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IODOXYBENZENE

A REMARKABLY CLOSE OZONE EQUIVALENT

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Abstract—Iodoxybenzene is isoelectronic to ozone and several of its reactions proceed via pathways remarkably similar to that of ozone. An attractive feature of iodoxybenzene mediated reactions is the direct formation of products and the transformation of the reagent to iodobenzene. The formation of benzil and iodobenzene in good yields from diphenylacetylene provides support for the anticipated intermediate arising from $\pi^4s + \pi^2s$ addition. Iodoxybenzene transforms phenanthrene to phenanthrenequinone as a result of the initially formed 4 + 2 adduct undergoing C–H rupture, in preference to the C–C rupture. This change is parallel to the transformation of phenanthrene 9-carboxylic acid to phenanthrenequinone with ozone. The expected C–C rupture of the initially formed adduct does take place with acenaphthylene leading to naphthalic anhydride. The reaction of pyrene with iodoxybenzene leads to nearly equal amounts of the 4–5, 1–6 and 3–6 quinones involving attack on the bond of the lowest bond localisation energy and the atom of the lowest atom localization energy. This behaviour is similar to the action of ozone on benzopyrene. Iodoxybenzene transforms anthracene, just like ozone, to anthraquinone, in good yields. The involvement of transannular addition of iodoxybenzene, as is partly the case with ozone, is proved unlikely by reaction with 9, 10 dimethylanthracene which gave 10-methyl 9-anthraldehyde and 10-carboxy 9-anthraldehyde, involving the insertion of elements of iodoxybenzene to the aryl C–H bond. This tendency of iodoxybenzene has been further demonstrated by the following changes: diphenylmethane→benzophenone; fluorene→fluorenone and tetralin→α-tetralone. Several of the transformations brought about with iodoxybenzene provide attractive synthetic routes, particularly to phenanthrenequinone, pyrenequinones and tetralone. Finally, just like the $2\,O_3 \rightarrow 3\,O_2$ change, iodoxybenzene, and even more so, 4-iodoxybiphenyl, thermally fragment to iodobenzene and 4-iodobiphenyl.

In sharp contrast to the high reactivity of ozone to π systems, the iso-electronic nitro group is inert to these functions. An examination of the various factors that may influence the course of such reactions has led to the conclusion that the exceptionally high ΔH_f^0 of ozone ($+34$ kcal mol^{-1}) is a major reason for its high reactivity. The resultant conclusion, that perturbed nitro systems, anticipated to be energy rich, are likely to mimic ozone has been somewhat substantiated.[1] On the basis of a thermochemical assessment, iodoxybenzene (**1**), possessing a functional group that can be considered to be isoelectronic to ozone and the nitro grouping can be anticipated to have a substantially positive ΔH_f^0, perhaps higher than any perturbed nitro systems that can be constructed.[2]

Additionally, the highly polarized I–O bond in iodoxybenzene could be expected to reduce the kinetic activation energy barrier.[3] Our earlier work[1] has led to the conclusion that it is this barrier which is responsible for the non-observance of the allowed $\pi^4s + \pi^2s$ additions involving the nitro function. Consequently, it was considered to be of interest to study the reaction of iodoxybenzene with π systems. The ensueing results, reported here, are of interest, particularly so, since, it projects iodoxybenzene as a reagent of promise and as an exceptionally useful one in certain cases. Further, the remarkably parallel behaviour exhibited by iodoxybenzene and ozone are of significance in the development of an effective ozone equivalent.

Whilst the preparation and reactions of higher valent organoiodine compounds have been described in early literature,[4] interest in their use as oxidants for organic synthesis is of relatively recent vintage. Iodosobenzene in particular, has been the subject of several communications within the past few years.[5] Indeed, it was only in 1982, whilst our own work was well under way, that Barton *et al.* specifically drew the attention relating to the potential of iodoxybenzene as a reagent for the oxidation of alcohols and sulfides.[3] Subsequently we communicated our own results on hydrocarbon systems to Prof. Barton.[6]

The envisaged iodoxybenzene cycloaddition to π functions would lead to an intermediate, remarkably similar to that formed with ozone or the nitro function. Further, this intermediate could rupture leading to carbonyl compounds and iodobenzene (I^1), reminiscent of the formation of carbonyl and nitrene from the nitro group adducts[1] (Chart I).

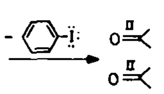

Chart I.

A major problem relating to the use of iodoxybenzene is the solubility of the reagent.[7] It is practically insoluble in most non-polar solvents and reacts violently with solvents such as DMSO, presumably due to ready oxidation. Ultimately, hot nitrobenzene turned out to be a satisfactory solvent. Most of the reactions with iodoxybenzene were, therefore, carried out in hot (~ 170°) nitrobenzene. In a typical experiment, a stirred mixture of the substrate and iodoxybenzene in nitrobenzene was held at 170° for 5–8 hr and the product(s) isolated by chromatography.

