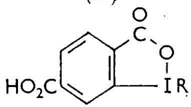

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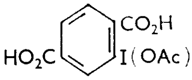
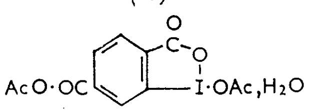


(VIIA)



(VIIB)

Abbes [5] showed that iodoterephthalic acid (V) gave a series of neutral salts (*e.g.*, disodium, disilver) and a mono- and a di-methyl ester; the iodoso-acid however gave only a series of " acid " metallic salts (*e.g.*, monosodium) and only an ill-defined unanalysed monoethyl ester, and hence was given the cyclic formula (VI; R = OH), with a possibility of tautomerism with the open structure.

Willgerodt [6] summarised the evidence for *o*-iodosobenzoic acid having the structure (II). (*a*) The compound has not the characteristic iodoso-odour; (*b*) it is stable to hot water, which converts normal iodoso-compounds into iodo- and iodoxy-compounds; (*c*) it is

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[1] V. Meyer and W. Wachter, *Ber.*, 1892, **25**, 2632.

[2] P. Askenasy and V. Meyer, *Ber.*, 1893, **26**, 1365.

[3] C. Hartmann and V. Meyer, *Ber.*, 1893, **26**, 1730.

[4] C. Willgerodt, *J. prakt. Chem.*, 1894, **49**, 466.

[5] H. Abbes, *Ber.*, 1893, **26**, 2951.

[6] C. Willgerodt, " Die Organischen Verbindungen mit Mehrwertigen Jod," p. 134, Verlag von Ferdinand Enke, Stuttgart, 1914.

unaffected by hot aqueous ethanol, whereas true iodoso-compounds oxidise ethanol to acetaldehyde; (*d*) it gives a monoacetyl derivative, whereas iodoso-compounds normally give diacetyl derivatives, *e.g.*, $PhI(OAc)_2$; it is a very weak acid ($K = 6 \times 10^{-7}$), much weaker than *o*-iodobenzoic acid ($K = 1{\cdot}3 \times 10^{-3}$) and benzoic acid ($K = 6 \times 10^{-5}$). (Most *o*-substituted benzoic acids have dissociation constants greater than that of benzoic acid.[7])

We have therefore sought chemical and infrared spectral evidence for the structure of compounds such as (II) and kindred compounds, bearing in mind that the stability of the ring could be due to strong hydrogen bonding between the hydrogen of the $\cdot CO_2H$ group and the oxygen of the ·IO group.

We find that, although the compound $PhI(OAc)_2$ cannot be converted by ethanol or sodium ethoxide into a compound $PhI(OEt)_2$, the 1-acetoxyiodoxolin-3-one (III; R = OAc) when boiled with methanol or with ethanol gives the crystalline 1-methoxy- and 1-ethoxy-derivative (III; R = OMe and OEt), respectively, and this provides a general method for the preparation of these "esters." The acetoxy-compound when heated with pyridine, quinoline, isoquinoline, *N*-methylpyrrole and other bases gives the anhydride (IV): this is also obtained more readily when the methoxy-compound (III; R = OMe) is heated with pyridine.

It is noteworthy that whereas the compound (II) gives the 1-acetoxy-derivative (III; R = OAc) with hot acetic anhydride and not with hot acetic acid, both the 1-hydroxy-5-nitro-1,2-benziodoxolin-3-one and its 6-nitro-isomer give the corresponding 1-acetoxy-derivatives with the anhydride or the glacial acid: each nitro-acetoxy-compound with hot methanol gives the corresponding 1-methoxy-derivative.

Iodosoterephthalic acid is an exception, however, being apparently unaffected by the anhydride, but with acetic acid giving a crystalline derivative of composition $C_{12}H_{11}IO_8$, which is stable in dry air but slowly decomposes on exposure to damp air regenerating the acid (VI; R = OH): chloroacetic acid similarly gives a derivative of composition $C_{12}H_9Cl_2IO_8$. The constitution of these products remains uncertain. The composition $C_{12}H_{11}IO_8$ corresponds to the diacetoxy-iodo-compound (VIIA), but the product reacts readily with numerous hot alcohols to give the corresponding 1-monoalkoxyiodoxolin-3-one derivatives (*e.g.*, VI; R = OEt): the product $C_{12}H_9Cl_2IO_8$ with ethanol gives the same 1-ethoxy-derivative. The infrared spectrum of the product gives no support to the structure (VIIA) but does provide some (indecisive) support for the monohydrated structure (VIIB).

