(2) Batterham, T. J., Highet, R. J., *Aust. J. Chem.*, **17**, 428 (1964).
(3) Bhacca, N. S., Johnson, L. F., Shooley, J. N., "Varian NMR Spectra Catalog", Spectrum No. 122, National Press, 1962.
(4) Bhacca, N. S., Johnson, L. F., Shooley, J. N., "Varian NMR Spectra Catalog", Spectrum No. 123, National Press, 1962.
(5) Canter, F. W., Curd, F. H., Robertson, A., *J. Chem. Soc.*, 1245 (1931).
(6) Diedrich, D. F., *J. Med. Pharm. Chem.*, **5**, 1054 (1962).
(7) Diedrich, D. F., *Arch. Biochem. Biophys.*, **117**, 248 (1966).
(8) Dutta, N. L., Bose, J. L., *J. Sci. Res. (Hardwar, India)*, **11B**, 413 (1952).
(9) Gulati, K. C., Seth, S. R., Venkataraman, K., *Org. Synth.*, **15**, 70 (1935).
(10) Jurd, L., *J. Org. Chem.*, **27**, 872 (1962).
(11) Szabó, V., Farkas, E., Lévai, A., *Acta Univ. Debrecen. Ludovico Kossuth Nominatae, Ser. Phys. Chim.*, 191 (1969/70).
(12) Venkataraman, K., *Proc. Natl. Inst. Sci. India*, **5**, 255 (1939).
(13) Vick, H., Diedrich, D. F., Baumann, K., *Am. J. Physiol.*, **224**, 552 (1973).

Received for review February 14, 1977. Accepted May 30, 1977. Part of this work was supported by Public Health Service Grant AM 06878.

Synthesis and Characterization of 3-Alkylbenzothiazolium Salts

P. J. Nigrey* and A. F. Garito
Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Six 3-alkyl substituted benzothiazolium iodides were synthesized by quaternization of benzothiazol with alkyl iodides. The above iodides were converted to corresponding perchlorate salts using silver perchlorate. UV, IR, and NMR spectral data are reported.

Although a few 3-alkylbenzothiazolium iodides have been known for some time, these were restricted to methyl- and ethyl-substituted (*3, 5*) ones, with the characterization of these having been poor and for many others unavailable. Recently, interest in cyanine dye studies (*4*), nucleophilic carbenes (*6*), catalysis (*1*), and charge-transfer complexes (*2*) has made the synthesis and systematic study of these types of compounds a worthwhile endeavor particularly since most studies to date have been restricted to methyl- and ethyl-substituted types. We report here a simple technique for the systematic synthesis of 3-alkylbenzothiazolium iodides and a novel scheme for the preparation of the corresponding perchlorates to give analytically pure samples in good yields.

Experimental Section

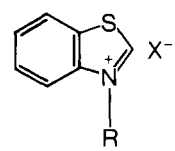
All melting points were taken on a Mettler FP5 melting point apparatus using a Mettler FP 52 microscope hot stage attachment and are uncorrected. Elemental chemical analysis were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Ultraviolet (UV) absorption spectra were recorded on a Cary 14 recording spectrophotometer in 10^{-5} M solutions in acetonitrile. Infrared (IR) spectra were recorded on a Perkin-Elmer 225 grating spectrophotometer in KBr pellets. Nuclear magnetic resonance (NMR) spectra were obtained at 60 MHz on a Varian A-60 spectrometer in deuterated dimethyl sulfoxide solutions with tetramethylsilane (Me_4Si) as the internal standard. All values for chemical shifts (δ) were reported downfield from Me_4Si in parts per million.

Materials. All reagents used in these studies were used as commercially available without further purification. Silver perchlorate (Alfa inorganics, anhydrous) was stored over desiccant prior to usage.

Preparation of 3-Alkylbenzothiazolium Salts. In the following representative methods for the synthesis of **1a, 5a,** and **5b** yields were not optimized.