Iodoxybenzene (**1**) was prepared essentially by procedures described in literature.[8] 4-Iodoxybiphenyl (**2**) was made by a similar sequence. The reaction of diphenylacetylene with **1** at 170° for 5 hr led to the isolation of benzil (83%) and iodobenzene (37%). The presence of the latter was definitely established by GC analysis and the yield reflects loss of the compound during chromatographic operations. The formation of these products could be readily rationalised on the basis of the involvement of the anticipated cycloadduct **3** followed by fragmentation (CHART II). By a similar sequence of changes 1, 1, 4, 4-tetraphenyl buta 1, 3-diene gave a 79% yield of benzophenone. The other fragment, namely, glyoxal, could not survive the reaction conditions. Diphenylacetylene is transformed to benzil (51%) on treatment with **1**, in the absence of solvents at 170° for 5 hr.

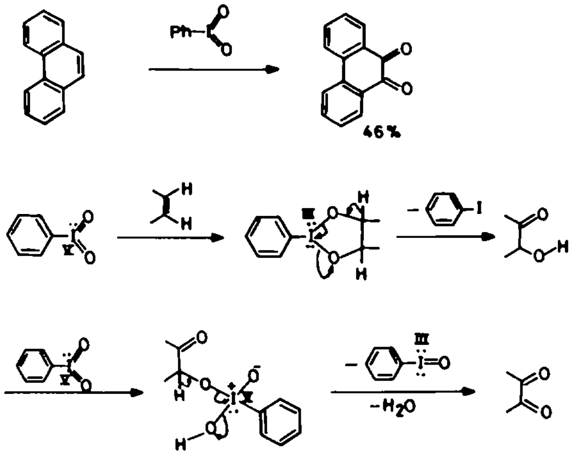

Chart IV.

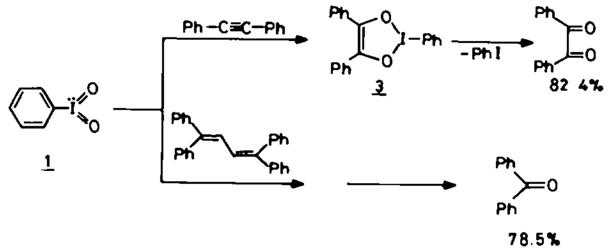

Chart II.

In endeavours to prepare, if possible, the cyclic intermediate **3**,[9] benzoin was reacted with two equivalents of NaH in DME and treated with one equivalent of $PhICl_2$ at 0°. Quenching followed by careful chromatography, gave only benzil (60%) and iodobenzene (35%) which could arise either *via* **3** or through an open intermediate (Chart III). The most convincing proof for **3**, therefore, is the formation of iodobenzene and benzil from diphenylacetylene and $PhIO_2$ (*vide supra*).

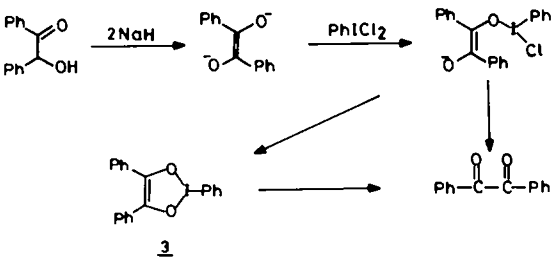

Chart III.

Reaction of phenanthrene with iodoxybenzene gave a 46% yield of phenanthrenequinone—whose properties were identical with those of an authentic sample—thus providing a most convenient method for its preparation. The phenanthrene → phenanthrenequinone change is rationalised on the basis of two sequential oxidations involving iodoxybenzene. The primary adduct fragments to an α-hydroxyketone, which, then undergoes further oxidation (Chart IV). The formation of the α-hydroxyketone is a result of C–H rupture of the primary adduct in favour of a C–C break as envisaged in Chart I, that would have led to a dicarbonyl compound. With a view to promote such a C–C break, iodoxybenzene was reacted with acenaphthylene. It was anticipated that in this case the primary product would undergo the scission of the strained C–C bond, in preference to the C–H. In the event, this turned out to be the case and the reaction gave a 22% yield of naphthalic anhydride—whose structural assignment is supported by IR, MS–resulting from further oxidation of the initially formed dialdehyde (Chart V).

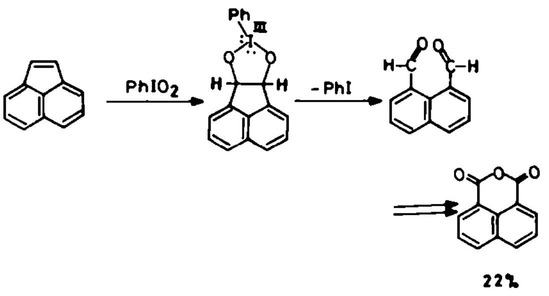

Chart V.

