51. *Oxidations with Phenyl Iodosoacetate. Part VI.* The Oxidation of Some Phenols Containing Electron-attracting Substituents.*

By A. R. FOX and K. H. PAUSACKER.

Several *p*-alkoxycarbonyl- or *p*-nitro-phenols have been oxidised with phenyl iodosoacetate in benzene solution; 4-alkoxycarbonyl- or 4-nitro-2-iododiphenyl ethers were formed. *p*-Nitrophenol also yielded 5-hydroxy-2 : 4'-dinitrodiphenyl ether. In acetic acid solution, *p*-nitrophenol gave a compound believed to be 2-hydroxy-5-nitrodiphenyliodonium acetate. The latter could readily be rearranged to 2-iodo-4-nitrodiphenyl ether.

SIEGEL and ANTONY [1] found that oxidation, by 2 equivalents of phenyl iodosoacetate, of a number of phenols gave the corresponding 4-acetoxyphenol when hydrogen or bromine was in the *para*-position. When four equivalents of oxidising agent were used, the corresponding *p*-benzoquinones were formed. 4-Hydroxybenzyl acetates were obtained from 4-alkylphenols.

Little information is available concerning the oxidation of phenols containing electron-attracting substituents but it has been shown that 2 : 6-disubstituted 4-nitrophenols are oxidised by lead tetra-acetate to 2 : 6-disubstituted *p*-benzoquinones [2] and that *o*-, *m*-, and *p*-nitro-, and *o*-carboxy-phenol do not react with lead tetra-acetate at room temperature.[3]

When *p*-nitrophenol was oxidised with phenyl iodosoacetate in benzene at room temperature, an amorphous precipitate was obtained and two compounds (A and B) could be isolated by chromatography of the solution on alumina or silica. The yield of compound A is increased by use of a solvent more polar than benzene; thus the yields in benzene, ether, chlorobenzene, and nitrobenzene are 6, 7, 14, and 38%, respectively. When acetic acid was the solvent, only 6% of compound A was formed together with 84% of a bright yellow precipitate (C).

Compound A, $C_{12}H_8O_3NI$, is insoluble in alkali, and yields *p*-aminodiphenyl ether on reduction. For comparison, the three *x*-iodo-4'-nitrodiphenyl ethers, were prepared by the condensation of *p*-fluoronitrobenzene with the appropriate iodophenol.[4] Compound A is not identical with any of these compounds and was proved to be 2-iodo-4-nitrodiphenyl ether, which was synthesised from phenol and 1-chloro-2-iodo-4-nitrobenzene (see ref. 4*b* for an alternative synthesis).

The unsubstituted phenyl group of compound A must come from phenyl iodosoacetate and not from the solvent (benzene) as the same compound, and compound B, were formed

---

* Part V, *J.*, 1954, 4502.

[1] Siegal and Antony, *Monatsh.*, 1955, **86**, 292.

[2] Jones and Kenner, *J.*, 1931, 1842.

[3] Wessely, Lauterbach-Keil, and Sinwel, *Monatsh.*, 1950, **81**, 811.

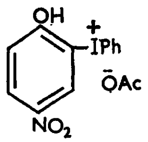
[4] (*a*) Rarick, Brewster, and Dains, *J. Amer. Chem. Soc.*, 1933, **55**, 1289; (*b*) Brewster and Strain, *ibid.*, 1934, **56**, 117.

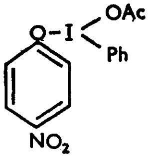
in chlorobenzene. Furthermore, a compound presumed to be 3-chloro-2′-iodo-4′-nitrodiphenyl ether and compound B were formed when *p*-nitrophenol was oxidised with *m*-chlorophenyl iodosoacetate in benzene. The iodine atom must also come from the phenyl iodosoacetate and not from its reduction product (iodobenzene) for approximately the same yield of compound A was obtained when a large excess of iodobenzene was added. In addition, *p*-nitrodiphenyl ether was kept for one month in benzene with benzoyl peroxide and the only possible iodinating agents, (*a*) iodine, (*b*) iodobenzene, and (*c*) phenyl iodosoacetate. No reaction was observed, even when the mixture (*a*) was irradiated with ultraviolet light for 36 hours.