The 1-alkoxy-derivatives (*e.g.*, VI; R = OEt) dissolve readily in cold dilute aqueous sodium hydroxide, and acidification then precipitates the initial compound (VI; R = OH).

The chemical evidence, and the infrared spectral evidence discussed later, show without reasonable doubt that the iodoxolin ring system does occur in the compounds formulated as (III) and (VI), where in each case R = OH, Oalkyl, or OAc. The ease of formation and the comparative stability of this system are apparently closely associated with the 5-membered ring. Other examples of 5-membered ring systems containing iodine are the simple 1,4-dichloro-iodoxolin-3-one (VIII; R = H) and its 5-carboxylic acid (VIII; R = CO_2H),[8] and the 2,2′-biphenylene compound (IX) [9] which is considerably more stable than triphenyliodine.[10] The 2,2′-biphenyleneiodonium salts (X) represent a rather different type of compound,[11] but the strong tendency of iodine to form a 5-membered ring is shown by the spontaneous conversion of 2,2′-di-iodosobiphenyl and of bis(2,2′-dichloro-iodo)biphenyl into the iodonium iodide (X; X = I), and by the direct formation of this salt when 2,2′-diaminobiphenyl is tetrazotised and treated with aqueous potassium iodide.

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[7] J. F. J. Dippy and R. H. Lewis, *J.*, 1937, 1421.

[8] J. Thiele and W. Peter, *Ber.*, 1905, **38**, 2844; *Annalen*, 1909, **369**, 119.

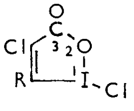
[9] K. Clauss, *Chem. Ber.*, 1955, **88**, 268.

[10] G. Wittig and M. Rieber, *Annalen*, 1949, **562**, 187; G. Wittig and K. Clauss, *ibid.*, 1952, **578**, 136.

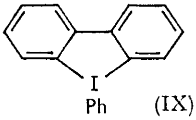
[11] L. Mascarelli, *Atti R. Acad. Lincei*, 1907, **16**, 562; 1908, **17**, 580; 1909, **18**, 190; 1910, **19**, 308; 1912, **21**, 617.

Two compounds, apparently containing iodine in a six- and seven-membered ring respectively, have been briefly investigated.

Raum[12] attempted to prepare *o*-iodosophenylacetic acid by the oxidation of *o*-iodophenylacetic acid (XI) but this process gave *o*-iodobenzoic acid. Chlorine readily united however with the acid (XI) to give the iodo-dichloride, which when hydrolysed with cold water gave a product, claimed by Raum to be the compound (XII). We have repeated this work, and our product had the same m. p. and composition as Raum's. (Ours was analysed for C and H; Raum analysed his for total halogen and chlorine only.) A less pure sample of this compound was obtained by dissolving the iodo-dichloride in aqueous sodium carbonate, and precipitating the product with acid. The compound (XII) is insoluble in ether, and when heated with acetic acid gave the acid (XI), and with acetic anhydride gave *o*-iodophenylacetic anhydride, with evolution of chlorine in each case. It dissolved in aqueous sodium hydroxide, and acidification gave an unidentified gum and a small proportion of the acid (XI). The compound liberated iodine from aqueous sodium iodide: this reaction, and more particularly the infrared spectral evidence (see later) supports the structure (XII).



(VIII)



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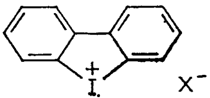

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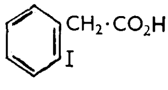

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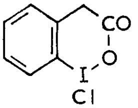
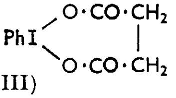


(XII)



(XIII)

We find that iodosobenzene in acetone reacts with succinic acid, and the iododichloride with silver succinate, to give a white product having the composition of iodosobenzene succinate (XIII): its investigation was restricted by its insolubility in all common solvents except 2-methoxy- and 2-ethoxy-ethanol. Its liberation of iodine from aqueous sodium iodide supports the structure (XIII). Boiling water decomposed the compound giving succinic acid and iodo- and iodoxy-benzene, clearly by an initial hydrolysis to its original components. Compounds analogous to the succinate (XIII) could not be obtained by the combination of *m*- or *p*-iodosobenzoic acid with succinic acid: this is not surprising, for whereas iodosobenzene forms a stable diacetate, the two iodosobenzoic acids do not form similar compounds.[13] Iodosobenzene did not combine similarly with phthalic acid.