It is interesting to note that the action of iodoxybenzene and ozone on phenanthrene, leads to, respectively, phenanthrene quinone and diphenic aldehyde, the latter arising from the expected C–C rupture.[10] Of particular significance is the observation that, in sharp contrast to its mode of action on phenanthrene, ozone transforms phenanthrene 9-carboxylic acid to phenanthrenequinone in 67% yield by pathways that closely parallel

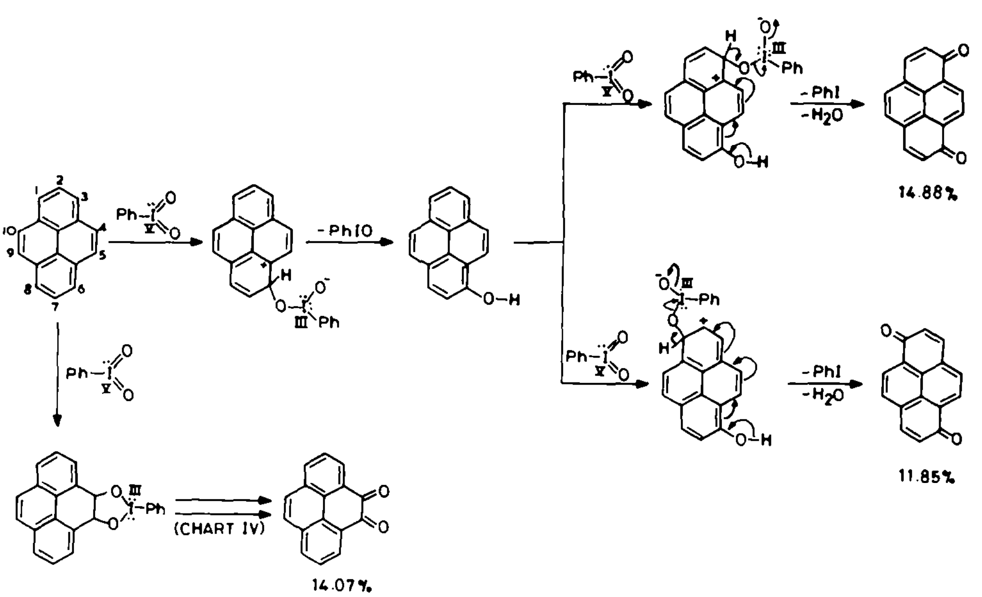

Chart VI.

the phenanthrene → phenanthrenequinone change brought about with **1**, wherein the carboxylate function brings about the C–O bond formation in preference to the C–C scission.[11]

The reaction of iodoxybenzene with pyrene in nitrobenzene at 170° for 8 hr gave interesting and useful results. A careful chromatographic analysis gave pyrene 4, 5-quinone (14%), pyrene 1, 6-quinone (12%) and pyrene 3, 6-quinone (15%). All the three crystalline quinones were characterized by MS, m.p. and possessed IR spectra identical with those reported.[12] In terms of simplicity and yields, this procedure, to the best of our knowledge, is the most advantageous for the preparation of pyrenequinones. It is of great interest to compare the reaction of ozone with pyrene and the benzo homolog, benzopyrene. Whilst the ozonization of pyrene takes an expected course, leading to π cleavage, that of the benzo homolog, benzopyrene, leads to, the exclusive formation of quinones. Thus, the reaction of iodoxybenzene with pyrene is similar to the ozonization of benzopyrene! However, the distribution of the quinones in the $PhIO_2$-pyrene reaction is quite different from that of the ozonolysis of benzopyrene. The latter reaction gives 1, 6-quinone and 3, 6-quinone in the ratio of 3:1 and only a trace of the 4, 5-quinone ($< 1\%$). This difference is a reflection of the similarities and differences in the properties of ozone and iodoxybenzene. The 4, 5-quinone arises in both cases by cyclo-addition to the 4–5 bond, the bond of lowest bond localization energy. This process competes with attack of either iodoxybenzene or ozone on atoms having the lowest atom localization energy leading to either the 1, 6 or the 3, 6 quinones (Chart VI).[13]

The reaction of two equivalents of iodoxy benzene with anthracene in nitrobenzene at 170° for 5 hr gave a 60% yield of anthraquinone, whose properties were identical to those of an authentic sample (IR, m.p., MS). It turns out that the yield of anthraquinone drops to 30% when only one equivalent of the reagent is employed. The reaction of iodoxybenzene with anthracene follows a course remarkably similar to that with ozone. The latter reagent also transforms anthracene to anthraquinone, both in protic and aprotic media. The best yields ($\sim 73\%$) are obtained when two equivalents of ozone are used. A detailed investigation of the ozonisation of anthracene has led to the delineation of two separate pathways leading to the product, namely, by electrophilic attack on positions of lowest atom localization energy (9, 10) and by transannular addition across the 9, 10-position. Indeed, the latter pathway is very significant in the ozonolysis of 9, 10-disubstituted anthracenes.[14] The absence of evidence of products arising from transannular addition of iodoxybenzene with 9, 10-dimethylanthracene (*vide infra*) coupled with the experimental observation that two equivalents of the reagent **1** are required, lead to the conclusion that the iodoxybenzene mediated anthracene → anthraquinone change follows via electrophilic attack on positions of lowest atom localization energy (Chart VII).