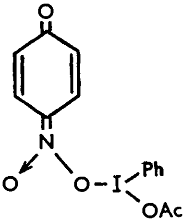
The oxidation of 3 : 4-dinitrophenol, and methyl and ethyl *p*-hydroxybenzoate with phenyl iodosoacetate in benzene solution gave compounds, believed to be 2-iodo-4 : 5-dinitrodiphenyl ether, 2-iodo-4-methoxycarbonyldiphenyl ether, and 4-ethoxycarbonyl-2-iododiphenyl ether, respectively. Compounds analogous to compound B were not isolated. 2 : 6-Dichloro-4-nitrophenol gave 2 : 6-dichloro-*p*-benzoquinone.

3-Methoxy-4-nitrophenol, *p*-ethoxycarbonylphenol, and 3 : 4-dinitrophenol (on heating) were oxidised in acetic acid solution to compounds which are believed to be 2-iodo-5-methoxy-4-nitrodiphenyl ether (95%), 4-ethoxycarbonyl-2-iododiphenyl ether (88%) and 2-iodo-4 : 5-dinitrodiphenyl ether (87%). The oxidation of *p*-nitrophenol with phenyl iodosobenzoate, in benzene saturated with benzoic acid, yielded compounds A and B only.

Compound C (m. p. 156°), $C_{14}H_{12}O_5NI$, rearranged to Compound A, in 88—95% yield, when heated above its melting point, or when refluxed with acetic acid, benzene, or ethanol. Its solution in hot sodium hydroxide was deep purple; this colour was discharged on acidification but was regenerated on basification. Only compound A (33%), which does not give these colour changes, could be isolated from the mixture although the odour suggested that iodobenzene was formed. A good yield (88%) of compound A was obtained when compound C was treated with diazomethane in dioxan.


(I)

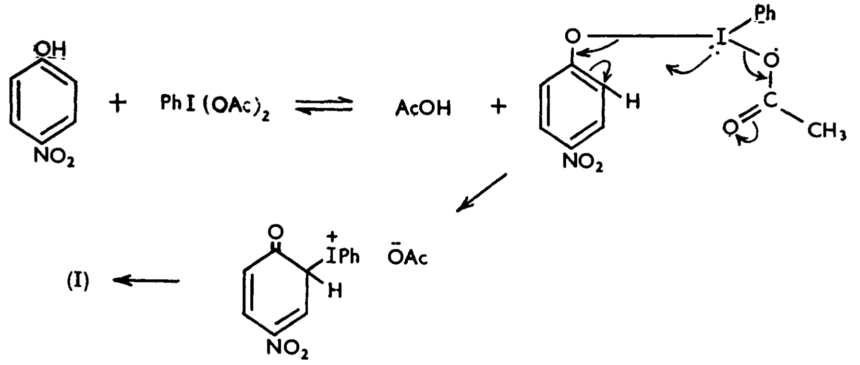

(II)


(III)

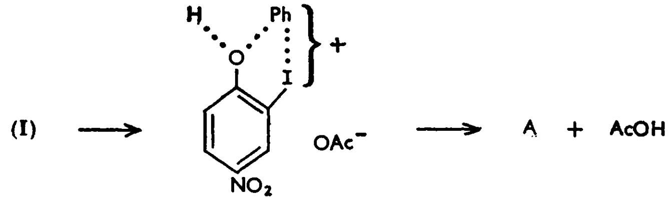
Three structural formulæ (I—III) were considered for compound C but 2-hydroxy-5-nitrodiphenyliodonium acetate (I) appears to be the only one that can explain (*a*) its yellow colour, (*b*) its insolubility in common organic solvents, (*c*) its reaction with hydrochloric acid to form a compound, $C_{12}H_9O_3NClI$, whose formula indicates that an acetoxy-radical has been replaced by chlorine, and (*d*) its failure to liberate iodine from acidified potassium iodide.