Infrared Spectra.—These have been measured for the following compounds: $PhICl_2$, PhIO, $PhI(OAc)_2$, (III; R = OH, OAc, OMe, OEt, Cl), (IV), (VI; R = OH, OMe, OEt), (VII), $PhIO_2$, *m*- and *p*-$C_6H_4(ICl_2)CO_2H$, *m*- and *p*-$C_6H_4(IO)CO_2H$, *o*-$C_6H_4(ICl_2)\cdot CH_2\cdot CO_2H$, (XII).

The salient features of these spectra between 3330 and 660 cm.$^{-1}$ are as follows.

(a) *The parent compounds.* Iodobenzene dichloride appears to have no absorption band that cannot be correlated with vibrations of the monosubstituted benzene ring. This is not unexpected, as the bond stretching frequencies of heavy atom bonds such as I–Cl would be expected to occur below 670 cm.$^{-1}$. In iodosobenzene, the only feature that can be attributed to the I–O linkage is a strong band at 734 cm.$^{-1}$. Iodoxybenzene ($PhIO_2$) shows extra absorption bands in the same region as that for iodosobenzene, and the two strongest, lying at 728 and 711 cm.$^{-1}$, may be tentatively attributed to bond stretching vibrations of the IO_2 group involving the I–O linkage.

If a mean value of 720 cm.$^{-1}$ is taken as characteristic of an I–O stretching vibration for the above examples, and if the I–O link is treated for purpose of calculation as a diatomic unit separate from the rest of the molecule (a reasonable approximation when

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[12] W. Raum, *Ber.*, 1894, **27**, 3232.

[13] C. Willgerodt, *Ber.*, 1894, **27**, 2328.

the linkage to the rest of the molecule is through a heavy atom), the stretching force constant of the bond, k_{I-O}, is 4·4 × 10^5 dynes cm.$^{-1}$. This value approaches that of a single bond (cf. C–C, 4·4 × 10^5; C=C, 10·9 × 10^5), but the C–I single bond (probably a better standard for comparison) has a much lower force constant (~2·3 × 10^5), so that I–O linkage may have a proportion of double-bond character.

Co-ordinate linkage, X → O	Type of compound and observed frequencies (cm.$^{-1}$)	Approximate force constants k_{X-O} (10^5 dynes/cm.$^{-1}$)	Corresponding values of k_{X-C} single bonds
S → O	Sulphones (1238)	9·6	3·0
	Sulphoxides (1050)	6·9	
P → O	Alkyl phosphates (1250)	9·7	2·8
Se → O	Selenoxide (838)[14]	5·5	2·6
I → O	Iodoso Iodoxy (720)	4·3	2·3

Further evidence can be derived by comparison of the force constants of other X–O co-ordinate-type linkages and those of the corresponding X–C linkages, derived by an approximate but consistent treatment.

The ratio k_{X-O}/k_{X-C} decreases markedly from the pair X = S and P to X = Se and I, suggesting that as the period of X increases, the amount of multiple-bond character decreases, but that k_{I-O} still corresponds to some considerable multiple-bond character.

(b) *Characteristic group frequencies. The* CO_2H *group.* Many of the compounds contain CO_2H groups linked to the benzene ring. With one exception, all which could contain this group have C=O absorption in the usual range (1760—1690 cm.$^{-1}$). Many also have general absorption in the 2860—2220 cm.$^{-1}$ region, and a broad band near 910 cm.$^{-1}$ characteristic of the acid OH group.

The ortho-*acids.* The only compound which might contain the CO_2H group but which does not have the characteristic CO_2H frequency near 1720 cm.$^{-1}$ is *o*-iodosobenzoic acid. This has a much lower C=O frequency (1633 cm.$^{-1}$), suggesting a very different structure such as (II). (This C=O band is too intense to be confused with aromatic absorption.) This compound also has two strong absorption bands at 2920 and 2420 cm.$^{-1}$, the first being normally masked by Nujol absorption in the spectra of mulls: these bands are clearly associated with the stretching vibration of the new type of OH group, involved in rather strong hydrogen bonding.

The silver and calcium salts have spectra very similar to that of the free acid (apart from the absence of the OH bands), suggesting that they also have the cyclic structure (III; R = OAg and OCa).

Iodosoterephthalic acid, which can be formulated as (VI; R = OH), has the same characteristic OH band at 2421 cm.$^{-1}$ and lower C=O frequency (1615 cm.$^{-1}$), in addition to the usual band at 1715 cm.$^{-1}$ due to the normal CO_2H group.