The reaction of iodoxybenzene with 9,

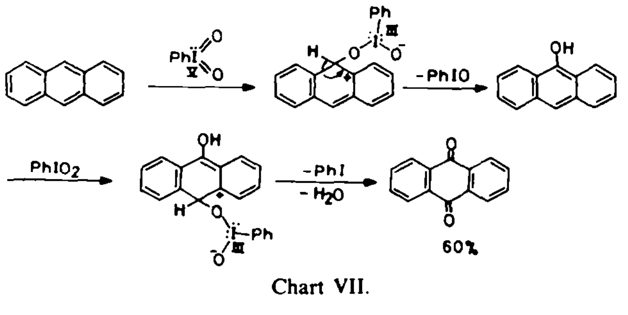

Chart VII.

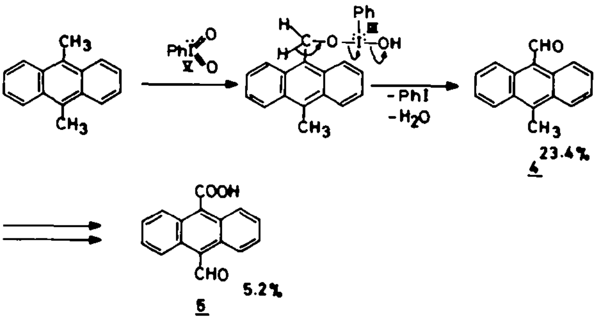

Chart VIII.

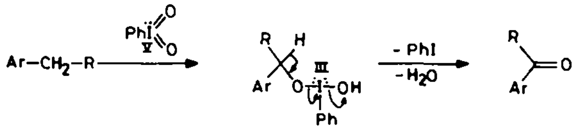

Chart IX.

10-dimethylanthracene followed a course in complete variance with that of ozone. The products isolated were, by treatment of iodoxybenzene with 9, 10-dimethylanthracene in nitrobenzene at 170°, 9-methylanthracene 10-carboxaldehyde (24%) (**4**)—whose structure was established by IR, MS, NMR, the latter identical with those reported and a 5% yield of 9–10 anthraldehydic acid (**5**) the structural assignment for which is based on IR, NMR and MS. As referred to earlier, ozonolysis of 9, 10-dimethylanthracene and related compounds proceed by prior formation of a 9–10 transannular ozonide, without oxidation of substituents! In sharp contrast, iodoxybenzene shows a preference for oxidation of aryl–alkyl groupings. The transformation of 9, 10-dimethylanthracene to **4** and **5** with iodoxybenzene can be rationalized on the basis of intermediate arising from the insertion of iodoxybenzene to the C–H σ bond either by a concerted pathway or involving intermediates (Chart VIII). That this pathway (Chart IX) is of major significance in the case of iodoxybenzene was clearly demonstrated with the oxidation of selected, activated methylene functions with iodoxybenzene in nitrobenzene at 170°, thus leading to an exceptionally easy route to ketones, particularly α-tetralone. The range and general nature of this novel reaction is reflected in the following transformations: diphenylmethane → benzophenone (75%), fluorene → fluorenone (24%) and tetralin → tetralone (45%) (Chart X). The structural assignment for the products are based on comparison with authentic samples or their derivatives. It appears therefore that the preference of ozone for π addition over C–H insertion is reversed in the case of iodoxybenzene.

An unexpected finding during the course of the above investigation was the thermal decomposition of iodoxybenzene to iodobenzene and, presumably oxygen, a pathway that competed, fortunately less effectively, with that of the reaction with the substrate. This was also inferred from the fact that whilst iodoxybenzene took about 2 hr to give a clear solution in nitrobenzene at 170°, the same was achieved within minutes when diphenylacetylene was present.

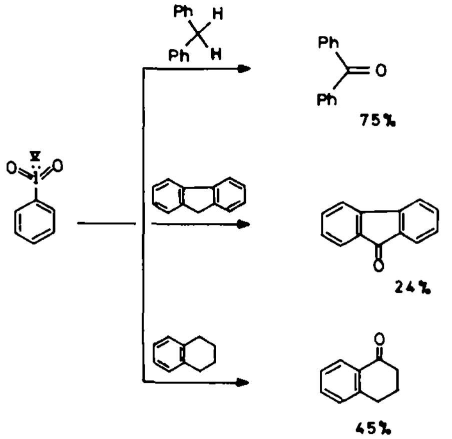

Chart X.