Dr. A. R. H. Cole has kindly measured the infrared absorption spectrum of compound C and has reported that there is no band between 1600 and 1700 cm.$^{-1}$ where the quinone carbonyl absorbs, thus eliminating formula (III). The carbonyl group of the acetate is shown by absorption near 1710 cm.$^{-1}$. There is also a very strong band, suggestive of a nitro-group, at 1570 cm.$^{-1}$ and no hydroxyl absorption. This evidence tends to support formula (II) rather than (I), but Dr. Cole points out that the absence of hydroxyl absorption does not necessarily mean that this group is not present for the sample was studied as a solid (mull) and the hydroxyl group would be involved in intermolecular hydrogen bonding which tends to broaden the hydroxyl absorption. In certain cases (*e.g.*, carboxylic acids), this makes the hydroxyl group barely detectable.

Compound C is probably formed by intramolecular rearrangement of the " ester " already postulated [5] as an intermediate in the reaction of phenols with phenyl iodosoacetate. The intramolecular nature seems likely as a mixture of *p*-nitrophenol and anisole reacts with phenyl iodosoacetate to form compound C (90%).



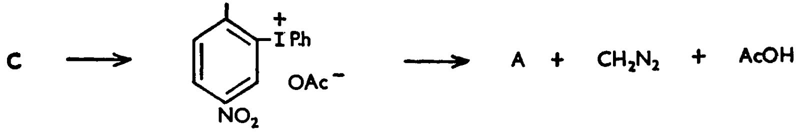
The rearrangement of compound C to compound A, either when heated alone or in inert solvents, appears to be an intramolecular rearrangement involving a phenyl cation :



As 3-methoxy-4-nitrophenol gives 2-iodo-5-methoxy-4-nitrodiphenyl ether under identical conditions, it is suggested that an intermediate analogous to compound C is formed initally, and that it rearranges very readily owing to increased electron density on the phenolic oxygen atom.

The reaction of compound C with sodium hydroxide may involve some thermal rearrangement (probably *via* the phenoxide ion) but nucleophilic attack of the hydroxide ion should also take place to form 4-nitrocatechol and iodobenzene. The colour observed would then be due to the reaction of alkali with either 4-nitrocatechol or its oxidation products. The other possible reaction products, *viz.*, phenol and 2-iodo-4-nitrophenol, are not considered likely to arise as it has been shown [9] that *o*- and *m*-nitrodiphenyliodonium bromide rearrange to form *o*- and *m*-bromonitrobenzene and iodobenzene instead of *o*- and *m*-iodonitrobenzene and bromobenzene.

The ease of rearrangement of compound C to compound A during attempted methylation with diazomethane in dioxan may be due to the intermediate formation of a phenoxide ion which would be expected to rearrange readily, *i.e.*,



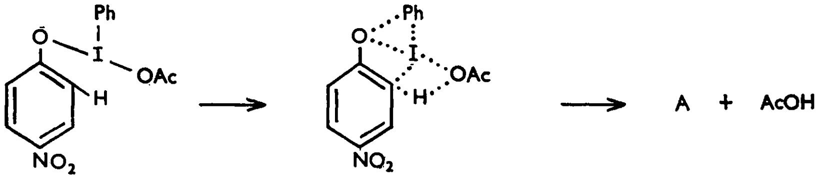
This is in accord with the mechanism [10] proposed for the reaction of phenols with diazomethane.

