Synthesis of 1-Alkyl and 1,3-Dialkyl-2-benzimidazolones from 1-Alkenyl-2-benzimidazolones using Phase-Transfer Catalysis Technique

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A general synthetic route to 1-alkyl and 1,3-dialkyl-2-benzimidazolones from 1-alkenyl-2-benzimidazolones using phase-transfer catalysis conditions is described.

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Introduction.

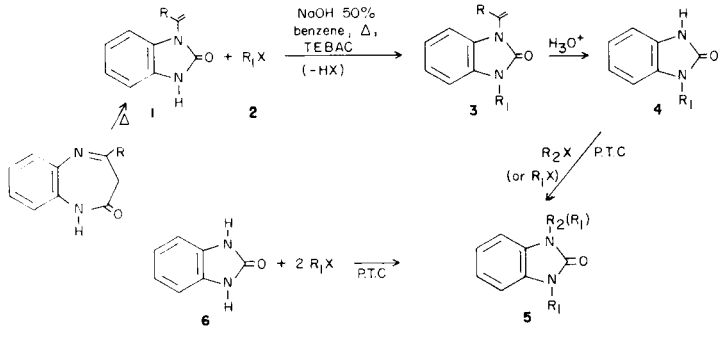
Three methods were reported concerning the preparation of titled compounds. Davoll (1) reported that alkylation of 1-alkenyl-2-benzimidazolones with alkyl halides and sodium ethoxide in ethanol yields monoalkyl-2-benzimidazole derivatives. The second method consists of condensation of *N*-alkyl-*o*-phenylenediamine with carbonyl sources, *e.g.*, urea (1,2), phosgene (3,4), or carbondioxide (5). The condensation of *N*-alkyl-*o*-aminobenzamide with phthalic anhydride was also reported (6); likewise the condensation of *N,N*-polymethylene (n = 5-12)-*o*-phenylenediamines with phosgen produced the appropriate 2-benzimidazolone (7). The third method of Cumper Pichering (8) depends upon direct alkylation of 2-benzimidazolone, but it leads to a mixture of mono- and dialkyl derivatives (9), thus necessitating separation by column chromatography. This method was recently used (10) for the cycloalkylation of benzimidazolone with α,ω-dihalides ($X-(CH_2)_n-X$) in the presence of sodium hydride in DMF at ambient temperature or with lithium hydride at 90°.

Since it has been reported that the second method involves difficulties in the selective monoalkylation of *o*-phenylenediamine (11), and owing to the pharmacological importance of 2-benzimidazolones (12), we attempted to prepare a series of *N*-monoalkylated and *N,N*-dialkylated derivatives (13). We describe here an effective alkylation procedure of 1-alkenyl-2-benzimidazolones using a phase-transfer catalysis technique (14), followed by acid hydrolysis according to Davoll's method (1a).

Results and Discussion.

The alkylation of 1-alkenyl-2-benzimidazolones **1** under phase transfer catalysis conditions [alkyl halide, 50% aqueous sodium hydroxide, benzene as the organic solvent and triethylbutylammonium chloride (TEBAC) as the catalyst] leads to the corresponding *N*-alkyl derivatives **3** in 80-95% yields. Hydrolysis in acid medium furnishes 1-alkyl-2-benzimidazolones **4** in almost quantitative yields.

A new alkylation of **4** following the same procedure (PTC) leads to 1,3-dialkyl-2-benzimidazolones ($R_1 \neq R_2$) or the symmetric derivatives ($R_1 = R_2$) (compound **5**, *cf.*, Scheme 1). Starting with the 2-benzimidazolones **6** we were able to obtain **5**. The structures of compounds **3**, **4** and **5** were confirmed by spectroscopic data. The ir spec-



Scheme 1

Synthetic Route using Phase-Transfer Catalysis of 1-(α-Methylvinyl)-, (α-Phenylvinyl)-2-benzimidazolones **1**, 1-Alkyl-2-benzimidazolones **4** and 2-Benzimidazolones **6**.