The ortho-*esters.* The methyl and ethyl esters of *o*-iodosobenzoic acid, like the *ortho*-acid, have their C=O absorption bands at much lower frequencies (1650 cm.$^{-1}$) than is normal for true esters (1730 cm.$^{-1}$) and this again supports the cyclic structures (III; R = OMe and OEt). These OMe and OEt groups appear to have the characteristic absorption bands: OMe, 1010s, 964s; OEt, 1015s, 873s.

The analogous derivatives of iodosoterephthalic acid (VI; R = OMe and OEt) also have the lower-frequency C=O band at 1618 and 1631 cm.$^{-1}$ and the normal C=O band at 1704 and 1733 cm.$^{-1}$, respectively. The OMe and OEt groups in these compounds have absorption bands analogous to those of (III; R = OMe and OEt): OMe, 1024m, 976s; OEt, 1026m, 873*s*.

The compound (III; R = OAc) has C=O absorption at 1660 and 1615 cm.$^{-1}$, the latter corresponding to the C=O group of the iodoxolin-3-one ring and the former to that of the

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[14] D. Barnard, J. M. Fabian, and H. P. Koch, *J.*, 1949, 2442.

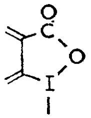
·IOCOMe group. This is supported by the spectrum of the compound $PhI(OCOMe)_2$, in which the C=O band of the ·I–O·CO·C group occurs at 1650 cm.$^{-1}$.

The compound (VIIB?) has bands at 1623, 1667, 1730, and 1764 cm.$^{-1}$, the first and second possibly being also the CO bands of the indoxolin-3-one ring and of the IOCOMe group, respectively: a band at 3225 cm.$^{-1}$ may indicate water of crystallisation.

The C=O groups of the anhydride (IV) give a band at 1680 cm.$^{-1}$: this rather anomalous value may reflect the influence of the unique ·O·I·O·I·O group to which the C=O groups are linked. If the compound (IV) were a true aryl carboxylic anhydride of the type R·CO·O·CO·R, it should have two bands at *ca.* 1825 and 1755 cm.$^{-2}$ the former being the more intense.

o-Iodophenylacetic acid dichloride has the normal C=O band (1715 cm.$^{-1}$) of the CO_2H group and has not undergone cyclisation, but the monochloro-compound has this band at 1653 cm.$^{-1}$ and therefore probably has the cyclic structure (XII).

Discussion.—The C:O frequencies (1650—1615 cm.$^{-1}$) of the "cyclic" compounds formulated as (III) and (VI), are very considerably lower than the normal C=O values in carboxylic acids and their esters. They are closer to, but always significantly higher than, the normal range of frequencies (1610—1550 cm.$^{-1}$) attributed to the ·COO$^-$ group. There is thus strong support for the cyclic structure, although the electronic structure within the ring may be intermediate between that of (XIV) and (XV).



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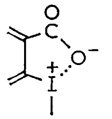
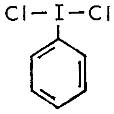


(XV)

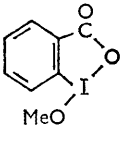
$o-I·C_6H_4·CO·O·O·CO·C_6H_4·R$ (XVI)

It is noteworthy that *oo'*-di-iodoperbenzoic anhydride (XVI; R = I-*o*) and *o*-iodo-*p*-nitroperbenzoic anhydride (XVI; R = NO_2-*p*) on thermal decomposition give the 1-*o*-iodobenzoxy- and the 1-*p*-nitrobenzoxy-iodoxolin-3-one (III; R = *o*-$I·C_6H_4·CO·O$ and R = *p*-$NO_2·C_6H_4·CO·O$), respectively.[15]

The stereochemistry of the 3-covalent iodine atom in the iodoxolin ring of compounds such as (III) and (VI) is of considerable interest. The 3-covalent iodine atoms in tetrakis-(triethylarsinemonoiodocopper), $[Et_3As,CuI]_4$, have their valencies directed to the three apices of a regular tetrahedron,[16] but this is probably a special case. Iodobenzene dichloride is approximately T-shaped (XVII) with the atomic distances I–Cl, 2·45; I–C, 2·00 Å, and the intervalency angle, Cl–I–C, 86°.[17] It may therefore be significant that a model of 1-methoxy-1,2-benziodoxolin-3-one constructed with the usual interatomic bond



(XVII)



(XVIII)

angles and distances, and with a C–I–OMe bond angle of 90° (XVIII) fits together without strain, the O–I–O angle being very nearly 180°, comparable to the Cl–I–Cl angle in (XVII).