In this respect also, iodoxybenzene behaves like ozone, which decomposes readily according to the equation $2O_3 \rightarrow 3O_2$. This was discovered during blank reactions that endeavoured to test the stability of iodoxybenzene in nitrobenzene. No iodoxybenzene could be recovered when it was held at 170° for 5 hr in nitrobenzene. Further, such solutions had no ability to react with substrates such as diphenylacetylene. Careful chromatographic analysis of the solution arising from nitrobenzene and iodoxybenzene, held for 5 hr at 170°, showed only traces of iodobenzene. In view of the difficulties pertaining to the isolation of iodobenzene under these conditions, 4 iodoxybiphenyl (**2**) was held at 170°, in nitrobenzene for 5 hr. Chromatographic analysis yielded a 65% yield of iodobiphenyl, characterised by NMR comparison with an authentic sample. Thus, it appeared that the self destruction of **2** is more important than **1**. This was further demonstrated by reaction of 4-iodoxybiphenyl with Ph–C≡C–Ph at 170°. In sharp contrast to iodoxybenzene, and as anticipated from blank reactions, only a 30% yield of benzil could be obtained in this case! The disproportionation of either iodoxybenzene or io-

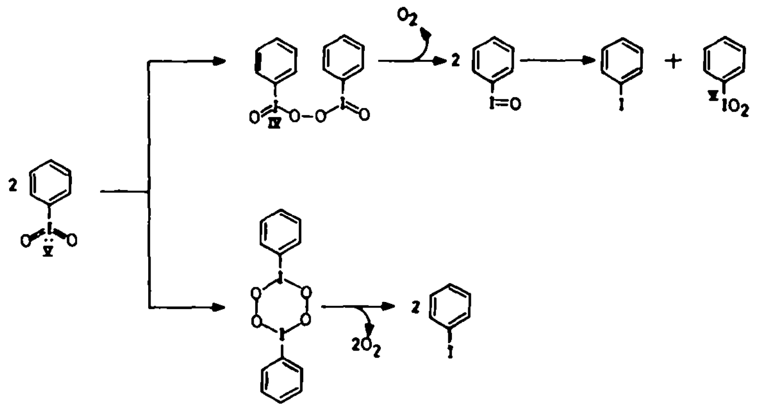

Chart XI.

doxybiphenyl could take place either in stages or via a cyclic dimeric intermediate (Chart XI).

We are hopeful that iodoxybenzene could be developed into an effective ozone equivalent by appropriate modifications that would enhance its reactivity and solubility and hopefully these could be realized by further substitution with electrophilic groupings to increase its activity and by affixing hydrophobic residues to improve the solubility.[15]

EXPERIMENTAL[16]

Iodoxybenzene (**1**)

Iodoxybenzene was prepared essentially as reported.[8] However, consistently good results could be obtained by handling smaller amounts of iodobenzene.

Dry Cl_2 was passed through an ice-salt cooled and vigorously stirred soln of iodobenzene (20.4 g, 0.1 mol) in dry $CHCl_3$ (30 ml) till an excess was present (~ 3 hr). The yellow crystalline iodobenzenedichloride was washed sparingly with $CHCl_3$, dried and used directly in the following experiment.

A mechanically stirred mixture of powdered iodobenzenedichloride (25 g, 0.09 mol), freshly prepared aqueous NaOCl (45 ml, 4M, 0.225 mol) and glacial AcOH (1 ml) was maintained at 65–75° for 1 hr, during which froathing takes place and the yellow $PhICl_2$ changes to white $PhIO_2$. The mixture was cooled in an ice bath, filtered, washed thoroughly with water followed by $CHCl_3$ (75 ml), air dried and finally in a vacuum desiccator to give 19.6 g (92%) of iodoxybenzene which could be crystallised from water, m.p. 238° (explodes). Lit.[8] m.p. 237°. IR: ν_{max}(KBr) cm^{-1}: 1465, 1430, 1078, 1040.

Reaction of iodoxybenzene with diphenyl acetylene

(a) *In nitrobenzene*: *Isolation of benzil and iodobenzene*. A stirred mixture of iodoxybenzene (0.708 g, 0.003 mol), diphenyl acetylene (0.534 g, 0.003 mol) and nitrobenzene (3 ml) was held at 170° for 5 hr, cooled and chromatographed on silica gel. Elution with hexane gave iodobenzene (0.06 g, 37%)—identical with an authentic sample on GC column OV-101—unchanged diphenylacetylene (0.39 g) and with benzene 0.140 g (82.4%) of benzil. m.p. 94–95° (lit. m.p. 94–95°). The IR was identical to that of an authentic sample. IR: ν_{max}(KBr) cm^{-1}: 1660 (C=O).

(b) *Without solvent*: *Isolation of benzil*. A mixture of diphenylacetylene (1.068 g; 0.006 mol) and iodoxybenzene (0.236 g, 0.001 mol) was held at 170° for 5 hr, cooled and chromatographed over silica gel. Elution with hexane gave unchanged diphenylacetylene (0.951 g) and with benzene: hexane: 3 : 1, 0.070 g (51%) of benzil m.p. 92°, whose properties were identical with those of an authentic sample.