It seemed possible that the formation of compound A when the oxidation is carried out in benzene at room temperature involves the intermediate production of compound C. However, compound C is sparingly soluble in benzene at room temperature and, when

---

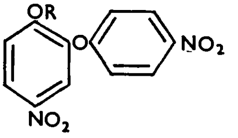
[5] (*a*) Cordner and Pausacker, *J.*, 1953, 102; (*b*) Pausacker, *J.*, 1953, 107.

suspended in this solvent, does not rearrange to compound A under the conditions of oxidation. It is therefore suggested that compound A is formed by intramolecular rearrangement of the initial " ester," *i.e.*,

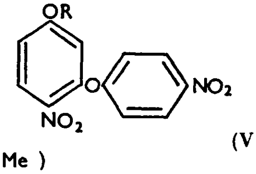


Compound B (14%; m. p. 121°), $C_{12}H_8O_6N_2$, is a bright yellow compound which gives a deep red solution in alkali, and forms only a monoacetate and a monomethyl ether. Although many previous workers [6] have found that diphenyls are formed when different phenols are oxidised by a wide variety of reagents this is apparently the first recorded example of diphenyl ether formation.

Of the two likely structures (IV*a* and V*a*) the former is already known and is not identical with compound B, which is provisionally assigned structure (V*a*). Attempts to prepare compound (V*b*) by the condensation of 5-methoxy-2-nitrophenol with either *p*-chloro- or *p*-fluoro-nitrobenzene were unsuccessful although compound (IV*a*) was readily prepared [7] by the condensation of 2-methoxy-5-nitrophenol with *p*-chloronitrobenzene.



(IV)



(V)

(*a*, R = H ; *b*, R = Me)

This difference is ascribed to the decreased electron-availability on the attacking phenoxide ion.

When the methyl ether of compound B was reduced, and the product deaminated, a low yield of *m*-methoxydiphenyl ether was obtained. A marked similarity was also noted between the ultraviolet absorption spectra of compound B, its methyl ether, 5-methoxy-2-nitrodiphenyl ether, and 3'-methoxy-4-nitrodiphenyl ether in ethanol (see Table). These facts appear to confirm structure (V*a*) for compound B.

	$\lambda_{max.}$ (Å)	log ε	$\lambda_{min.}$ (Å)	log ε
Compound B	2900	4·11	2550	3·91
Methyl ether of B	3000	4·13	2500	3·82
5-Methoxy-2-nitrodiphenyl ether	2950	3·84	2580	3·71
3'-Methoxy-4-nitrodiphenyl ether	3050	4·08	2480	3·55

The following mechanism is proposed for the formation of compound B :

$$\begin{tikzcd}
p\text{-}NO_2\cdot C_6H_4\cdot OH + PhI(OAc)_2 \arrow[r, rightleftharpoons] & p\text{-}NO_2\cdot C_6H_4\cdot OI(OAc)Ph + AcOH \arrow[d] \\
B + PhI + AcOH & p\text{-}NO_2\cdot C_6H_4\cdot O\cdot + PhI\cdot OAc \arrow[l, "p\text{-}NO_2\cdot C_6H_4\cdot OH"']
\end{tikzcd}$$

The first stage is identical with that already assumed in the formation of compound A, the second involves homolytic fission of the " ester," [5, 8] and the third the attack of the

---

[6] Wacek and Kessel, *Monatsh.*, 1954, **85**, 1; Albert, *J. Amer. Chem. Soc.*, 1954, **76**, 4983; Cavill, Cole, Gilham, and McHugh, *J.*, 1954, 2785; Burton and Hopkins, *J.*, 1952, 2445; Moore and Waters, *J.*, 1954, 243; Bacon, Grime, and Munro, *J.*, 1954, 2275; Cosgrove and Waters, *J.*, 1951, 388, 1726.

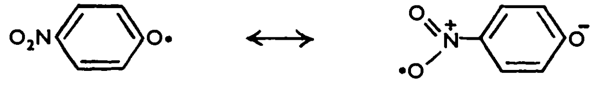
[7] Buchan and Scarborough, *J.*, 1934, 705.

[8] Pausacker, *J.*, 1953, 1989.