Method I. A 25-mm medium-wall Pyrex tube was filled with benzothiazol (8.68 g, 64.3 mmol) and methyl iodide (11.4 g, 80.3 mmol). The contents of the tube were solidified in liquid nitrogen (−196 °C), sealed off, allowed to warm to room temperature, and then placed in an oven at 140 °C for 15 min. After cooling to room temperature, the tube was again cooled to −196 °C and

Table I. Physical Properties of 3-Alkylbenzothiazolium Salts[a]



	R	X^-	Method of prep	Reaction time, h	Mp, °C	Yield, %	Solvent of recryst
1a	CH_3	I	I	0.25	216.3–217.1	71	A/E
1b	CH_3	ClO_4	III		144.6–145.5	85	A/EA
2a	C_2H_5	I	I	1	140.4–141.0	75	A/E
2b	C_2H_5	ClO_4	III		91.4–92.1	95	A/EA
3a	*n*-C_3H_7	I	II	1	158.1–158.5	70	A/EA
3b	*n*-C_3H_7	ClO_4	III		88.4–88.7	78	A/EA
4a	*i*-C_3H_7	I	I	4	131.3–132.2	74	A/EA
4b	*i*-C_3H_7	ClO_4	III		108.1–109.1	72	AC/EA
5a	*n*-C_4H_9	I	I	0.50	114.6–115.2	67	A/EA
5b	*n*-C_4H_9	ClO_4	III		97.7–98.0	60	A/EA
6a	*n*-C_5H_{11}	I	I	0.50	119.0–120.0	70	A/EA
6b	*n*-C_5H_{11}	ClO_4	III		99.4–99.9	90	A/EA

[a] Elemental analyses (C,H,N,Cl,I,O,S) were in agreement with theoretical values and submitted for review. [b] Key: A = acetonitrile, E = ethanol, EA = ethyl acetate, AC = acetone.

Table II. IR and UV Absorption Data for 3-Alkylbenzothiazolium Salts[a]

	Aromatic CH str, cm^{-1}	Aliphatic CH str, cm^{-1}	C=C, C=N str, cm^{-1}	Aromatic CH out-of-plane bend, cm^{-1}	λ_{max}, nm (log ϵ)
1a	3040 w	2990 s	1580 m, 1515 m, 1450 m, 1430 m	887 s, 760 s	206 (4.49)
2a	3080 m	3000 m	1580 m, 1500 m, 1427 s	882 s, 762 s	207 (4.51)
3a	3050 m	2995 m	1580 m, 1510 m, 1455 m	900 m, 743 s	206 (4.51)
4a	3020 s	2990 s	1575 m, 1496 m, 1434 m	901 m, 752 s	206 (4.54)
5a	3060 w	2970 s	1575 w, 1510 w, 1438 m	909 m, 900 m, 759 s	205 (4.55)
6a	3065 m	2940 m	1573 w, 1505 w, 1424 s	888 s, 764 s	205 (4.50)
1b	3040 m	3010 m	1580 m, 1518 m, 1445 m	900 m, 885 m, 765 s	208 (4.08)
2b	3060 m	2980 m	1580 m, 1520 m, 1440 m	890 m, 745 s	208 (4.12)
3b	3085 m	2965 w	1581 m, 1520 w, 1455 m	907 m, 754 s	208 (4.04)
4b	3090 m	2990 m	1576 m, 1500 m, 1435 m	905 m, 755 s	208 (4.09)
5b	3080 s	2960 s	1579 m, 1505 m, 1455 m	909 m, 760 s	209 (4.08)
6b	3070 m	2960 m	1580 m, 1509 m, 1429 m	903 m, 764 s	207 (4.16)

[a] Key: s = strong, m = medium, w = weak.