Reaction of iodoxybenzene with 1, 1, 4, *4-tetraphenyl* 1, *3-butadiene*

Isolation of benzophenone. A stirred mixture of iodoxybenzene (0.236 g, 0.001 mol), 1, 1, 4, 4-tetraphenyl 1, 3-butadiene (0.180 g, 0.0005 mol) and nitrobenzene (2 ml) was held at 170° for 5 hr, cooled and chromatographed on silica gel. Elution with hexane gave unreacted butadiene (0.04 g) and with benzene 0.105 g (78.5%) of benzophenone, m.p. 45–46° (lit. m.p. 48–49.5°) whose IR was identical with that of an authentic sample. IR: ν_{max}(KBr) cm^{-1}: 1650 (C=O).

Reaction of benzoin di-anion with $PhICl_2$

Attempted isolation of cyclic intermediate **3**

Isolation of benzil. Under N_2, ice-cooling and stirring, 50% mineral oil dispersion of NaH (2.4 g, 0.05 mol) was added to a soln of benzoin (5.3 g, 0.025 mol) in dry DME (30 ml). The mixture was left stirred for 0.25 hr, admixed with $PhICl_2$, (6.9 g, 0.025 mol), left stirred overnight, neutralized with glacial acetic AcOH (3 ml), solvents evaporated and the residue chromatographed on silica gel. Elution with hexane gave iodobenzene (1.248 g, 35%), with benzene:hexane::1:1, 2.210 g (60%) of benzil and with benzene, 1.636 g of unchanged benzoin.

Reaction of iodoxybenzene with phenanthrene

Isolation of 9, *10-phenanthrenequinone*. A stirred mixture of iodoxybenzene (4.720 g, 0.02 mol), phenanthrene (1.780 g, 0.01 mol) and nitrobenzene (15 ml) was held at 170° for 5 hr, cooled and chromatographed on silica gel. Elution with hexane gave unreacted phenanthrene (0.160 g) and with benzene: EtOAc (19:1), 0.870 g (46%) of 9, 10-phenanthrene quinone which was crystallised from EtOH m.p. 209° (lit.[17] m.p. 209–11°). The IR spectrum was identical to that of an authentic sample. IR: ν_{max}(KBr) cm^{-1}: 1670 (C = O).

Reaction of iodoxybenzene with acenaphthylene

Isolation of 1, *8-naphthalic anhydride*. A stirred mixture of iodoxybenzene (1.180 g, 0.005 mol), freshly sublimed acenaphthylene[18] (0.760 g, 0.005 mol) and nitrobenzene (5 ml) was held at 170° for 5 hr, cooled and the mixture chromatographed over silica gel. Elution with benzene: hexane (8:2) gave 0.2 g (22%) of naphthalic anhydride which was crystallised from *o*-dichlorobenzene m.p. 270° (lit.[19] m.p. 273°). IR: ν_{max}(KBr) cm^{-1}: 1790, 1740, 1720 (C=O); Ms: *m*/*e*: 198 (M^+), 182 ($M^+ - O$), 154 ($M^+ - CO_2$), 126 (M^+–(CO–O–CO)).

Reaction of iodoxybenzene with pyrene

Isolation of pyrene quinones. A mixture of iodoxybenzene (6.06 g, 0.026 mol), pyrene (1.73 g, 0.098 mol) and nitrobenzene (15 ml) was held at 170° for 8 hr, cooled and chromatographed on silica gel. Elution with hexane gave unreacted pyrene (0.55 g), benzene: EtOAc (98:2) 0.190 g (14%) of pyrene 3, 6-quinone which on crystallisation from benzene gave red crystals m.p. 265–267° (lit.[20] m.p. 270°). IR: ν_{max}(KBr) cm^{-1}: 1760, 1745, 1670 (C = O); Ms: *m/e*: 232 (M$^+$), 204 (M$^+$–CO), 176 (M$^+$–2CO).

Further elution with benzene: EtOAc (19:1) gave 0.160 g (12%) of pyrene 1, 6-quinone which was crystallised from benzene m.p. 300° (lit.[20] m.p. 309°). IR: ν_{max}(KBr) cm^{-1}: 1760, 1745, 1630 (C = O); Ms: *m/e*: 232 (M$^+$), 204 (M$^+$–CO), 176 M$^+$–2CO).

Finally elution with benzene: EtOAc (9:1) gave 0.201 g (15%) of pyrene 4–5 quinone which on crystallisation from benzene:hexane gave red crystals m.p. 308° (lit.[20] m.p. 310°). IR: ν_{max}(KBr) cm^{-1}: 1745, 1630 (C = O); Ms: *m/e*: 232 (M$^+$), 204 (M$^+$–CO), 176 (M$^+$–2CO). All the three quinones exhibited IR identical with those that reported.[12]

Reaction of iodoxybenzene with anthracene

Isolation of 9, 10-*anthraquinone*. A stirred mixture of iodoxybenzene (0.944 g, 0.004 mol), anthracene (0.356 g, 0.002 mol) and nitrobenzene (5 ml) was held at 170° for 5 hr, cooled, and chromatographed on silica gel. Elution with benzene gave 0.240 g (60%) of anthraquinone which on crystallisation from benzene gave pale yellow needles m.p. 283° (lit. m.p. 284–85°), the IR of which was identical to that of an authentic sample. IR: ν_{max}(KBr) cm^{-1}: 1662 (C=O); Ms: *m/e*: 208 (M$^+$), 180 (M$^+$–CO), 152 (M$^+$–2CO).