A brief *X*-ray crystal structure examination of the compounds (III; R = OMe), (VI; R = OMe), 1-methoxy-5-nitro-1,2-benziodoxolin-3-one and its 6-nitro-isomer, by Dr. W. Cochran, showed that the main stereochemical features of these compounds could not unfortunately be established without a full structure analysis, for which facilities were not available.

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[15] J. E. Leffler, R. D. Faulkner, and C. C. Petropoulous, *J. Amer. Chem. Soc.*, 1958, **80**, 5435; W. Honsberg and J. E. Leffler, *J. Org. Chem.*, 1961, **26**, 733.

[16] F. G. Mann, D. Purdie, and A. F. Wells, *J.*, 1936, 1503.

[17] E. M. Archer and T. E. D. van Schalkwyk, *Acta Cryst.*, 1953, **6**, 88.

EXPERIMENTAL

All compounds, unless otherwise described, were colourless.

Consistent m. p. could be obtained for certain compounds only by the use of evacuated sealed tubes (denoted as E.T.) or by immersion of the tube in a pre-heated bath, the temperature of immersion being denoted as (T.I.°). Difficulty in obtaining consistent m. p.s for some iodoso-compounds in particular has been recorded.[2, 3]

Iodobenzene dichloride, iodosobenzene, and iodoxybenzene were prepared by standard methods.[18]

Iodosobenzene Diacetate.—A mixture of freshly prepared iodosobenzene (4 g.) and acetic acid (12 ml.) was heated to give a clear solution, which when cooled and diluted with ether (120 ml.) deposited the crystalline diacetate (3·8 g., 65%), m. p. 157—159° (lit.,[19] 156—157°) from benzene.

o-*Iodobenzoic Acid.*—Prepared by diazotising anthranilic acid in dilute sulphuric acid, and adding the filtered solution to potassium iodide, also in the dilute acid, the crude brown acid (92%) was converted into the ethyl ester,[20] b. p. 150—151°/13 mm. (71%) which on hydrolysis with ethanolic potassium hydroxide gave the pure acid, m. p. 163°, in almost theoretical yield.

o-*Iodosobenzoic Acid* (1-*Hydroxy*-1,2-*benziodoxolin*-3-*one*, II).—Chlorine was passed into a cold solution of *o*-iodobenzoic acid (15 g.) in chloroform (400 ml.) until separation of the yellow crystalline iodo-dichloride (16 g., 82%) was complete: the crystals were collected and dissolved in aqueous sodium hydroxide, which on careful acidification deposited the acid (II), (10 g., 76%) m. p. 231—232° (decomp.).

The acid dissolved in warm aqueous ammonia but crystallised unchanged on cooling: a solution in warm methanolic ammonia on cooling deposited the rather unstable *ammonium salt*, m. p. 134° (decomp.) (T.I. 130°) (Found: N, 5·1. $C_7H_8INO_3$ requires N, 5·0%). The calcium salt had m. p. 260° (decomp.) (Found: C, 29·75; H, 1·7. Calc. for $C_{14}H_8CaI_2O_6$: C, 29·7; H, 1·4%).

1-*Acetoxy*-1,2-*benziodoxolin*-3-*one* (III; R = OAc).—A mixture of the 1-hydroxy compound (III; R = OH) (15 g.) and acetic anhydride (40 ml.) was gently boiled under reflux for 5 min., giving a clear solution, which on cooling deposited the acetoxy-compound (16·1 g., 91%), m. p. 167—169° (lit.,[2] 166—167°) (from acetic anhydride).

1-*Methoxy*-1,2-*benziodoxolin*-3-*one* (III; R = OMe).—A mixture of the acetoxy-compound (1 g.) and methanol (5 ml.), when boiled under reflux for 10 min. and cooled, deposited the 1-*methoxy-derivative* (0·8 g.), m. p. 166—168° (T.I. 160°), resolidifying and remelting at *ca.* 190° (from methanol) (Found: C, 34·75; H, 3·0; I, 45·6. $C_8H_7IO_3$ requires C, 34·55; H, 2·6; I, 45·6%). A mixture of the compounds (III; R = OAc) and (III; R = OMe) had m. p. 134°. The 1-*ethoxy-compound* (III; R = OEt), similarly prepared using ethanol, had m. p. 126—128°, also resolidifying and remelting at *ca.* 190° (Found: C, 37·3; H, 3·3; I, 43·6. $C_9H_9IO_3$ requires C, 37·00 H, 3·1; I, 43·45%).