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Table 1

Preparation of 1-Alkyl-3-(α-methylvinyl) and 3-(α-Phenylvinyl)-2-benzimidazolones (3) through Alkylation with Phase-Transfer Catalysis

(1a) R-CH_3	(2) R'X	(3)	M.p. °C	Yield %	Formula	Analysis: Calcd./Found % C	H	N	Tlc (b) R_F (i)	(ii)	Ir λ max cm^{-1} (C=O)
	2c CH_3I	**3ac**	liquid	90	$C_{11}H_{12}N_2O$	70.14	6.38	14.88	0.37	0.55	1705
						70.32	6.15	14.69			
	2d C_2H_5Br	**3ad**	51	90	$C_{12}H_{14}N_2O$	71.18	6.92	13.84	0.40	0.60	1700
						71.35	6.73	13.60			
	2e $CH_2=CH-CH_2-Br$	**3ae**	20	95	$C_{13}H_{14}N_2O$	72.80	6.53	13.07	0.48	0.68	1710
						72.65	6.22	12.71			
	2f *n*-C_3H_7Br	**3af**	liquid	95	$C_{13}H_{16}N_2O$	72.12	7.40	12.94	0.50	0.70	1705
						71.92	7.62	13.09			
	2g *i*-C_3H_7Br	**3ag**	liquid	80	$C_{13}H_{16}N_2O$	72.12	7.40	12.94	0.51	0.73	1700
						72.40	7.28	12.24			
	2h *n*-C_4H_9Br	**3ah**	liquid	90	$C_{14}H_{18}N_2O$	72.95	7.82	12.16	0.56	0.78	1710
						73.20	7.68	11.98			
	2i *i*-C_4H_9Br	**3ai**	liquid	85	$C_{14}H_{18}N_2O$	72.95	7.82	12.16	0.55	0.78	1712
						73.15	7.98	12.22			
	2j $C_6H_5CH_2Cl$	**3aj**	liquid	95	$C_{17}H_{16}N_2O$	77.19	6.05	10.59	0.64	0.81	1715
						77.36	6.24	10.73	(iii)	(iv)	
(1b) R-C_6H_5	**2c** CH_3I	**3bc**	108	95	$C_{16}H_{14}N_2O$	76.71	5.59	11.19	0.24	0.35	1700
						76.85	5.28	11.32			
	2d C_2H_5Br	**3bd**	78	90	$C_{17}H_{16}N_2O$	77.19	6.05	10.59	0.32	0.46	1715
						77.38	5.88	10.36			
	2e $CH_2=CH-CH_2Br$	**3be**	52	95	$C_{18}H_{16}N_2O$	78.26	5.80	10.14	0.41	0.56	1710
						78.39	5.59	10.30			
	2f *n*-C_3H_7Br	**3bf**	93	95	$C_{18}H_{18}N_2O$	77.61	6.47	10.06	0.41	0.56	1695
						77.51	6.59	10.25			
	2g *i*-C_3H_7Br	**3bg**	78	85	$C_{18}H_{18}N_2O$	77.61	6.47	10.06	0.45	0.59	1710
						77.22	6.22	9.88			
	2h *n*-C_4H_9Br	**3bh**	115	90	$C_{19}H_{20}N_2O$	77.98	6.84	9.58	0.51	0.65	1710
						78.10	7.02	9.66			
	2i *i*-C_4H_9Br	**3bi**	59	80	$C_{19}H_{20}N_2O$	77.98	6.84	9.58	0.51	0.65	1708
						77.77	6.98	9.40			
	2j $C_6H_4CH_2Cl$	**3bj**	70	95	$C_{22}H_{18}N_2O$	80.88	5.51	8.58	0.61	0.72	1715
						80.61	5.65	8.72			
	2k $HOCH_2CH_2Br$	**3bk**	105	95	$C_{17}H_{16}N_2O_2$	72.84	5.71	9.99	0.10	0.15	1705
						72.61	5.88	10.09			
	2l $BrCH_2CH_2Br$	**3bl**	liquid	95	$C_{17}H_{15}BrN_2O$	59.44	4.37	8.16	0.35	0.50	1710
						59.72	4.48	8.35			