[9] Beringer, Brierley, Drexler, Gindler, and Lumpkin, *J. Amer. Chem. Soc.*, 1953, **75**, 2708.

[10] Eistert, " Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, 1947, p. 513.

p-nitrophenoxy-radical (VI) on *p*-nitrophenol in the position *ortho* to the nitro-group. It is suggested that (VI) is nucleophilic owing to contributing forms of structure (VI*a*) to the resonance hybrid.



(VI) (VI*a*)

EXPERIMENTAL

Oxidation of p-*Nitrophenol in Benzene*.—Solutions of *p*-nitrophenol (5·4 g.) and phenyl iodosoacetate (9·7 g.) in dry, thiophen-free benzene (300 ml. and 450 ml., respectively) were mixed and set aside at room temperature until reaction was complete (48 hr.). A brown amorphous precipitate (2·0—2·2 g.) (Found: C, 51·4—53·3; H, 2·4—2·9; N, 7·7—8·0; I, 5·1—7·8%) was filtered off, and the filtrate was chromatographed on silica. The first (colourless) band yielded compound A (0·8 g.) which crystallised as needles, m. p. 61°, from methanol or light petroleum (b. p. 60—80°) (Found: C, 42·2; H, 2·3; N, 4·2; I, 36·9. Calc. for $C_{12}H_8O_3NI$: C, 42·2; H, 2·3; N, 4·1; I, 37·2%). Its m. p. was undepressed with a sample of 2-iodo-4-nitrodiphenyl ether (for preparation, see below). The second (yellow) band yielded *compound B* (0·6 g.) which crystallised as yellow plates, m. p. 120°, from ethanol (Found: C, 52·3; H, 3·0; N, 9·9. $C_{12}H_8O_6N_2$ requires C, 52·2; H, 2·9; N, 10·1%). The *monoacetyl derivative* formed brown prisms (from ethanol), m. p. 126° (Found: C, 53·3; H, 3·5; N, 8·7; Ac, 13·7. $C_{14}H_{10}O_7N_2$ requires C, 52·9; H, 3·1; N, 8·8; Ac, 13·5%), and the *monomethyl ether*, colourless needles (from ethanol), m. p. 128° (Found: C, 53·8; H, 3·7; N, 10·0; OMe, 9·0. $C_{13}H_{10}O_6N_2$ requires C, 53·8; H, 3·4; N, 9·7; 1 OMe, 10·7%).

When only compound A was required, alumina was used as an adsorbent, as it gave a more rapid and efficient separation from compound B which was strongly adsorbed and could only be removed by dissecting the column and extracting the alumina with ethanol.

With *m*-chlorophenyl iodosoacetate as oxidising agent the products were (*a*) benzene-insoluble material (2·0 g.), (*b*) *3′(?)-chloro-2-iodo-4-nitrodiphenyl ether* (1·0 g.), needles (from methanol), m. p. 64° (Found: N, 3·4; Cl, 9·7; I, 34·1. $C_{12}H_7O_3NClI$ requires N, 3·7; Cl, 9·3; I, 33·9%), and (*c*) compound B (0·4 g.), m. p. and mixed m. p. 119°.

m-*Chlorophenyl Iodosoacetate*.—Hydrogen peroxide (39%; 12 ml.) and acetic anhydride (53 ml.) were stirred for 4 hr. at 40°. *m*-Chloroiodobenzene (10 g.) was added to the solution which slowly deposited *m*-chlorophenyl iodosoacetate (15 g.; m. p. and mixed m. p. 154°). This is an adaptation of the method given for the preparation of phenyl iodosoacetate.[5b]

