Drozdov and Stavrovskaya.[13] Into a 1-l. three-necked flask equipped with a stirrer, condenser, Glascol and thermometer were charged 150 ml. of 95% ethanol, 10 g. (0.166 mole) of glacial acetic acid, 250 g. of water and 50 g. (0.89 mole) of 100 mesh iron powder. This slurry was stirred and heated to 80–85° in one-half hour and then 21.0 g. (0.1 mole) of 2-chloro-6-nitrobenzothiazole added in small portions in the course of one hour. The dark slurry was held at 80° an additional hour and 200 ml. of 95% ethanol and 10 g. of Darco G-60 added. This mixture was refluxed an additional one-quarter hour and filtered hot through a heated funnel into 250 ml. of water. The filtrate was chilled in an icebox and the solid filtered off and dried *in vacuo* at 50°. The weight of material, m.p. 155–157° (lit.,[13] m.p. 162°), was 13.8 g. (75%). This material was pure enough to be used without further purification.

6-Acetylamino-2-chlorobenzothiazole (IX).—Into a 300-ml. three-necked flask equipped with a sealed stirrer, dropping funnel and ice-bath were charged 18.4 g. (0.1 mole) of 6-amino-2-chlorobenzothiazole and 70 ml. of pyridine. The solution was stirred and at 10° 10.8 g. (0.16 mole) of acetyl chloride was added dropwise in the course of 20 minutes. The reaction mixture was stirred at 0–10° an additional one-half hour and poured into 800 ml. of ice and water. The heavy white slurry was stirred to dissolve the ice and the white solid collected on a Buchner funnel. The cake was washed with 500 ml. of water and dried *in vacuo* at 50°. The weight of material, m.p. 118–121°, was 21.6 g. (95%). A sample was recrystallized twice by dissolving in a minimum amount of 95% ethanol, filtering, and adding the filtrate to 40 volumes of hot water. Fine white needles separated, melting at 131–132°.

Anal. Calcd. for $C_9H_8ON_2SCl$: C, 47.47; H, 3.51; N, 12.20. Found: C, 47.56; H, 3.18; N, 12.57.

6-Acetylamino-2-hydrazinobenzothiazole (**X**).—Into a 600-ml. beaker on a hot-plate was placed 150 g. (85% real, 2.55 moles) of hydrazine hydrate. The liquid was stirred and heated to boiling and 42.5 g. (0.186 mole) of 6-acetylamino-2-chlorobenzothiazole added quickly. A heavy slurry was formed. The slurry was diluted with a 125 ml. of hot water, held at the boil for an additional five minutes, cooled by adding 150 g. of ice, and filtered. The cake was washed with water and dried *in vacuo* at 50°. The weight of material, m.p. 215–219°, was 38.3 g. (93%). A sample was recrystallized from aqueous methanol, m.p. 233–235°.

Anal. Calcd. for $C_9H_{10}ON_4S$: C, 48.64; H, 4.50; N, 25.22. Found: C, 48.90; H, 4.39; N, 24.49.

Condensation of 6-Acetylamino-2-hydrazinobenzothiazole with Aromatic Aldehydes.—Into a 250-ml. beaker on a hot-plate were charged 3.0 g. (0.0135 mole) of 6-acetylamino-2-hydrazinobenzothiazole and 100 ml. of 25% acetic acid. The slurry was heated to boiling and a solution was obtained. To the yellow solution at the boil was added 3.0 g. (0.024 mole) of *p*-hydroxybenzaldehyde. A thick slurry was obtained almost immediately. This was stirred manually for 10 minutes, cooled, filtered, and the cake washed with water. The yield of material, m.p. 274–277°, was 3.4 g. (77%).

6-Amino-2-hydrazinobenzothiazole (XI).—Into a 100-ml. beaker were charged 10 g. (0.054 mole) of 6-amino-2-chlorobenzothiazole and 50 g. (85% real, 0.85 mole) of hydrazine hydrate. The slurry was heated to boiling and stirred manually. A straw-colored solution was formed which was boiled five minutes longer and cooled to 20°. The bulky precipitate was collected on a Buchner funnel, washed with 200 ml.of water, and dried *in vacuo* at 55°. The weight of pale yellow crystals was 8.6 g. (88%), m.p. 208–210°. A sample recrystallized twice from isopropyl alcohol melted at 209.5–211°.

Anal. Calcd. for $C_7H_8N_4S$: C, 46.66; H, 4.45; N, 31.03. Found: C, 47.12; H, 4.24; N, 30.84.

2-Chloro-6-phenylsulfonamidobenzothiazole.—In a 50-ml. beaker on a hot-plate were mixed 20 ml. of pyridine, 1.3 g. (0.007 mole) of 6-amino-2-chlorobenzothiazole, and 2.0 g. (0.0114 mole) benzenesulfonyl chloride. The mixture was heated to boiling and the cherry-red fluorescent solution obtained was cooled and poured into 150 ml. of water. The light red solid was collected on a Buchner funnel and recrystallized from aqueous ethanol. The weight of material melting point 175–177° was 2.1 g. or 95% of theory. A sample was recrystallized once again from aqueous ethanol, m.p. 176–177.5°.

