Phenyliodine(III) Bis[phthalimidate]: A Novel Polyvalent Iodine Compound

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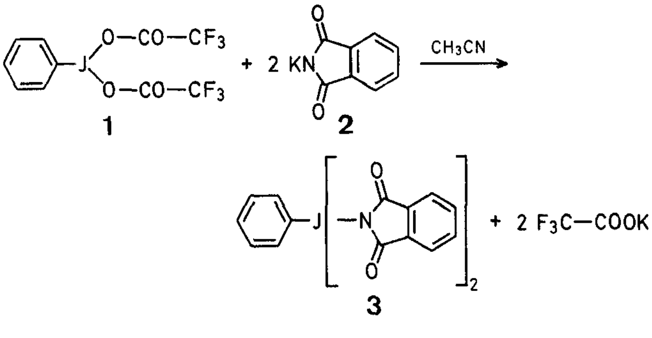
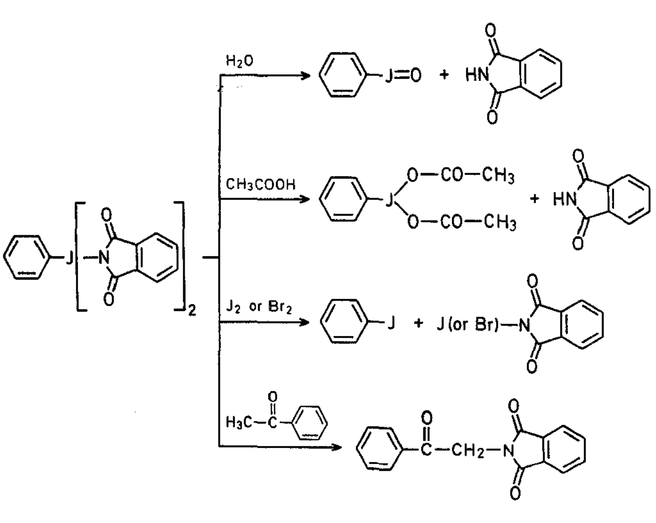
Although aryliodine(III) dicarboxylates are well-known derivatives of trivalent iodine[1], no analogues with two iodine-nitrogen bonds have been described. We now report the first example of a stable compound of this type: phenyliodine(III) bis[phthalimidate] (**3**) which is prepared by the reaction of phenyliodine(III) bis[trifluoroacetate] (**1**) with potassium phthalimidate (**2**) in acetonitrile.

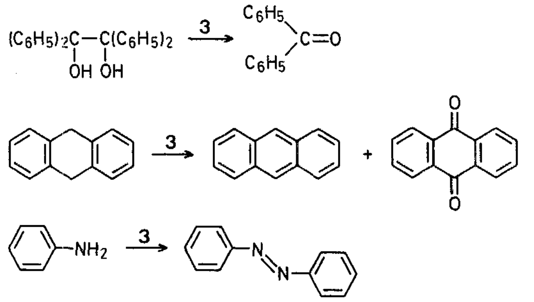


Compound **3** was characterised by microanalysis and mass spectrometry. An alternative structure with iodine-oxygen bonds from the tautomeric form of phthalimide is very unlikely because of the lack of an absorption assignable to the C=N group in the I.R. spectrum and the anti-aromatic character of the 5-membered ring of such a system.

The product **3** is fairly stable thermally; it is hydrolysed slowly by atmospheric moisture and rapidly in solvents containing traces of water to iodosobenzene and phthalimide. It is insoluble in common organic solvents and reactions are generally performed with suspensions of **3** in acetonitrile or carbon tetrachloride. With acetic acid, **3** reacts to give phenyliodine(III) bis[acetate] and phthalimide; with iodine or bromine, iodobenzene and *N*-iodo- or *N*-bromophthalimide, respectively, are formed. *N*-Iodophthalimide had not been adequately characterised previously[2]. Similar reactions are known to occur between **1** and halogens[3]. Another interesting reaction of **3** is that with acetophenone to give *N*-phenacylphthalimide in low yield.



Compound **3** exhibits mild oxidising properties, e.g. it cleaves benzopinacol to benzophenone in fair yield. This reaction is slow but can be catalysed by addition of dibenzoyl peroxide, demonstrating its free-radical character. Although **3** is less efficient than **1** in this reaction[4], it is more effective in reaction with 9,10-dihydroanthracene affording a mixture of anthracene and 9,10-anthraquinone (30 and 12% yields, respectively, using dibenzoyl peroxide and equimolar amounts of the reactants). Compound **3** also oxidises aniline to *trans*-azobenzene in 62% yield.