Synthesis and Reactions of Compound A.—2-Chloro-5-nitroacetanilide (3·5 g.) and copper[11] (0·1 g.) were added to a mixture of phenol (5·3 g.) and potassium hydroxide (3·6 g.) which had previously been heated to 140°. After being heated at 150—160° (0·5 hr.), the mixture was poured into a solution of sodium hydroxide (5 g.) in ice-water (50 ml.). The mixture was extracted with ether and *2-acetamido-4-nitrodiphenyl ether* (2·5 g.) was obtained as needles (from methanol), m. p. 123° (Found: C, 61·9; H, 4·1; N, 10·4. $C_{14}H_{12}O_4N_2$ requires C, 61·7; H, 4·4; N, 10·3%). When this amide (2·2 g.) was refluxed with hydrochloric acid (20%; 20 ml.) and then basified, 2-amino-4-nitrodiphenyl ether (m. p. 106°; lit.[4b] 107°) was obtained. After diazotisation the product was treated with potassium iodide,[12] and 2-iodo-4-nitrodiphenyl ether (60%) was obtained as needles (from methanol), m. p. 61° (lit.[4b] 61°). Its m. p. was undepressed on admixture with compound A.

Compound A (0·58 g.) was hydrogenated with Raney nickel (5 ml.) and potassium hydroxide (0·3 g.) in ethanol (25 ml.) to give a 20% yield of 4-aminodiphenyl ether (m. p. and mixed m. p. 81°).

2-, 3-, *and 4-Iodo-4′-nitrodiphenyl Ether*.—*o*-Iodophenol (1·8 g.) was heated with *p*-fluoronitrobenzene (1·2 g.) and potassium hydroxide (0·5 g.) at 160° for 0·5 hr. The mixture was poured into sodium hydroxide solution and 2-iodo-4′-nitrodiphenyl ether, m. p. 104° (lit.[4b] 104°), was obtained. *3-Iodo-4′-nitrodiphenyl ether*, yellow needles (from methanol), m. p. 84° (Found: C, 42·1; H, 2·4; N, 4·0. $C_{12}H_8O_3NI$ requires C, 42·2; H, 2·3; N, 4·1%), and 4-iodo-4′-nitrodiphenyl ether, m. p. 64° (lit.[4b] 70°), were prepared similarly. The latter liquefied on admixture with compound A.

---

[11] Brewster and Groening, *Org. Synth.*, 1946, Coll. Vol. II, 445.

[12] Cf. Bennett and Turner, *J.*, 1926, 476.

Degradation of Compound B.—Compound B (1·15 g.) was hydrogenated in ethanol (25 ml.) with Raney nickel (5 ml.), and the crude amine (0·88 g.) was diazotised (0·5°) in concentrated hydrochloric acid (10 ml.). A 20-molar excess of hypophosphorous acid (50%) was cooled to 0° and added to the diazonium solution which was kept at 2° (48 hr.). The reaction mixture was extracted with ether, and the extract was washed several times with alkali, and then with water. After distillation, *m*-methoxydiphenyl ether (b. p. 145°/3 mm.; lit.[13] b. p. 175°/20 mm.) was obtained (Found: C, 77·8; H, 6·1; O, 15·4. Calc. for $C_{13}H_{12}O_2$: C, 78·0; H, 6·0; O, 16·0%). It could not be crystallised. *o*-Methoxydiphenyl ether [14] has m. p. 77°.

3-Methoxy-4'-nitrodiphenyl Ether.—This compound was prepared from *m*-methoxyphenol and *p*-chloronitrobenzene by Brewster and Groening's method.[11] *3-Methoxy-4'-nitrodiphenyl ether* crystallised as plates (from ethanol), m. p. 88° (Found: C, 64·2; H, 4·5; N, 5·7 $C_{13}H_{11}O_4N$ requires C, 63·7; H, 4·5; N, 5·7%).

Other Oxidations in Benzene.—(*a*) 3 : 4-Dinitrophenyl (4·6 g.), phenyl iodosoacetate (8·1 g.), and benzene (400 ml.) were refluxed (9·25 hr.) until the reaction was complete. The solution was chromatographed on alumina; the first (yellow) band yielded 2(?)-*iodo*-4 : 5-*dinitrodiphenyl ether* (0·71 g.) as light yellow needles (from *cyclo*hexane), m. p. 115° (Found: C, 37·7; H, 2·1; N, 7·1; O, 21·0; I, 33·0. $C_{12}H_7O_5N_2I$ requires C, 37·3; H, 1·8; N, 7·3; O, 21·2; I, 32·9%).