The 1-acetoxy-compound when similarly warmed with benzyl alcohol was largely unaffected, and with 2-methylbutan-1-ol and cyclohexanol was converted into the 1-hydroxy-compound (II).

When the 1-acetoxy-compound was mixed with aniline, methylaniline, or piperidine, heat was evolved with considerable darkening. When however the acetoxy-compound (1 g.) was warmed with quinoline, isoquinoline, pyridine, 4-methoxypyridine, *N*-methylpyrrole, or 2-methylbenzothiazole (5 ml.), it dissolved and on continued heating at 100—110° each solution became very dark and slowly deposited the 1-hydroxy-1,2-benzindoxolin-3-one anhydride (IV), m. p. 225° (decomp.) (T.I. 210°) (lit.,[2] 220°), from dimethylformamide (Found, in the pyridine reaction, C, 33·3; H, 1·9; I, 49·7. Calc. for $C_{14}H_8I_2O_5$: C, 33·0; H, 1·6; I, 49·8%). This anhydride dissolved in warm aqueous sodium hydroxide and the cold solution on acidification deposited the 1-hydroxy-compound. With aqueous sodium iodide it gave iodine only on warming, in marked contrast to the immediate liberation of iodine by the 1-hydroxy-compound.

When the 1-methoxy-compound (1 g.) was heated under reflux with pyridine (5 ml.) at 105° for 4 hr., it gave a clear almost colourless solution which slowly deposited the anhydride, m. p. and mixed m. p. 227° (decomp.) (T.I. 210°) (Found: C, 33·1; H, 1·6; I, 49·8%).

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[18] *Org. Synth.*, Coll. Vol. 3, 1955, pp. 482, 483, 485.
[19] C. Willgerodt, *Ber.*, 1892, **25**, 3498.
[20] J. B. Cohen and H. S. Raper, *J.*, 1904, **85**, 1272.

m-Iodosobenzoic acid and the *p*-isomer[13] were prepared from the corresponding iododichlorides: the *p*-acid was initially contaminated with the iodoxy-acid.

Iodoterephthalic Acid (V).—Following Kloeppel,[21] *p*-toluic acid was nitrated to 2-nitro-*p*-toluic acid (86%), reduced to 2-amino-*p*-toluic acid (85%), which on diazotisation and treatment with sodium iodide gave 2-iodo-*p*-toluic acid (70%), m. p. 205—207° after vacuum sublimation and recrystallisation from ethanol. Oxidation by alkaline permanganate[5] gave the acid (V) (78%), m. p. 299—301° (lit.,[5] 274—276°) from aqueous ethanol (Found: C, 33·2; H, 2·0; I, 43·8. Calc. for $C_8H_5IO_4$: C, 32·9; H, 1·7; I, 43·5%).

Iodosoterephthalic Acid (6-*Carboxy*-1-*hydroxy*-1,2-*benziodoxolin*-3-*one*) (VI; R = OH).—The acid (V) (6 g.) was added to stirred fuming nitric acid (60 ml.) at 15°, and after 30 min. the mixture was poured into water (300 ml.). The acid (VI; R = OH) (4·5 g., 70%), when collected, thoroughly washed with hot water, ethanol, and ether, had m. p. 283° (decomp.) (T.I. 280°) (lit.,[5] 260°): the m. p. depends markedly on the temperature of immersion.

1-*Acetoxy*-6-*acetoxycarbonyl*-1,2-*benziodoxolin*-3-*one Monohydrate* (VIIB?).—A solution of the acid (VI; R = OH) (3 g.) in boiling acetic acid (90 ml.) when cooled deposited the *compound* (VIIB?) (3·1 g., 77%), m. p. 279—281° (decomp.) from acetic acid (Found: C, 35·3; H, 2·7; I, 31·1. $C_{12}H_9IO_7,H_2O$ requires C, 35·1; H, 2·7; I, 31·0%). On exposure to damp air it is slowly converted into the acid (VI; R = OH): a sample which has not been kept sufficiently dry may analyse deceptively for an intermediate monoacetoxy-acid.

When the acid (VI; R = OH) (1 g.) was heated with chloroacetic acid (4 g.) for 10 min. at 120°, the cooled solution rapidly deposited the *di*(*chloroacetoxy*)-*compound* (as VIIB?), m. p. 260° (decomp.) after extraction with boiling toluene to eliminate chloroacetic acid (Found: C, 30·7; H, 1·6. $C_{12}H_7Cl_2IO_7,H_2O$ requires C, 30·2; H, 1·9%). This compound is readily soluble in ethanol, in which the acid (VI; R = OH) is almost insoluble.