Reaction of iodoxybenzene with 9, 10-*dimethylanthracene*

Isolation of 9-methylanthracene-10-*carboxaldehyde* 4 *and* 9, 10-*anthraldehydic acid* 5. A stirred mixture of iodoxybenzene (1.416 g, 0.006 mol), 9, 10-dimethyl anthracene (1.236 g, 0.006 mol) and nitrobenzene (5 ml) was held at 170° for 5 hr, cooled and chromatographed on silica gel. Elution with hexane gave 9, 10-dimethylanthracene (0.2 g) and with benzene: hexane (9:1) 0.309 g (23.4%) of 9-methylanthracene 10-carboxaldehyde m.p. 171–72°. (lit.[21] m.p. 171–72°). IR: ν_{max}(KBr) cm^{-1}: 1630 (C=O); NMR: δ (CDCl$_3$): 11.4 (s, 1H, $C\underline{H}O$), 9.00–8.75 (m, 2H, aromatic 1,8), 8.35–8.1 (m, 2H, aromatic 4, 5), 7.7–7.3 (m, 4H, aromatic 2, 3, 6 and 7), 3.2 (s, 3H, $C\underline{H}_3$). The above spectrum was in excellent agreement with that of an authentic sample.[22] Ms: *m/e*: 220 (M$^+$), 191 (M$^+$–CHO).

Further elution with benzene gave 0.078 g (5.2%) of 9, 10-anthraldehydic acid, m.p. 280° (lit.[23] m.p. 286–87°). IR: ν_{max}(KBr) cm^{-1}: 1660 (C=O); NMR: δ (CDCl$_3$): 11.4 (s, 1H, $C\underline{H}O$), 8.8–8.69 (m, 2H, aromatic 1, 8), 8.42–8.2 (m, 2H, aromatic 4, 5), 7.95–7.24 (m, 4H, aromatic 2, 3, 6 and 7).

Reaction of iodoxybenzene with diphenylmethane

Isolation of benzophenone. A stirred mixture of iodoxybenzene, (0.236 g, 0.001 mol) and diphenylmethane (0.840 g, 0.005 mol) was held at 170° for 5 hr, cooled and chromatographed on silica gel. Elution with hexane gave unchanged diphenylmethane (0.74 g) and with benzene 0.081 g (75%) of benzophenone, m.p. 46–47° (lit. m.p. 48–49.5°) whose IR was identical to that of an authentic sample. IR: ν_{max}(KBr) cm^{-1}: 1650 (C=O).

Reaction of iodoxybenzene with fluorene

Isolation of fluorenone. A stirred mixture of iodoxybenzene (0.708 g, 0.003 mol), fluorene (0.498 g, 0.003 mol) and nitrobenzene (3 ml) was held at 150°, cooled and chromatographed on silica gel. Elution with hexane gave unchanged fluorene (0.07 g) and with benzene: hexane (3:2), 0.110 g (24%) of fluorenone, m.p. 82–84° (lit. m.p. 82–85°) whose IR was identical to that of an authentic sample.

Reaction of iodoxybenzene with tetralin

Isolation of α-tetralone. A stirred mixture of iodoxybenzene (0.708 g, 0.003 mol) and tetralin (1.980 g, 0.015 mol) was held at 170° for 5 hr, cooled and chromatographed on silica gel. Elution with hexane gave unchanged tetralin (1.86 g) and with benzene:hexane (1:1) 0.06 g (45%) of α-tetralone characterised as its semicarbazone m.p. 211° (lit. m.p. 217°). IR: ν_{max}(neat) cm^{-1}: 1675 (C=O): Ms: *m/e*: (of semicarbazone), 204 (M$^+$ + 1), 203 (M$^+$), 159 (M$^+$–CONH$_2$), 144 (M$^+$–NH–CONH$_2$).

4-Iodoxybiphenyl (2). In the present work, 4-iodoxybiphenyl was prepared by procedure similar to that for iodoxybenzene. In the literature it is prepared by peracetic acid oxidation of iodobiphenyl.

Concentrated HNO$_3$ (4.8 ml) was added over 1 hr, to a stirred mixture of biphenyl (38.5 g, 0.25 mol), glacial AcOH (100 ml), concentrated H$_2$SO$_4$ (27.5 ml) and I$_2$ (31.8 g, 0.3 mol), diluted with water, steam distilled to remove biphenyl, the residue filtered, dried and crystallised from ethanol to give 45.0 g (64.3%) of 4-iodobiphenyl, m.p. 113° (lit.[24] m.p. 113°).

