The Synthesis of Some Substituted Benzyl Iodides and Related Compounds[1]

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Several additional benzyl iodides were required for use in studies on the exchange of benzyl iodides with radioactive iodide ion. The exchange studies are being carried out by Milton Kahn and associates in this laboratory.

The two methods previously described[2] were used to prepare the benzyl iodides, namely, method A involving the exchange of the aryl halide with sodium iodide in acetone and method B involving the reaction of a benzyl alcohol with concentrated hydriodic acid. The benzyl iodides prepared together with their properties and analytical data are shown in Table I.

TABLE I

Substituted Benzyl Iodides—$RC_6H_4CH_2I$ or $R_2C_6H_3CH_2I$

R	Procedure	Recryst. Solvent	Appearance	M.P., °C.	Formula	Iodine Analysis Calc'd	Iodine Analysis Found
o-F	A		Pale yellow oil[a,b]		C_7H_6FI	53.77	53.68
o-Cl[c]	A	Petroleum ether with Norit (A)	Colorless needles	26–27	C_7H_6ClI	50.25	50.35
o-Br	A	Petroleum ether with Norit (A)	Pale yellow needles	47.5–48.5[d]	C_7H_6BrI	42.74	43.28
o-I	A	Petroleum ether with Norit (A)	Pale yellow needles	71–74	$C_7H_6I_2$	36.90[e]	36.58
m-Cl	A		Pale yellow oil[f]		C_7H_6ClI	50.25	50.23
2,6-diCl	B	Petroleum ether with Norit (A)	Pale yellow needles	71–72.5	$C_7H_5Cl_2I$	44.23	43.85

[a] Rapidly liberates iodine on exposure to light. [b] B.P., 71–74° at 0.4 mm. [c] *o*-Chlorobenzyl iodide is mentioned by Scott, U. S. Patent 2,481,044, but no constants or analytical data are given. [d] Reported m.p. 47° in reference (4). [e] Calculated only for aliphatic (reactive) iodine in the molecule. [f] B.P., 141° at 22 mm., solidifies in the refrigerator at about 15°.

For the preparation of 2,6-dichlorobenzyl iodide, the corresponding alcohol was required. This was obtained by lithium aluminum hydride reduction of 2,6-dichlorobenzaldehyde in quantitative yield. The aldehyde was prepared by treatment of 2,6-dichlorobenzal chloride with aqueous alcoholic silver nitrate.

EXPERIMENTAL[3]

Procedures A and B are illustrated in reference (2). Intermediate benzyl bromides used in procedure A were obtained as follows: *o*-fluorobenzyl bromide,[4] *o*-bromobenzyl bromide,[5] *o*-iodobenzyl bromide,[6] and *m*-chlorobenzyl bromide[7–10] were all prepared by N-bromosuccinimide bromination of the corresponding halogenated toluenes. The physical constants of these agree well with those listed in the references cited. The *o*-chlorobenzyl chloride was obtained from the Eastman Kodak Co.

2,6-Dichlorobenzaldehyde. To a stirred solution of 229.9 g. (1 mole) of 2,6-dichlorobenzal chloride (Eastman Kodak Co.) dissolved in 2 l. of ethanol and 500 ml. of water was added 339.8 g. (2 moles) of silver nitrate dissolved in 2 l. of 50% aqueous ethanol. The silver chloride precipitated immediately but stirring was continued for several hours. The silver chloride was removed by filtration. The filtration process was repeated several times as more silver chloride continued to precipitate. The filtrate was evaporated to low volume under reduced pressure until the aldehyde began to separate as long needles contaminated with silver chloride. The aldehyde-silver chloride mixture was separated by dissolving the aldehyde in ether, drying the ether solution over sodium sulfate and evaporating the ether. There was obtained 61 g. of 2,6-dichlorobenzaldehyde which after recrystallization from ethanol melted at 71–72.5°.[11]

2,6-Dichlorobenzyl alcohol. To a suspension of 12.2 g. (0.32 mole) of lithium aluminum hydride in 400 ml. of anhydrous ether was added with stirring 28 g. (0.16 mole) of 2,6-dichlorobenzaldehyde dissolved in 350 ml. of absolute ether over a period of $1^1/_2$ hours. The slurry was allowed to stir for an additional two hours. The excess lithium aluminum hydride was cautiously decomposed with water, acidified with dilute hydrochloric acid, and the ether layer was separated and dried over sodium sulfate. The white crystalline mass on evaporation of the ether amounted to 28 g., m.p. 86–90°. A sample purified for analysis melted at 97–98.5°.

Anal. Calculated for $C_7H_6Cl_2O$: C, 47.49; H, 3.42. Found: C, 47.50; H, 3.57.

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(2) Daub and Castle, *J. Org. Chem.*, **19**, 1571 (1954).

(3) All melting points are uncorrected.

(4) Shoesmith and Slater, *J. Chem. Soc.*, 214 (1926).

(5) Goerner and Nametz, *J. Am. Chem. Soc.*, **73**, 2940 (1951).

(6) Mabery and Robinson, *Amer. Chem. J.*, **4**, 101 (1882).

(7) Sprung, *J. Am. Chem. Soc.*, **52**, 1640 (1930).

(8) Jenkins, *J. Am. Chem. Soc.*, **55**, 2896 (1933).

(9) Bernstein, Roth, and Miller, *J. Am. Chem. Soc.*, **70**, 2310 (1948).

(10) Baker, *J. Chem. Soc.*, 1448 (1936).

(11) Gindraux, *Helv. Chim. Acta*, **12**, 933 (1929).