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An Alternative Synthetic Method for Polycyclic Aromatic Iodides

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Polycyclic aromatic iodides **2** and **4** are prepared from readily available bromides **1** and **3** via the copper(I) iodide-mediated halogen exchange with iodide ion in hot hexamethylphosphoric triamide.

Although polycyclic aromatic hydrocarbons readily undergo halogenation with molecular chlorine or bromine to give the expected halogen derivatives, the corresponding reaction with molecular iodine fails. Due to the low oxidation potential of substrates as well as the high oxidizing ability of electron-deficient iodine species, the use of stronger iodinating agents usually results in the extensive formation of quinone or quinol derivatives rather than nuclear iodination. Thus the common laboratory methods for the synthesis of polycyclic aromatic iodides involve the diazotization of corresponding amines followed by treatment with alkali metal iodide[1,2,3], or initial conversion of aromatic bromides to aryllithium or arylmagnesium compounds and subsequent treatment with molecular iodine[4,5,6].

We now report a convenient direct route to some polycyclic aryl iodides, which is based on the halogen exchange of readily available bromides with iodide ion in the presence of copper(I) iodide. When 2-bromonaphthalene (**1a**) is heated with a large excess of potassium iodide and copper(I) iodide in hexamethylphosphoric triamide (HMPT), bromine is replaced by iodine to give 2-iodonaphthalene (**2a**) isolated in 70–75% yield. 9-Bromoanthracene (**1b**), 9-bromophenanthrene (**1d**), and 1-bromopyrene (**1e**) react similarly, giving 9-iodoanthracene (**2b**), 9-iodophenanthrene (**2d**), and 1-iodopyrene (**2e**), respectively, in 70–84% yields (Table). The reaction is clean and no side reactions are observed. Without copper(I) iodide, the conversion of bromides to iodides does not take place. Since the halogen exchange occurs under non-aqueous neutral conditions, many sensitive functional groups would survive during the reaction. Unfortunately, the present method is not applicable to polycyclic aromatic chlorides.

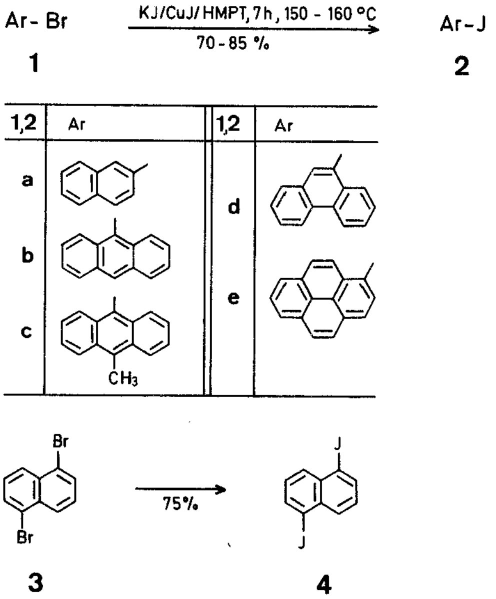

Table. Polycyclic Aromatic Iodides **2a–e** and **4** prepared[a]

Product	Yield[b] [%]	m.p. [°C]	Molecular Formula[c] or Lit. m.p. [°C]	I.R. (KBr) ν [cm^{-1}]	^{1}H-N.M.R. (CDCl$_3$/TMS) δ [ppm]
2a	70–75	53–54°	54.5°[7]	1580, 1500, 1130, 940, 860, 820, 740	7.2–7.7 (m, 6H); 8.0 (br. s, 1H)
4	75[d]	144–146°	147°[7]	1580, 1480, 1380, 1320, 1210, 1195, 780, 680	7.12 (t, 2H, *J* = 7.5 Hz); 7.98 (d, 4H, *J* = 7.5 Hz)
2b	70–80	79–81°	82–83°[5]	1260, 1250, 955, 910, 880, 840, 765, 730	7.07–7.53 (m, 4H); 7.56–7.87 (m, 2H); 8.07–8.37 (m, 3H)
2c	85	135–137° (decomp.)	$C_{15}H_{11}J$[e,f] (318.2)	1260, 1160, 955, 900, 880, 840, 765, 725	3.04 (s, 3H); 7.05–7.60 (m, 4H); 7.96–8.30 (m, 4H)
2d	80	85–88°	87°[4]	900, 880, 845, 755, 745, 720	7.07–7.66 (m, 4H); 7.80–8.09 (m, 2H); 8.21 (s, 1H); 8.27–8.52 (m, 2H)
2e	84	85–87°	$C_{16}H_9J$[g] (328.2)	1580, 1000, 960, 840, 830, 810, 750, 700	7.6–8.5 (m)

[a] All reactions were carried out at 150–160°C under a nitrogen atmosphere.
[b] Yield of isolated product.
[c] Satisfactory microanalyses were obtained: C ±0.5, H ±0.1.
[d] Double the amount of the reagents were used to obtain the diiodination product.
[e] Decomposes gradually on storage.
[f] M.S.: *m/e* = 318 (M$^+$).
[g] M.S.: *m/e* = 328 (M$^+$).

1-Iodopyrene (2e); Typical Procedure:

A mixture of 1-bromopyrene; 2.00 g, 7.11 mmol), copper(I) iodide (6.77 g, 35.5 mmol), potassium iodide (12.5 g, 75.4 mmol), and hexamethylphosphoric triamide (25 ml) is stirred for 6 h at 150–160 °C under nitrogen. The progress of the reaction is monitored by G.L.C. The reaction is quenched by the addition of dilute hydrochloric acid (40 ml) followed by benzene (40 ml) and the resulting mixture is freed from insoluble copper(I) salts by filtration. The organic phase is separated, washed with water (2 × 40 ml) and evaporated to leave a pale yellow solid; which is purified by recrystallization from benzene/ethanol (1/2) to give pure **2e**; yield: 1.95 g (84%); m.p. 85–87 °C (Table).

$C_{16}H_9J$	calc.	C 58.56	H 2.76
(328.2)	found	58.07	2.86

M.S.: $m/e = 328$ (M^+).

Received: December 17, 1984

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