Dry Cl$_2$ was passed through a vigorously stirred and ice-salt cooled soln of 4-iodobiphenyl (28 g, 0.1 mol) in dry CHCl$_3$ (30 ml) till excess was present (~ 2.5 hr), the precipitated yellow orange 4-iodobiphenyldichloride collected, washed with chilled CHCl$_3$ and dried (yield 26 g, 74%), m.p. 85° (lit.[25] m.p. 85–87°).

A mechanically stirred mixture of powdered, freshly prepared 4-iodobiphenyldichloride (26 g, 0.07 mol), NaOCl (60 ml, 4M, 0.3 mol) and glacial AcOH (1 ml) was held at 70° for 1.5 hr, cooled in ice, filtered, washed with water, CHCl$_3$ and dried to give 12 g (52%) of **2** m.p. 213° (explodes!) (lit.[26] m.p. 210°).

Thermolysis of 4-iodoxybiphenyl in nitrobenzene

Isolation of iodobiphenyl. A stirred mixture of 4-iodoxybiphenyl (0.210 g, 0.007 mol) and nitrobenzene was held at 170° for 5 hr. Complete soln was attained in 2 hr. The mixture was cooled and chromatographed over silica gel. Elution with hexane gave 0.140 g (72%) of 4-iodobiphenyl whose structure was established by comparison of IR and NMR with an authentic sample.

Reaction of 4-iodoxybiphenyl with diphenylacetylene

Isolation of 4-iodobiphenyl and benzil. A stirred mixture of 4-iodoxybiphenyl (1.248 g, 0.004 mol), diphenylacetylene (0.712 g, 0.004 mol) and nitrobenzene (15 ml) was held at 170° for 5 hr, cooled and chromatographed on silica gel. Elution with hexane gave 1.1 g (98%) of 4-iodobiphenyl and with benzene: hexane::3:1, 0.290 g (34.5%) of benzil.

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[2] Data is not available in the literature to thermochemically compute the ΔH_f^0 of iodoxybenzene, on the basis of group additivity principle. The expectation that the ΔH_f^0 of iodoxybenzene could be substantially positive is based on several considerations. Iodoxybenzene could be construed as arising from addition of oxygen to iodobenzene. The ΔH_f^0 of iodobenzene is +27 kcal mol^{-1}, an exceptionally high value, particularly when compared with the ΔH_f^0 of the related halogen family: Fluorobenzene, −36.13; chlorobenzene, 2.58; bromo benzene, 14.5. Oxidation of iodobenzene to iodoxybenzene could be expected to lead to a further higher value (D. R. Stull, E. R. Westrum and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*. Wiley, New York (1969). Salts of iodic acid, closely resembling iodoxybenzene, has been demonstrated to be an effective electrophile. It accepts lone pairs to form intermediates involving d-orbitals which readily fragment

with the transfer of $2e^-$ from the substrate resulting in a facile $I^V \rightarrow I^{III}$ change. (T. W. Evans and W. M. Dehn, *J. Am. Chem. Soc.* **52**, 3649 (1930).

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[6] Letter dated July 20, 1982. We are most grateful to Prof. Barton for his suggestions contained in his reply dated August 16, 1982, particularly pertaining to the study of the reaction of pyrene with iodoxybenzene which was subsequently done on his advice.

[7] "....... while it is slightly soluble in water, it is still less so in chemically inert organic solvents. These refractory qualities are shared by all the iodoxy compounds of which some seventy are described in Willgerodt's monograph of 1914 ("Die Organischen Verbindugen mit Mehrwertigem Iod" Enke, Stuttgart) and so they are characteristic of the group, $-IO_2$...." (I. Masson, E. Race and F. E. Pounder, *J. Chem. Soc.* 1669 (1935).

[8] H. J. Lucas and E. R. Kennedy *Org. Syn. Coll.* Vol. III, p. 482; H. J. Lucas and E. R. Kennedy *Ibid.* Vol. III, p. 485; M. W. Formo and J. R. Johnson, *Ibid.* Vol. III, p. 486.

[9] Interestingly, such an intermediate is postulated in the transformation of pyrocatechols to *o*-quinones with PhI $(OAc)_2$.

[10] The monumental, 2 volume treatise by P. S. Bailey (*Ozonation in organic chemistry* Vol. I, 1978; Vol. II., 1982, Academic Press, New York) must be the major source of information pertaining to the properties of ozone. This help is acknowledged. Wherever appropriate, secondary references have been taken from these books.

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[15] Reaction of iodoxybenzene with camphene gave a mixture of carbonyl containing products. The same was the outcome when $PhIO_2$ was reacted with excess refluxing cyclohexene. No reaction was observed with dicyclopentadiene and indene.

[16] M.p. are not corrected. IR spectra were recorded in a PE 580 instrument as KBr discs. NMR spectra were obtained on 10–15% solutions in $CDCl_3$ on a FT R600 instrument. The chemical shifts are reported in ppm with TMS at 0.00 as internal standard. Ms were obtained in a Jeol instrument. Silicagel (Acme) was used for TLC and column chromatography was done on silica gel (Acme 100–200 mesh). Reactions are monitored wherever possible, by TLC.

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