6-*Carboxy*-1-*methoxy*-1,2-*benziodoxolin*-3-*one* (VI; R = OMe).—When the compound (VIIB?) was warmed with methanol, it gave a clear solution from which the 1-*methoxy-compound* (VI; R = OMe), m. p. 300° (decomp.) (T.I. 295°) rapidly separated (Found: C, 33·5; H, 2·25; I, 39·1. $C_9H_7IO_5$ requires C, 33·5; H, 2·2; I, 39·4%). The following *derivatives*, all melting with decomposition, were similarly prepared.

Compound (VI)		Found (%)				Required (%)		
R	M. p.	C	H	I	Formula	C	H	I
OEt	296° (T.I. 290°)	35·8	2·75	37·9	$C_{10}H_9IO_5$	35·75	2·7	37·8
OPr^n	280° (T.I. 270°)	38·1	3·5	36·3	$C_{11}H_{11}IO_5$	37·75	3·2	36·25
OPr^i	290° (T.I. 280°)	38·2	3·1					
O·CH$_2$·CHMeEt	280° (T.I. 270°)	41·35	3·95		$C_{13}H_{15}IO_5$	41·3	4·0	
O·CH$_2$·Ph	258—261° (T.I. 250°) *	44·8	3·1		$C_{15}H_{11}IO_5$	45·2	2·8	

* Recrystallised from benzyl alcohol–benzene.

The di(chloroacetoxy)-compound (as VIIB?), when similarly warmed with ethanol, also gave the 1-ethoxy-compound (Found: C, 35·3; H, 2·4; I, 38·0%).

1-*Hydroxy*-6-*nitro*-1,2-*benziodoxolin*-3-*one*.—4-Nitroanthranilic acid was converted into 2-iodo-4-nitrobenzoic acid, which with chlorine gave the iodo-dichloride: hydrolysis then gave the above benziodoxolin-3-one, m. p. 201° (decomp.) (T.I. 180°) (lit.,[22] 190, 196, 201°).

The 1-hydroxy-compound, heated with acetic acid or anhydride, gave 1-*acetoxy*-6-*nitro*-1,2-*benziodoxolin*-3-*one*, m. p. 198—200° (decomp.) (T.I. 190°) (Found: C, 30·7; H, 2·0; N, 4·3; I, 36·0. $C_9H_6INO_6$ requires C, 30·8; H, 1·7; N, 4·0; I, 36·15%). This compound when briefly heated with methanol gave the 1-*methoxy-derivative*, cream coloured needles, m. p. 189—191° (decomp.) (T.I. 180°) (Found: C, 29·9; H, 1·9; I, 39·5. $C_8H_6INO_5$ requires C, 29·8; H, 1·9; I, 39·3%): the 1-*n-propoxy-derivative*, similarly prepared, formed needles, m. p. 179—180° (decomp.) (T.I. 170°) (Found: C, 34·1; H, 2·75. $C_{10}H_{10}INO_5$ requires C, 34·2; H, 2·85%).

1-*Hydroxy*-5-*nitro*-1,2-*benziodoxolin*-3-*one*.—2-Iodo-5-nitrobenzoic acid[23] was converted into the iodo-dichloride and then into the above benziodoxolin-3-one, m. p. 216° (decomp.) (T.I. 210°) (lit.,[23] 197°) after crystallisation from much hot water (Found: C, 27·0; H, 1·5. Calc. for $C_7H_4INO_5$: C, 27·2; H, 1·3%).

This compound with hot acetic anhydride gave the 1-acetoxy-derivative, m. p. 196—197°

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[21] E. Kloeppel, *Ber.*, 1893, **26**, 1733.

[22] C. Willgerodt and R. Gartner, *Ber.*, 1908, **41**, 2820.

[23] H. Goldstein and A. V. Grampoloff, *Helv. Chim. Acta*, 1930, **13**, 312; 1932, **15**, 1102.