tra of **3** exhibits ν C=O between 1695 and 1715 cm^{-1}, and at 1700 cm^{-1} in the monosubstituted derivatives **4**. The dialkyl compounds **5** show ν C=O between 1695 and 1710 cm^{-1}. In the ^{1}H-nmr spectra, the α-methylvinyl group in compounds **3ax** was identified by the chemical shift of vinyl protons at 5.17-5.20 ppm (*cis*, multiplet) and at 5.07 ppm (*trans*, multiplet), while that of the methyl group appears at 2.25 ppm. In compounds **3bx** (R = C_6H_5) the two vinyl protons appear as two singlets at 5.50 and 5.80 ppm. The chemical shifts of alkyl substituents fixed on the nitrogen atom(s) in compounds **4** and **5** gave the characteristic signals corresponding to these groups.

The 2-benzimidazolones **3**, **4** and **5** were analyzed on silica gel nanoplates hptlc 5 μ, using tlc according to classical method of Stahl. The relative values of R*f* show the following order in decreasing mobility **5** > **4** > **3** > **6**. In each series of compounds, a decrease in the adsorption energy of the molecule was observed as a function of the steric hindrance of alkyl groups attached to the nitrogen atom(s). The following order of decreasing mobility was observed in series **3**: $C_6H_5CH_2$ > *i*-C_4H_9 ≥ *n*-C_4H_9 > *i*-C_3H_7 ≥ *n*-C_3H_7 > $CH_2CH_2{=}CH_2$ > C_6H_5 > CH_3.

EXPERIMENTAL

Melting points are uncorrected and were determined using a Kofler hot stage; tlc analyses were performed either on silica gel nanoplates hptlc 5 μ or in silica gel HF 254 + 366 Merck in a saturated atmosphere; eluents are reported in Table 1. ^{1}H-nmr spectra were recorded at 100 MHz or at 60 MHz using a Varian XL 100 and an EM 360 A spectrophotometer; ir spectra were recorded on a Perkin Elmer 225 in potassium bromide or in dichloromethane solution.