The free-radical character of the reactions of **3** is further demonstrated by the polymerisation of vinyl acetate on being stirred with **3** for 72 h.

Phenyliodine(III) Bis[phthalimidate] (3):

Phenyliodine(III) bis[trifluoroacetate] (**1**; 4.5 g, 1.04 mmol) and potassium phthalimidate (**2**; 3.7 g, 2.0 mmol) in acetonitrile (100 ml) are stirred at room temperature for 12 h. The off-white precipitate is collected, washed with acetonitrile, and dried in vacuo; yield: 3.6 g (74%). Because of its reactivity and insolubility in organic solvents, an analytical sample is prepared from very dilute solutions of the reactants and thorough washing of the precipitate with various dry solvents, followed by drying in vacuo; m.p. 210–215 °C (dec.).

$C_{22}H_{13}JN_2O_4$	calc.	C 53.23	H 2.62	N 5.65
(496.3)	found	53.12	2.60	5.64

I.R. (KBr): $\nu = 1730$, 1695, 1680, 1600 cm^{-1}.

M.S.: $m/e = 496$ (M$^+$, 0.2%); 350 (1.2%); 204 (79%); 147 (45%); 127 (39%).

***N*-Halophthalimides:**

Compound **3** (496 mg, 1 mmol) and iodine (254 mg, 1 mmol) in carbon tetrachloride (25 ml) are stirred for 12 h. A precipitate which cannot be recrystallised because of decomposition (liberation of iodine in chloroform) is obtained; yield: 321 mg (72%); m.p. 236–242 °C (dec).

I.R. (Nujol): $\nu = 1755$, 1705, 1605 cm^{-1}.

M.S.: $m/e = 273$ (35%); 229 (7%); 155 (14%); 147 (87%); 141 (34%).

N-*Bromophthalimide* is obtained similarly; yield: 66%; m.p. 205–206 °C (Ref.[5], m.p. 206–207 °C).

***N*-Phenacylphthalimide:**

Compound **3** (0.5 g, 1.1 mmol) and acetophenone (0.5 g, 5 mmol) are heated at 70 °C for 30 min. The mixture is then triturated with carbon tetrachloride (15 ml) and the product is isolated from the filtrate by column chromatography on silica gel eluting with petroleum ether/chloroform; yield: 58 mg (20%); m.p. 165–166 °C (Ref.[6], m.p. 165–167 °C).

Reaction of 3 with Benzopinacol:

Compound **3** (0.5 g, 1.1 mmol) and benzopinacol (366 mg, 1 mmol) are suspended in carbon tetrachloride (25 ml) and the suspension is stirred for 3 days in the presence of dibenzoyl peroxide (10 mg). The mixture is filtered, the filtrate evaporated, and the residue dissolved in ethanol. Addition of a solution of 2,4-dinitrophenylhydrazine gives benzophenone 2,4-dinitrophenylhydrazone; yield: 240 mg (64%); m.p. 235–239 °C (Ref.[7], m.p. 238 °C).

The reaction also occurs under reflux (6 h) in the absence of the dibenzoyl peroxide catalyst; yield: 57%.

Reaction of 3 with Aniline:

Compound **3** (496 mg, 1 mmol) and aniline (93 mg, 1 mmol) in carbon tetrachloride (20 ml) are stirred for 2 days. The filtered solution is evaporated to dryness and the residue subjected to column chromatography on silica gel eluting with petroleum ether/chloroform to give *trans*-azobenzene; yield: 56 mg (62%); m.p. 62–65 °C (Ref.[7], m.p. 67–68 °C).

Reaction of 3 with 9,10-Dihydroanthracene:

Compound **3** (496 mg, 1 mmol) and 9,10-dihydroanthracene (180 mg, 1 mmol) are stirred in carbon tetrachloride (15 ml) in the presence of dibenzoyl peroxide (10 mg) for 24 h. The mixture is then filtered, the filtrate evaporated to dryness, and the residue column chromatographed on silica gel eluting with petroleum ether/chloroform to give anthracene [yield: 54 mg; (30%); m.p. 212–213 °C (Ref.[7], m.p. 215–216 °C)] and 9,10-anthraquinone [yield: 25 mg (12%); m.p. 282–285 °C (Ref.[7], m.p. 286 °C)].

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