(decomp.) (T.I. 190°) (lit.,[23] 187—188°) (Found: C, 30·9; H, 1·65; N, 4·3. Calc. for $C_9H_6INO_6$: C, 30·8; H, 1·7; N, 4·0%). Goldstein and Grampoloff regarded this derivative as a mixed anhydride of the 2-iodoso-5-nitro-benzoic and acetic acids.[23]

The acetoxy-derivative, when dissolved in much boiling methanol, deposted 1-*methoxy*-5-*nitro*-1,2-*benziodoxolin*-3-*one*, prisms, m. p. 212° (decomp.) (T.I. 200°) (Found: C, 30·1; H, 2·1. $C_8H_6INO_5$ requires C, 29·8; H, 1·9%), and with propan-1-ol gave the 1-*n*-*propoxy*-homologue, prisms, m. p. 187—188° (decomp.) (T.I. 180°) (Found: C, 34·3; H, 2·8. $C_{10}H_{10}INO_5$ requires C, 34·2; H, 2·85%).

o-*Iodophenylacetic Acid Dichloride*.—*o*-Iodophenylacetic acid (XI),[12, 24] when treated in chloroform with chlorine, deposited the pale yellow dichloride (84%), m. p. 104° (decomp.) (T.I. 95°) (Found: C, 28·75; H, 1·9. Calc. for $C_8H_7Cl_2IO_2$: C, 28·85; H, 2·1%). The powdered dichloride, when shaken vigorously with cold water, was converted into the flocculent white 1-chloro-1,2-benziodoxin-3(4*H*)-one (XII), m. p. 118° (decomp.) (T.I. 115°) (lit.,[12] 119°), after thorough washing with water and ether (Found: C, 32·35; H, 1·95. Calc. for $C_8H_6ClIO_2$: C, 32·4; H, 2·05%): the presence of chlorine was confirmed.

Dilute aqueous sodium carbonate readily dissolved the dichloride, and acidification deposited a less pure sample of the compound (XII). Dilute aqueous sodium hydroxide also readily dissolved the dichloride, but acidification liberated chlorine and deposited a gummy solid, freely soluble in ether, unlike the iodoso-acid and the compound (XII). Attempted crystallisation of this solid from much hot water gave only the acid (XI).

The monochloro-compound (XII) also dissolved readily in cold dilute sodium hydroxide, and acidification gave a gum: extraction with boiling light petroleum (b. p. 60—80°) gave a small amount of the acid (XI) and a gum which could not be crystallised.

The compound (XII) in acetic acid, when boiled under reflux for 30 min., evolved chlorine and gave a clear solution: removal of the acetic acid under reduced pressure gave a residue of the acid (XI) (60% after recrystallisation from petroleum). The compound (XII) behaved similarly with acetic anhydride, but the residue, also recrystallised from petroleum, gave o-*iodophenylacetic anhydride*, m. p. 98—100° (Found: C, 38·1; H, 2·7. $C_{16}H_{12}I_2O_3$ requires C, 37·95; N, 2·4%). The acid (XI) when boiled with acetic anhydride gives the anhydride, hence its formation in this experiment.

2-*Phenyl*-2,1,3-*iodadioxepan*-4,7-*dione* (XIII).—Iodosobenzene (6·60 g.) was added to a solution of succinic acid (3·45 g., 1 mol.) in acetone (75 ml.), which was shaken vigorously until the initially thick milky liquid became clear (*ca.* 5 min.). The solution, filtered to remove a small amount of sticky material, was allowed to evaporate spontaneously, depositing an amorphous solid. (Evaporation on a water-bath caused deposition of an oil, which solidified on cooling and stirring.), The crude solid (7 g.) was boiled with acetone (75 ml.) for 5 min. to remove succinic acid, and the residual 2-*phenyl*-2,1,3-*iodadioxepan*-4,7-*dione* (XIII) (5 g.) collected and washed with hot acetone: it had m. p. 173—175° (decomp.) (Found: C, 36·8; H, 2·7; I, 40·3. $C_{10}H_9IO_4$ requires C, 37·5; H, 2·8; I, 39·7%).

A mixture of iodobenzene dichloride (1·4 g.) and disilver succinate (1·7 g., 1 mol.) in acetone (30 ml.) was shaken for 1 hr., filtered and evaporated. The pale yellow residue was powdered and extracted with boiling acetone, leaving the white insoluble 1-phenyl-2,1,3-iodadioxepan-4,7-dione (XIII), m. p. and mixed m. p. 174—176° (decomp.).

The dione (XIII) is insoluble in, or decomposed by, most boiling organic solvents. A sample which crystallised very slowly from 2-ethoxyethanol had m. p. 172—174° (decomp.) but had apparently undergone slight decomposition (Found: C, 37·6; H, 3·1; I, 41·8%).

No satisfactory product was obtained by the interaction of iodosobenzene and succinic anhydride, and with oxalic and malonic acid vigorous oxidation occurred.

Infrared spectra. These were obtained using a Perkin-Elmer model 21 spectrometer with a rock-salt prism.

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[24] W. S. Rapson and R. G. Shuttleworth, *J.*, 1941, 489.