Table 1 continued

Compound No.	^{1}H-Nmr Spectra of **3** (carbon tetrachloride/TMS) (c) δ ppm
3ac	6.97 (s, 4H), 5.17 (m, 1H), 5.07 (s, 1H), 3.30 (s, N-CH_3), 2.24 (s, 3H)
3ad	6.95 (s, 4H), 5.20 (m, 1H), 5.07 (s, 1H), 3.83 (q, J7, 2H), 1.33 (t, J7, 3H)
3ae	6.93 (s, 4H), 6.30-5.50 (m, 1H), 5.43-4.90 (m, 4H), 4.40 (d, J6, 2H), 2.25 (s, 3H)
3af	6.97 (s, 4H), 5.17 (m, 1H), 5.07 (s, 1H), 3.77 (t, J7, 3H), 2.27 (s, 3H), 1.73 (sex, J7, 2H), 0.95 (t, J7, 3H)
3ag	7.30-6.70 (m, 4H), 5.17 (m, 1H), 5.07 (s, 1H), 4.60 (sept, J7, 1H), 2.23 (s, 3H), 1.50 (d, J7, 6H)
3ah	6.97 (s, 4H), 5.17 (m, 1H), 5.07 (s, 1H), 3.78 (t, J7, 2H), 2.23 (s, 3H), 2.0-1.10 (m, 4H), 0.93 (t, J7, 3H)
3ai	6.94 (s, 4H), 5.17 (m, 1H), 5.07 (s, 1H), 3.57 (d, J7, 2H), 2.60-1.70 (m, 4H), 0.95 (d, J7, 6H)
3aj	7.45-6.70 (m, 9H), 5.32 (s, 1H), 5.20 (s, 1H), 5.04 (s, 2H, N-CH_2), 2.25 (s, 3H) (deuteriochloroform)
3bc	7.30 (s, 5H), 7.10-6.30 (m, 4H), 5.76 (s, 1H), 5.50 (s, 1H), 3.43 (s, 3H)
3bd	7.30 (s, 5H), 7.10-6.20 (m, 4H), 5.80 (s, 1H), 5.50 (s, 1H), 3.90 (q, J7, 2H), 1.37 (t, J7, 3H)
3be	7.30 (s, 5H), 7.10-6.30 (m, 4H), 6.30-5.60 (m, 2H), 5.50 (s, 1H), 5.40-4.95 (m, 2H), 4.45 (d, J6, 2H)
3bf	7.30 (s, 5H), 7.10-6.30 (m, 4H), 5.8 (s, 1H), 5.5 (s, 1H), 3.83 (t, J7, 2H), 1.87 (sex, J7, 2H), 1.03 (t, J7, 3H)
3bg	7.3 (s, 5H), 7.1-6.3 (m, 4H), 5.8 (s, 1H), 5.5 (s, 1H), 4.7 (sept, J7, 1H), 1.57 (d, J7, 6H
3bh	7.3 (s, 5H), 7.1-6.3 (m, 4H), 5.77 (s, 1H), 5.5 (s, 1H), 3.85 (t, J7, 2H), 2.1-1.2 (m, 4H), 1.0 (t, J7, 3H)
3bi	7.3 (s, 5H), 7.1-6.3 (m, 4H), 5.77 (s, 1H), 5.47 (s, 1H), 3.65 (d, J7, 2H), 2.23 (m, 1H), 0.97 (d, J6, 3H)
3bj	7.5-7.18 (m, 10H), 7.02-6.6 (m, 4H), 5.94 (s, 1H), 5.6 (s, 1H), 5.12 (s, 2H) (deuteriochloroform)
3bk	7.38 (s, 5H), 7.22-6.45 (m, 4H), 5.96 (s, 1H), 5.5 (s, 1H), 4.2-3.6 (m, 4H), 2.63 (s, 1H, CH) (acetone-d_6
3bl	7.3 (s, 5H), 7.16-6.3 (m, 4H), 5.83 (s, 1H), 5.5 (s, 1H), 4.22 (t, 2H, J7), 3.63 (t, J7, 2H)

(a) Most of the obtained products were oily liquids. (b) The purity of the compounds were checked by tlc on silica gel HF 254 + 366. Eluents: i) benzene/acetonitrile 9/1; ii) benzene/acetonitrile 7/3; iii) benzene/ethylacetate 9/1; iv) benzene/ethylacetate 6/1. (c) Spectra were registered using a Varian EM 360 A spectrophotometer (60 MHz).

1-(α-Methylvinyl)-2-benzimidazolone (**1a**).

This compound was obtained by dry fusion of equimolar amounts of *o*-phenylenediamine and ethyl acetoacetate (20 mmoles) for 5 minutes at 150°, yield 75%, m.p. 121° [lit. (1a,12) m.p. 121°]; nmr (deuteriochloroform): δ ppm 12.50 (s, 1H, NH), 7.02 (s, 4H), 5.24 (m, 1H), 5.17 (s, 1H), 2.3 (s, 3H); ir (dichloromethane): ν cm^{-1} 3430 (NH), 1740-1660 (C=O).

Anal. Calcd. for $C_{10}H_{10}N_2O$ (174.1): C, 62.5; H, 6.2; N, 14.6. Found: C, 62.3; H, 6.1; N, 14.4.

2-Methylbenzimidazole (m.p. 174-176°) was alos obtained as a by-product.

1-(α-Phenylvinyl)-2-benzimidazolone (**1b**).