Anal. Calcd. for $C_{13}H_9O_2N_2S_2Cl$: C, 48.07; H, 2.76; N, 8.63. Found: C, 48.71; H, 3.02; N, 8.55.

2-Hydrazino-6-phenylsulfonamidobenzothiazole.—In a 50-ml. beaker on a hot-plate were mixed 2.1 g. (0.0065 mole) of 2-chloro-6-phenylsulfonamidobenzothiazole and 20 g. (85% real, 0.34 mole) of hydrazine hydrate. When this mixture was heated to boiling a pale yellow solution was obtained. This solution was boiled an additional five minutes, cooled, and neutralized to litmus paper with 6 *N* sulfuric acid. Fifty milliliters of water was added and the solid was collected on a Buchner funnel. The cake was washed with water and air dried. The weight of material, m.p. 212–216°, was 1.7 g. (82%). A sample was recrystallized twice from toluene-alcohol. Pale yellow crystals were obtained melting at 214–216°.

Anal. Calcd. for $C_{13}H_{12}O_2N_4S_2$: C, 48.75; H, 3.75; N, 17.50. Found: C, 49.33; H, 3.75; N, 17.60.

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[13] N. S. Drozdov and V. I. Stavrovskaya, *J. Gen. Chem.* (*U. S. S. R.*), **9**, 409 (1949), or *C. A.*, **34**, 103 (1940).

NOTES

Preparation of 1,3-Dichlorohexafluoropropane

BY B. L. BAKER AND A. M. WHALEY[1]

It became necessary during the course of a program concerning stability studies on various fluorochlorides to prepare highly fluorinated materials. One of the compounds synthesized was 1,3-dichlorohexafluoropropane, $CF_2Cl-CF_2-CF_2Cl$, and the procedure reported represents a practical three-step method from commercially available 1,2-dichloro-2-propene. The low boiling point and the indicated stability coupled with the below reported method of preparation of the fluoride would seem to make it worthy of further study as a possible refrigerant.

There has been considerable confusion in the literature regarding the structure of the 1,2- and 1,3-dichlorohexafluoropropanes. The first correct accounts of the synthesis of the 1,3-dichloride are those of Downing, *et al.*,[2] who chlorinated $CHF_2-CF_2-CHF_2$ and Young and Murray[3] who chlorinated $CHF_2-CF_2-CF_2Cl$ and also fluorinated $CFCl_2-CF_2-CFCl_2$.

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[1] Halogen Chemicals, Inc., 616 King St., Columbia, S. C.

[2] F. B. Downing, *et al.*, U. S. Patent 2,413,696.

[3] E. G. Young and W. S. Murray, THIS JOURNAL, **70**, 2814 (1948).

Both the 1,1- and 1,2-dichlorohexafluoropropanes have been prepared by Henne and Waalkes.[4,5]

In our work the 1,3-dichloride was made by first adding hydrogen fluoride to 1,2-dichloro-2-propene to form the difluoromonochloride, then chlorinating this to the hexachlorodifluoride and finally fluorinating the latter to the hexafluorodichloride.

Experimental

Preparation of CH_3–CF_2–CH_2Cl.—The procedure used was similar to that of Henne and Haeckl[6] with the important exceptions that the temperature was kept at 100°, by means of a steam-bath, instead of at 50–60° and that hydrogen chloride was bled off at a pressure of 270 lb. per sq. in. gage. This process resulted in a 60% yield of difluorochloride.

Preparation of CCl_3–CF_2–CCl_3.—Ten moles (1145 g.) of CH_3–CF_2–CH_2Cl was chlorinated in sunlight at 75–85° until the theoretical weight of chlorine had been absorbed. The crude material was fractionated to give a practically quantitative yield of CCl_3–CF_2–CCl_3, boiling range 193–195°.[7]

Preparation of CF_2Cl–CF_2-CF_2Cl.—In a steel pressure cylinder eight moles (1430 g.) of antimony trifluoride was treated with four moles (284 g.) of chlorine. Four moles (1147 g.) of CCl_3–CF_2–CCl_3 was added and the mixture was heated in an oil-bath at 210° for one hour, 230° for four hours and 250° during two hours. The pressure eventually rose to 300 lb. per sq. in. gage. The organic material was distilled from the cylinder, washed with concd. hydrochloric acid, neutralized and fractionated. There were obtained 370 g. of CF_2Cl–CF_2–CF_2Cl, b.p. 35.8°, $n^{20}D$ 1.3030, d^{20}_4 1.5730[8] and 300 g. of $CFCl_2$–CF_2–CF_2Cl intermediate, which can be converted to the above hexafluorodichloride.

Acknowledgment.—Part of the funds for this project was made available by the University of South Carolina Research Committee.

