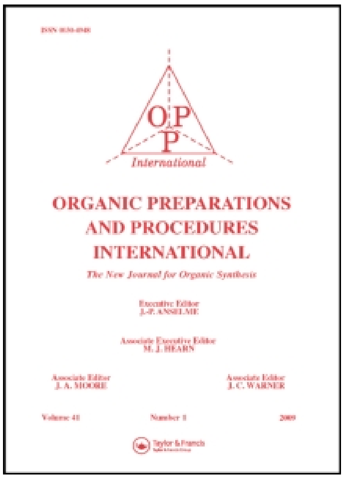

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IODIDE SALTS OF NITROGEN HETEROCYCLES BY BROMIDE-IODIDE EXCHANGE

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Submitted by (03/30/87)
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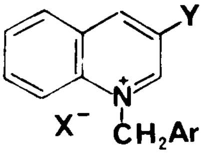
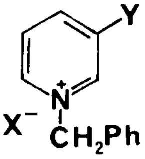
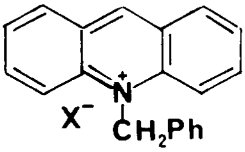
The choice of procedure for the preparation of 1-substituted benzyl-3-cyanoquinolinium iodides (2a-k) seems to be very limited.[1] We now report an ion exchange procedure in a specially chosen solvent mixture which optimizes the yields of iodide salts of nitrogen containing heterocyclic aromatic compounds.







X: 1 = Br, 2 = I

Y: a-h = CN, i-j = $CONH_2$, k = H

Ar: a = C_6H_5, b = p-$CH_3C_6H_4$

c = p-FC_6H_4, d = m-FC_6H_4

e = p-BrC_6H_4, f = p-$CF_3C_6H_4$

g = m-$CF_3C_6H_4$, h = p-CNC_6H_4

i = C_6H_5, j = p-FC_6H_4, k = C_6H_5

X: 3 = Br, 4 = I

Y: a = $CONH_2$, b = H

X: 5 = Br

6 = I

The 1-substituted benzyl-3-cyanoquinolinium bromides (1a-k) were prepared by heating 3-cyanoquinoline and corresponding benzyl bromides.[2-4] The key feature is the replacement of bromide ion by iodide ion in a mixed solvent system of ethanol-water (10:1 v/v). Ethanol alone was not suitable because of the low solubility of potassium bromide in it. On the other hand, excess water was not desirable because the products were too soluble.

These iodide salts have not been reported previously and their characterization is rather difficult because their spectra are nearly identical to those of the corresponding bromide salts. However, melting points and elemental analyses seemed to be satisfactory for the purpose.

TABLE 1. Elemental Analysis Data

Compd	Mol. Form.	Calcd (Found)			
		C	H	N	I
2a	$C_{17}H_{13}IN_2$	54.86 (54.88)	3.52 (3.52)	7.53 (7.53)	34.09 (33.89)
2b	$C_{18}H_{15}IN_2$	55.98 (55.77)	3.91 (3.78)	7.26 (7.26)	32.86 (32.99)
2c	$C_{17}H_{12}FIN_2$	52.33 (52.25)	3.10 (3.14)	7.18 (7.01)	32.52 (32.65)
2d	$C_{17}H_{12}FIN_2$	52.33 (52.22)	3.10 (3.03)	7.18 (7.00)	32.52 (32.83)
2e	$C_{17}H_{12}BrIN_2$	45.26 (45.23)	2.68 (2.39)	6.21 (6.00)	28.13 (29.22)
2f	$C_{18}H_{12}F_3IN_2$	49.11 (49.00)	2.75 (2.58)	6.36 (6.27)	28.83 (29.07)
2g	$C_{18}H_{12}F_3IN_2$	49.11 (49.05)	2.75 (2.66)	6.36 (6.08)	28.83 (29.20)
2h	$C_{18}H_{12}IN_3$	54.43 (54.48)	3.04 (3.00)	10.08 (10.33)	31.95 (31.85)
2i	$C_{17}H_{15}IN_2O$	52.33 (52.20)	3.87 (3.69)	7.18 (7.03)	32.52 (32.68)
2j	$C_{17}H_{14}FIN_2O$	50.02 (49.88)	3.46 (3.29)	6.86 (6.66)	31.09 (31.23)
2k	$C_{16}H_{14}IN$	55.35 (55.25)	4.06 (4.00)	4.03 (3.92)	36.55 (36.73)
4a	$C_{13}H_{13}IN_2O$	45.90 (45.68)	3.85 (3.80)	8.24 (8.25)	37.31 (37.55)
4b	$C_{12}H_{12}IN$	48.51 (48.69)	4.07 (4.28)	4.71 (4.55)	42.71 (42.89)
6	$C_{20}H_{16}IN$	60.47 (60.66)	4.06 (4.21)	3.53 (3.28)	31.94 (31.89)

TABLE 2. Yields and Melting Points[2,4] of 1-6

Bromides			Iodides		
Compd	Yield (%)	mp (°C)	Compd	Yield (%)	mp (°C)
1a	70	181-182	2a	75	165
1b	80	198	2b	75	122 (dec.)
1c	80	178-179	2c	80	134 (dec.)
1d	80	203-204	2d	80	173
1e	80	185	2e	70	162-164
1f	70	192	2f	75	147-148
1g	70	196-197	2g	70	145
1h	75	184	2h	80	170
1i	80	224-225 (dec.)	2i	80	204
1j	80	223-225 (dec.)	2j	60	200
1k	95	188	2k	60	158-160
3a	90	211-213	4a	75	139-140
3b	95	165	4b	70	135
5	48	208	6	70	190

EXPERIMENTAL SECTION

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by the M-H-W Laboratories, Phoenix, Arizona.

1-Benzyl-3-cyanoquinolinium Iodide. General Procedure.- A mixture of KI (2 mmoles) and ethanol (30 mL) was stirred until complete solution resulted at room temperature. The bromide 1 (1 mmole) was added to this solution. Reaction took place immediately and the pale yellow solution turned reddish orange in all the cases in this series. After stirring for 30 min, distilled water (3 mL) was added and the mixture was warmed on a hot plate just enough to give a clear solution. Upon cooling to room temperature, an orange precipitate formed and was collected and recrystallized from absolute ethanol to give the iodide salt 2.

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SYNTHESIS OF 3-METHYL- AND 3-tert-BUTYLPHENANTHRENE

Submitted by R. C. Bansal[†], S. A. Samad[†], J. S. Thomson[††],
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3-Methylphenanthrene (5) was needed as an analytical standard and for precise thermodynamic studies as a model monomethyl tricyclic fossil-fuel constituent.[1] The Bogert-Cook synthesis shown below is a well-known route