Similarly dry fusion (5 minutes, 200°) of *o*-phenylenediamine with ethylbenzoylacetate affords **1b**, yield 80%, m.p. 170-172° [lit. (12) m.p. 140-150° dec.]; nmr (deuteriochloroform): δ ppm 12.95 (s, 1H, NH), 7.33 (s, 5H), 7.2-6.5 (m, 4H), 6.0 (s, 1H), 5.6 (s, 1H); ir (dichloromethane): ν cm^{-1} 3400 (NH), 1720-1680 (C=O); ^{13}C-nmr (deuteriochloroform): δ ppm 155.2, 139.5, 135.2, 130.6, 129.1, 128.8, 128.3, 122.1, 131.3, 114.5, 110.1.

Anal. Calcd. for $C_{15}H_{12}N_2O$ (252.2): C, 76.3; H, 5.1; N, 11.9. Found: C, 76.3; H, 5.26; N, 11.7.

1-Alkyl-3-(α-methylvinyl) **3ax** and 1-Alkyl-3-(α-phenylvinyl) **3bx**-2-benzimidazolones.

General Procedure.

A mixture of **1** (20 mmoles) in benzene (40 ml.), 50% aqueous sodium hydroxide (15 ml.), triethylbutylammonium chloride TEBAC (1 mmole) and alkyl halide **2** (30 mmoles) was stirred for about 1 hour at 60°. The reaction was monitored by tlc. After completion of the reaction, the mixture was left to cool and the organic layer was separated, washed thoroughly with water and dried over anhydrous magnesium sulphate. The benzene was then evaporated *in vacuo*. The residue which solidified on cooling was collected, washed with petroleum ether and crystallized from the appropriate solvent. Liquids were purified by column chromatography on silica gel 60 eluted with a mixture of benzene-ethyl acetate (8:2). Results are reported in Table 1. R*f* values were recorded on silica gel nanoplates hplc 5 μ with benzene-acetonitrile (a, 9:1) and (b, 7:3 v/v) and with benzene-ethylacetate (c, 9:1) and (d, 6:1) as eluents for the **3ax** and **3bx** series, respectively.

Hydrolysis of Alkenyl-2-benzimidazolones **3**.

1-Alkyl-2-benzimidazolones **4**.

General Procedure.

To a stirred suspension of **3** (10 mmoles) in water (30 ml.), 5 ml. of concentrated hydrochloric acid was added and the mixture was heated for 1 hour at 60°. The reaction mixture was extracted with ether; the extract was washed with water, dried over anhydrous magnesium sulphate and evaporated *in vacuo*. The residue was precipitated by addition of a mixture of petroleum ether:benzene (9:1). The white solid thus obtained was filtered, dried and crystallized from the precipitation mixture.

1,3-Dialkyl-2-benzimidazolones **5**.

General Procedure.

The same general method was applied as that for alkylation of alkenyl-2-benzimidazolones **3**, but the reaction time was raised to 4-5 hours. The symmetric dialkyl derivatives (**5**, $R_1 = R_2$) were easily obtained from 2-benzimidazolone **6** by adding alkyl halide in excess.

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Table 2

Preparation of 1-Alkyl-2-benzimidazolones (**4**) by Acid Hydrolysis of 1-Alkyl-, 3-(α-Methylvinyl)- or 3-(α-Phenylvinyl)-2-benzimidazolones (**3**)