Table III. NMR Data for 3-Alkylbenzothiazolium Salts[a]

	Aliphatic H, δ	Aromatic H,[b] δ	H-2, δ
1a	4.46 s	7.78–8.70 m	10.6 s
2a	1.64 t, 4.95 q	7.80–8.77 m	10.7 s
3a	1.00 t, 2.06 h, 4.95 t	7.83–8.32 m	10.8 s
4a	1.74 d, 5.56 t	7.85–8.78 m	10.8 s
5a	0.95 t, 1.12–1.66 bm, 1.68–2.21 bm, 4.97 t	7.83–8.78 m	10.8 s
6a	0.90 t, 1.13–1.62 bm, 1.77–2.28 bm, 4.97 t	7.85–8.88 m	10.8 s
1b	4.46 s	7.78–8.65 m	10.6 s
2b	1.65 t, 4.92 q	7.78–8.67 m	10.6 s
3b	0.98 t, 2.04 h, 4.87 t	7.82–8.67 m	10.6 s
4b	1.74 d, 5.48 qn	7.80–8.67 m	10.6 s
5b	0.95 t, 1.12–1.65 bm, 1.70–2.18 bm, 4.88 t	7.80–8.67 m	10.6 s
6b	0.89 t, 1.07–1.58 bm, 1.70–2.18 bm, 4.88 t	7.80–8.68 m	10.6 s

[a] Key: s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, h = hextet, m = multiplet, bm = broad multiplet. [b] Aromatic protons in AA'BB' system.

carefully opened. The contents were slurried with acetone/ethyl ether (3:7 v/v), filtered, and recrystallized from a minimum volume of acetonitrile/ethanol (1:1 v/v) to give 12.6 g (71%) of **1a** as bright orange needles.

Method II. A mixture of benzothiazol (11.2 g, 82.6 mmol) and 1-iodobutane (16.0 g, 87.0 mmol) was refluxed under an argon atmosphere for 30 min. The resulting solution was allowed to cool to room temperature, slurried with acetone/ethyl ether, filtered, and recrystallized from acetonitrile/ethyl acetate (1:1 v/v) to give 17.6 g (67%) of **5a** as yellow needles.

Method III. To a solution of **5a** (9.57 g, 30.0 mmol) in 50 mL of absolute methanol was added silver perchlorate (6.22 g, 30.0 mmol) in 50 mL of absolute methanol. The resulting mixture was heated slightly (45 °C) and filtered through Celite while warm. The filter cake was washed with 10 mL of warm methanol and filtrate stored overnight at 0 °C. The solid obtained was recrystallized from minimum acetonitrile/ethyl acetate (1:1 v/v) to give 4.65 g (60%) of **5b** as colorless crystals. Although perchlorates are known explosion hazards, these salts failed to explode when tested by dropping a 5.5-kg weight 2.1 m into tubes containing samples.

Physical properties of title compounds are given in Table I. Spectral characterizations are given in Tables II and III.

Literature Cited

(1) Bartsch, R. A., Hünig, S., Quast, H., *J. Am. Chem. Soc.*, **92,** 6007 (1970).
(2) Buvet, R., DuPuis, P., Néel, J., Périchon, J., *Bull. Chim. Soc. Fr.*, 3991 (1969).
(3) Hofman, A. W., *Ber.*, **13,** 8 (1880).
(4) Leifer, A., Bonis, D., Collins, M., Dougherty, P., Fusco, A. J., Koral, M., Lu Valle, J. E., *Spectrochim. Acta*, **20,** 909 (1964).
(5) Mills, W. H., *J. Chem. Soc.*, **121,** 455 (1922).
(6) Wanzlick, H. W., Kleiner, H. J., Lasch, I., Füldener, H. U., Steinmaus, H., *Justus Liebigs Ann. Chem.*, **708,** 155 (1967).

Received for Review March 21, 1977. Accepted May 30, 1977. Supported in part by the National Science Foundation, MRL Program under Grant No. DMR-76-80994.