(*b*) (With R. W. RISEBOROUGH). The oxidation of methyl *p*-hydroxybenzoate (3·8 g.) with phenyl iodosoacetate (1 and 2 mol.) in benzene at room temperature gave 2(?)-*iodo*-4-*methoxycarbonyldiphenyl ether* (1·9 g. and 3·1 g., respectively), m. p. 63° (from methanol) (Found: C, 47·5; H, 3·2; O, 13·9; I, 35·2. $C_{14}H_{11}O_3I$ requires C, 47·5; H, 3·1; O, 13·6; I, 35·9%).

(*c*) (With R. W. RISEBOROUGH). Similarly the oxidation of ethyl *p*-hydroxybenzoate (4·2 g.) gave 4-*ethoxy*-2(?)-*iododiphenyl ether* (1·6 g. and 3·1 g., respectively), b. p. 215°/1·3 mm. (Found: C, 49·3; H, 3·6. $C_{15}H_{13}O_3I$ requires C, 49·6; H, 3·9%). When this compound and the compound obtained in section (*b*) above were hydrolysed with aqueous-alcoholic sodium hydroxide, 4-*carboxy*-2(?)-*iododiphenyl ether* (70%) was obtained as needles (from methanol), m. p. 160° (Found: C, 46·1; H, 2·9; O, 14·3. $C_{13}H_9O_3I$ requires C, 45·9; H, 2·9; O, 14·1%).

(*d*) (By JOAN MITCHELL). 2 : 6-Dichloro-4-nitrophenol (8·8 g.) and phenyl iodosoacetate (16·1 g.) in benzene (1 l.) were kept at 45° for 50 days. The solution was chromatographed on alumina; the first (red) band yielded 2 : 6-dichloro-1 : 4-benzoquinone (crude yield, 3·55 g.), which crystallised from light petroleum (b. p. 55—100°) as orange needles, m. p. 123° (Found: C, 40·8; H, 1·4; Cl, 40·3. Calc. for $C_6H_2O_2Cl_2$: C, 40·7; H, 1·1; Cl, 40·1%). Its m. p. was undepressed when mixed with an authentic sample.[15]

Oxidation of p-*Nitrophenol in Acetic Acid.*—Solutions of *p*-nitrophenol (4·4 g.) and phenyl iodosoacetate (12·0 g.) in acetic acid (50 ml.) were mixed and set aside (36 hr.). The yellow crystalline precipitate (9·0 g.) was filtered off, and a second crop (1·0 g.) was obtained by concentration of the filtrate under reduced pressure (temp. <35°). The remainder of the acetic acid was distilled off, and the residue was refluxed (2 hr.) with benzene. Chromatography on alumina yielded compound A (0·6 g.), m. p. and mixed m. p. 61°. The combined precipitates (*compound C*) were washed with ether and had m. p. 156° (Found: C, 42·4; H, 3·3; N, 3·4; I, 31·6. $C_{14}H_{12}O_5NI$ requires C, 42·0; H, 3·0; N, 3·5; I, 31·6%).

Reactions of Compound C.—(*a*) When compound C was heated at 164° for several hours, it was converted into compound A in 95% yield. Similarly, when compound C (0·55 g.) was refluxed (2 hr.) with ethanol, acetic acid, or benzene (25 ml.) it was converted into compound A in yields of 83, 87, and 92%, respectively.

(*b*) Compound C (1·8 g.) was refluxed (2 hr.) with sodium hydroxide solution (2N; 50 ml.) and extracted with ether. Compound A (0·5 g.) was obtained from the ether extract. The aqueous solution was acidified and continuously extracted with ether and an intractable brown tar (0·7 g.) was obtained.