3	4	(R^1)	M.p. °C (a)	Yield %	Lit. M.p. °C (lb)	Formula	Analysis: Calcd./Found % C	H	N	Tlc (b) Rf (ii)	(iv)
3bc	**4c**	CH_3	190*	95	—	$C_8H_8N_2O$	64.82	5.40	18.91	0.21	0.08
							64.66	5.56	19.07		
3bd	**4d**	C_2H_5	122*	95	83	$C_9H_{10}N_2O$	66.58	6.17	17.26	0.28	0.12
							66.32	6.41	17.35		
3ae	**4e**	$CH_2=CH-CH_2$	95*	95	75	$C_{10}H_{10}N_2O$	68.89	5.74	16.07	0.38	0.18
							68.67	5.61	16.28		
3af	**4f**	n-C_3H_7 (c)	102*	95	74	$C_{10}H_{12}N_2O$	68.10	6.81	15.89	0.35	0.14
							68.37	6.70	15.70		
3ag	**4g**	i-C_3H_7	129	95	—	$C_{10}H_{12}N_2O$	68.10	6.81	15.89	0.39	0.17
							68.29	6.66	16.06		
3ah	**4h**	n-C_4H_9	98*	95	82	$C_{11}H_{14}N_2O$	69.40	7.36	14.72	0.41	0.19
							69.13	7.51	14.63		
3ai	**4i**	i-C_4H_9 (d)	130	95	—	$C_{11}H_{14}N_2O$	69.40	7.36	14.72	0.41	0.19
							69.21	7.18	14.50		
3bj	**4j**	$C_6H_5CH_2$	198*	95	82	$C_{14}H_{12}N_2O$	74.90	5.35	12.48	0.45	0.21
							74.68	5.17	12.30		

^{1}H-Nmr Spectra of **4** (deuteriochloroform/TMS) (e)

Compound No.	δ ppm
4c	10.77 (s, NH), 7.3-6.8 (m, 4H), 3.47 (s, N-CH_3)
4d	10.55 (s, NH), 7.3-6.8 (m, 4H), 3.98 (q, J7, 2H), 1.4 (t, J7, 3H)
4e	10.94 (s, NH), 7.3-6.7 (m, 4H), 6.2-5.6 (m, 1H), 5.4-4.86 (m, 2H), 4.52 (d, J6, 2H)
4f	10.72 (s, Nh), 7.3-6.8 (m, 4H), 3.87 (t, J7, 2H), 1.82 (sex, J7, 2H), 0.99 (t, J7, 3H)
4g	10.8 (s, Nh), 7.3-6.9 (m, 4H), 4.78 (sept, J7, 1H), 1.58 (d, J7, 6H)
4h	10.8 (s, NH), 7.3-6.8 (m, 4H), 3.9 (t, J7, 2H), 1.94-1.2 (m, 4H), 0.96 (t, J7, 3H)
4i	10.84 (s, NH), 7.3-6.8 (m, 4H), 3.7 (d, J7, 2H), 2.5-1.98 (m, 1H), 1.0 (d, J7, 6H)
4j	10.73 (s, NH), 7.27 (s, 5H), 7.1-6.7 (m, 4H), 4.98 (s, 2H).

(a) The melting points of products (*) were identical with those reported in the literature (1) ± 1°; compounds **3ag** and **3ai** were not previously prepared. (b) *Cf.* footnote Table 1b. (c) Ir (potassium bromide): ν (C=O) 1700 cm^{-1}, in 2-benzimidazolone (**6**) (C=O) 1700 cm^{-1}. (d) Ir (potassium bromide): ν (C=O) 1700 cm^{-1}. (e) *Cf.* footnote Table 1c.

Table 3

Preparation of 1,3-Dialkyl-2-benzimidazolones (**5**) by Alkylation using Phase-Transfer Catalysis of 1-Alkyl-2-benzimidazolones (**4**) and 2-benzimidazolone (**6**)