[4] A. L. Henne and T. P. Waalkes, THIS JOURNAL, **67**, 1639 (1945).

[5] A. L. Henne and T. P. Waalkes, *ibid.*, **68**, 496 (1946).

[6] A. L. Henne and F. W. Haeckl, *ibid.*, **63**, 2692 (1941).

[7] A. L. Henne and M. W. Renoll, *ibid.*, **59**, 2434 (1937).

[8] Young and Murray[9] found the freezing range of this compound to be −126.3 to −125.4°.

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Some Quaternary Salts of 8-Hydroxyquinoline[1]

BY CARL T. BAHNER, LLOYD A. WALKER, FRANCES PIERCE AND EMMA KITE

The preparation of quaternary salts of substituted quinolines[2] has been extended to include salts of 8-hydroxyquinoline.

The salts were prepared by heating a mixture of the base and the appropriate organic halide at 100°, dissolving the resulting dark amorphous mass in hot alcohol, and adding ethyl acetate, ethyl ether or petroleum ether to throw out crystals of the product which was then recrystallized to a constant melting point before analysis. A 30-minute reaction period sufficed for the phenacyl bromides, but β-phenylethyl iodide required 48 hours and β-cyclohexylethyl bromide did not react satisfactorily even when heated 96 hours. The products were yellow, crystalline solids which were not readily soluble in water. The melting points and analytical data are shown in Table I.

Acknowledgments.—We wish to express our appreciation to Dr. M. J. Shear and Dr. J. L. Hartwell of the National Cancer Institute for arranging to screen these compounds against tumors in mice, and to Mr. George Biggerstaff and Mr. Lilburn Norton for assisting in the purification and analysis of one of these products.

TABLE I

8-HYDROXYQUINOLINIUM SALTS

Salt of 8-hydroxyquinoline with:	Empirical formula	M.p., °C.	Yield, %[a]	Analyses, % ionic halogen Calcd.	Found[b]
β-Phenylethyl iodide	$C_{17}H_{16}INO$	168.5–169[c]	85	33.64	33.46
Phenacyl bromide	$C_{17}H_{14}BrNO_2$	234–235	58	23.21	22.98
p-Methylphenacyl bromide	$C_{18}H_{16}BrNO_2$	223.5–224	46	22.26	22.09
p-Bromophenacyl bromide	$C_{17}H_{13}Br_2NO_2$	244.5–245	50	18.89	18.78
p-Iodophenacyl bromide	$C_{17}H_{13}BrINO_2$	257–258	58	16.99	16.68
p-Methoxyphenacyl bromide	$C_{17}H_{16}BrNO_3$	230	10	21.35	21.19
β-Naphthacyl bromide	$C_{21}H_{16}BrNO_2$	234–235	42[d]	20.02	19.93

[a] Crude yield of crystalline material unless otherwise indicated. [b] Average of two Volhard analyses for ionic halogen. After final recrystallization from acetic acid. [d] Yield of pure material.

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[1] This investigation was supported in part by a research grant from the National Cancer Institute, of the National Institutes of Health, Public Health Service, for which we are grateful.

[2] C. T. Bahner, W. K. Easley, M. D. Pickens, H. D. Lyons, L. L. Norton, B. G. Walden and G. Biggerstaff, THIS JOURNAL, **73**, 3499 (1951).

Morpholinium Salts[1]

BY CARL T. BAHNER, EMMA KITE, FRANCES PIERCE, LYDIA MOORE RIVES, MADGE DEEL PICKENS AND CLIFFORD MYERS

In extending the study of analogs of quaternary pyridinium salts as possible anti-cancer agents[2] we have synthesized tertiary amine hydrohalides and quaternary ammonium salts containing a morpholine ring. Lutz and his associates[3] have prepared a number of N-substituted morpholines for use as intermediates or for testing as anti-malarials and Hazard, Corteggiani and Renard[4] have reported that 4-methyl-4-(2-phenylethyl)-morpholinium iodide produced marked hypertension in dogs at a dose of 5 mg./kg.

The tertiary amine hydrohalides were obtained by reaction of morpholine with the appropriate organic halide in equimolecular proportions and the quaternary salts were prepared from N-substituted morpholines in the same manner. The time required for reaction varied from a few minutes to a

[1] This investigation was supported in part by a research grant from the National Cancer Institute, of the National Institutes of Health, Public Health Service, for which we are grateful.

[2] *Cf.*, C. T. Bahner, M. Fielden, L. M. Rives and M. D. Pickens, THIS JOURNAL, **73**, in press (1951).

[3] Robert E. Lutz, Rufus K. Allison, Gilbert Ashburn, Philip S. Bailey, Marion T. Clark, John F. Codington, Adolf J. Deinet, James A. Freek, Robert H. Jordan, Norman H. Leake, Tellis A. Martin, Kent C. Nicodemus, Russell J. Rowlett, Jr., Newton H. Shearer, Jr., J. Doyle Smith and James W. Wilson, III, *J. Org. Chem.*, **12**, 617 (1947).

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