(*c*) Compound C (5·0 g.) was refluxed in hydrochloric acid (10%; 60 ml.) until the yellow solid had become white (30 min.). The *product* (4·7 g.) was filtered off and washed with water; it had m. p. 210° [Found: C, 38·2; H, 2·4; N, 3·4; O, 13·5; Total halogen (as I), 48·4; Ac, *ca.* 1. $C_{12}H_9O_3NICl$ requires C, 38·3; H, 2·4; N, 3·7; O, 12·8; Total halogen (as I), 48·0%].

(*d*) Compound C was suspended in dioxan, and an excess of ethereal diazomethane added. After 10 days, the solvent was evaporated and compound A (88%) was obtained.

---

[13] Lea and Robinson, *J.*, 1926, 411.

[14] Ullmann and Stein, *Ber.*, 1906, **39**, 622.

[15] Armstrong, *Ber.*, 1874, **7**, 922.

Other Oxidations in Acetic Acid.—(*a*) 3-Methoxy-4-nitrophenol (0·56 g.) was oxidised with phenyl iodosoacetate (1·12 g.) in acetic acid (50 ml.). After the reaction had ceased (4 hr.), the acetic acid was distilled off under reduced pressure, to give 2(?)-*iodo-5-methoxy-4-nitrodiphenyl ether* (0·93 g.) which crystallised from methanol as needles, m. p. 103° (Found : C, 42·2; H, 2·8; N, 3·5. $C_{13}H_{10}O_4NI$ requires C, 42·0; H, 2·7; N, 3·8%).

(*b*) *p*-Ethoxycarbonylphenol (1·0 g.) was similarly oxidised for 13 hr. 4-Ethoxycarbonyl-2(?)-iododiphenyl ether (2·0 g.) was obtained which, on hydrolysis, gave 4-carboxy-2(?)-iododiphenyl ether (m. p. and mixed m. p. 160°).

(*c*) 3 : 4-Dinitrophenol (2·0 g.), phenyl iodosoacetate (3·64 g.), and acetic acid (50 ml.) were heated at 78° for 5 hr. 2(?)-Iodo-4 : 5-dinitrodiphenyl ether (3·41 g.), m. p. 118° (methanol), was obtained (Found : N, 6·9%).

Oxidation of p-*Nitrophenol with Phenyl Iodosobenzoate.*—Solutions of *p*-nitrophenol (1·3 g.) and phenyl iodosobenzoate (2·4 g.) in benzene saturated with benzoic acid (100 ml. and 150 ml., respectively) were mixed and set aside for 15 hr. The insoluble portion (0·2 g.) was filtered off and the filtrate was extracted with sodium hydrogen carbonate solution. Chromatography of the (dried) benzene layer on alumina yielded compound A (0·4 g.).

Phenyl Iodosobenzoate (By B. M. Lynch).—Finely powdered phenyl iodosoacetate (40 g.) was stirred in a solution of benzoic acid (100 g.) in dry ether (800 ml.). After 30 min., the phenyl iodosoacetate dissolved, and within a few minutes precipitation of phenyl iodosobenzoate began. Stirring was continued for a further 2 hr., and the product (51 g., 92%) was filtered off and washed with dry ether; it had m. p. 161° (lit.[16] 158°) (Found : equiv., 219. Calc. for $C_{20}H_{15}O_4I$: equiv., 223). This method is superior to Arbuzov's method.[16]

We thank Dr. A. R. H. Cole for measuring the infrared absorption spectrum. One of us (A. R. F.) thanks the Dafydd Lewis Trust for the award of a scholarship. Microanalyses are by Dr. K. W. Zimmermann.

University of Melbourne, N.3, Victoria, Australia. [*Received, June 27th*, 1956.]

[16] Arbuzov, *J. prakt. Chem.*, 1931, **131**, 357. Cf. Hey, Stirling, and Williams, *J.*, 1955, 3963.