4 or 6	2	R'X	5	M.p. °C	Yield %	Formula	Analysis: Calcd./Found % C	H	N	Tlc (a) Rf ii	iv	Ir ν max cm⁻¹	¹H (carbon tetrachloride/TMS (b) δ ppm
6	**2c**	CH_3I	**5cc**	102 (c)	95	$C_9H_{10}N_2O$	66.58 66.77	6.17 6.31	17.26 17.35	0.44	0.31	1703	7.20-6.60 (m, 4H), 3.35 (s, 6H)
4f	**2c**	CH_3I	**5cf**	liquid	90	$C_{11}H_{14}N_2O$	69.40 69.21	7.36 7.18	14.72 14.66	0.58	0.44	1710	7.20-6.68 (m, 4H), 3.84 (t, J7, 2H), 3.42 (s, 3H), 1.78 (sex, J7, 2H), 0.97 (t, J7, 3H)
6	**2d**	C_2H_5-Br	**5dd**	68	95	$C_{11}H_{14}N_2O$	69.40 69.57	7.36 7.56	14.72 14.90	0.58	0.47	1695	6.90 (s, 4H), 3.85 (q, J7, 4H), 1.34 (t, J7, 6H)
4e	**2d**	C_2H_5-Br	**5de**	liquid	95	$C_{13}H_{14}N_2O$	71.22 71.40	6.92 7.11	13.85 14.07	0.66	0.55	1706	7.30-6.80 (m, 4H), 6.16-5.74 (m, 1H), 5.40-5.10 (m, 2H), 4.66-4.36 (m, 2H), 3.97 (q, J7, 2H), 1.38 (t, J7, 3H)
4i	**2c**	CH_3I	**5ci**	liquid	80	$C_{13}H_{14}N_2O$	70.48 70.53	7.83 7.92	13.71 13.85	0.65	0.53	—	7.30-6.80 (m, 4H), 3.64 (d, J7, 2H), 2.46-1.96 (m, 1H), 0.94 (d, J7, 6H)
6	**2e**	CH_2=CH-CH_2Br	**5ee**	54	90	$C_{15}H_{14}N_2O$	72.80 73.08	6.53 6.80	13.07 13.30	0.72	0.63	—	6.90 (s, 4H), 6.30-5.43 (m, 1H), 5.43-4.84 (m, 2H), 4.38 (d, J6, 2H)
6	**2f**	*n*-C_3H_7Br	**5ff**	liquid	85	$C_{12}H_{16}N_2O$	71.46 71.79	8.25 8.60	12.83 12.61	0.72	0.65	—	6.90 (s, 4H), 3.75 (t, J7, 4H), 1.72 (sex, J7, 4H), 0.92 (t, J7, 6H)
6	**2g**	*i*-C_3H_7Br	**5gg**	liquid	80	$C_{12}H_{16}N_2O$	71.46 71.72	8.25 8.41	12.83 13.06	0.70	0.65	—	6.95 (s, 4H), 5.0-4.2 (m, 2H), 1.53 (d, J7, 12H)
6	**2h**	*n*-C_4H_9Br	**5hh**	liquid	80	$C_{15}H_{22}N_2O$	68.10 68.28	8.32 8.65	10.59 10.39	0.81	0.77	—	6.90 (s, 4H), 3.75 (t, J7, 4H), 2.0-1.07 (m, 8H), 0.95 (t, J7, 6H)
6	**2i**	*i*-C_4H_9Br	**5ii**	50	85	$C_{15}H_{22}N_2O$	68.10 68.33	8.32 8.52	10.59 10.37	0.80	0.77	—	6.87 (s, 4H), 3.60 (d, J7, 4H), 2.50-1.80 (m, 2H), 0.96 (d, J7, 12H)
4j	**2h**	*n*-C_4H_9Br	**5hj**	liquid	85	$C_{19}H_{20}N_2O$	77.03 77.31	7.13 7.41	9.99 10.11	0.90	0.85	1704	7.30 (s, 5H), 7.20-6.76 (m, 4H), 5.08 (s, N-CH_2), 4.92 (t, J7, 3H), 1.92-1.10 (m, 4H), 0.97 (t, J7, 3H)
6	**2j**	$C_6H_5CH_2$Br	**5jj**	110	90	$C_{21}H_{18}N_2O$	80.15 80.39	5.73 5.90	8.91 9.17	0.87	0.85	—	7.45-7.20 (m, 10H), 7.05-6.80 (m, 4H), 5.12 (s, 4H)

(a) *Cf.* footnote Table 1, b. (b) *Cf.* footnote Table 1, c. (c) Lit. (14) m.p. 107°.

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