for 30 min. The mixture was extracted with EtOAc (20 mL) and the organic solution was washed with H_2O (2 × 5 mL), dried (Na_2SO_4), and distilled in vacuo to yield a colorless solid. The solid was recrystallized from EtOAc–petroleum ether to produce 20.5 mg (77%) of **11** as colorless crystals, mp 237–239 °C dec; ^1H NMR (360 MHz, DMSO-d_6) δ 2.11 (s, 3), 2.19 (s, 3), 4.76 (t, 1, H_9), 5.78 (dd, 1, H_8), 6.07 (m, 1, H_{10}), 6.35 (d, 1, H_7), 6.43 (d, 1, OH), 7.38 (d, 1, H_5), 7.63 (dd, 1, H_3), 8.02 (d, 1, H_6), 8.42 (dd, 1, H_4), 9.00 (dd, 1, H_2), $J_{2,3}$ = 4.1, $J_{2,4}$ = 1.7, $J_{3,4}$ = 8.3, $J_{5,6}$ = 8.6, $J_{7,8}$ = 8.5, $J_{8,9}$ = 2.7, $J_{9,10}$ = 3.2, $J_{10,OH}$ = 5.0 Hz.

A mixture of 15 mg of the bromohydrin **11**, ca. 5 mg of NaOMe, and dry THF (5 mL) was stirred at 0–5 °C for 30 min. EtOAc (15 mL) was added and the organic phase was washed with ice-cold H_2O (5 mL), dried (Na_2SO_4), and evaporated in vacuo to yield 5 mg (57%) of a colorless solid which decomposed without melting at 133 °C: ^1H NMR (360 MHz, DMSO-d_6) δ 3.82 (m, 1, H_9), 4.10 (m, 1, H_8), 4.64 (m, 1, H_7), 4.71 (d, 1, OH_7), 5.12 (d, 1, H_{10}), 5.51 (d, 1, OH_8), 7.59 (dd, 1, H_3), 7.65 (d, 1, H_5), 7.99 (d, 1, H_6), 8.40 (dd, 1, H_4), 9.00 (dd, 1, H_2), $J_{2,3}$ = 4.1, $J_{2,4}$ = 1.7, $J_{3,4}$ = 8.3, $J_{5,6}$ = 8.4, $J_{7,8}$ = 4.0, $J_{8,9}$ = 2.0, $J_{9,10}$ = 4.0, $J_{7,OH}$ = 8.2, $J_{8,OH}$ = 4.6 Hz; mass spectrum, m/e 229 (M^+).

***trans*-8-Bromo-7-hydroxy- and *trans*-9-Bromo-10-hydroxy-7,8,9,10-tetrahydrobenzo[*h*]quinoline (15 and 16).** A mixture of 7,8,9,10-tetrahydrobenzo[*h*]quinoline[18] (**12**, 0.7g, 3.8 mmol), *N*-bromosuccinimide (0.7g, 3.9 mmol), and α,α'-azobis(isobutyronitrile) [AIBN, 5.0 mg] in dry CCl_4 (40 mL) was stirred at 70–75 °C under argon for 45 min. The mixture was cooled to 10 °C and filtered, and the filtrate was concentrated under reduced pressure to yield a mixture of **12**, **13**, and **14** (1.03 g). This mixture was stirred with LiF (1.0 g) and Li_2CO_3 (1.5 g) in redistilled HMPA (5 mL) at 80–85 °C for 60 min under argon. The reaction mixture was cooled to room temperature, diluted with ether (50 mL), and filtered. The filtrate was washed with water (5 × 25 mL), dried (Na_2SO_4), and concentrated to give a dark oil (0.62 g).

The above oil (0.62 g), *N*-bromoacetamide (NBA, 0.50 g), and 2 drops of concentrated HCl were dissolved in a mixture of THF (30 mL) and water (6 mL) and stirred at 0–5 °C under Ar for 4 h. The mixture was diluted with water (25 mL) and extracted with EtOAc (2 × 50 mL). The combined EtOAc extracts were dried (Na_2SO_4) and concentrated in vacuo. The crude product, thus obtained, was chromatographed on a dry column grade silica gel (Merck) using $CHCl_3$ as eluant to give 0.15 g (14%) of **16** [mp 165–167 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.8 (br s, exchangeable with D_2O, OH), 2.20–2.70 (m, 2 H_8), 3.10 (m, 2 H_7), 4.60 (m, H_9), 5.76 (d, H_{10}), 7.10–7.85 (m, H_3, H_5, and H_6), 8.17 (d, H_4), 9.83 (m, H_2), $J_{3,4}$ = 8.2, $J_{9,10}$ = 6.6; mass spectrum, m/e 276.97, 278.94 (M^+)] and 80 mg (8%) of **15** [mp 135–137 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 2.25–2.73 (m, 2 H_9), 3.15 (br s, exchangeable with D_2O, OH), 3.25–3.70 (m, 2 H_{10}), 4.45 (m, H_8), 5.07 (d, H_7), 7.40–7.72 (m, H_3, H_5, H_6), 8.13 (dd, H_4), 8.92 (dd, H_2), $J_{2,3}$ = 4.3, $J_{2,4}$ = 1.6, $J_{3,4}$ = 8, $J_{7,8}$ = 7 Hz; mass spectrum, m/e 277, 279 (M^+)].

7,8,9,10-Tetrahydro-7,8-epoxybenzo[*h*]quinoline (6). To a stirred solution of a mixture of bromohydrin **15** (25 mg) in acetone (5 mL) was added 10% NaOH (0.4 mL) under argon. The mixture was stirred at room temperature for 30 min and extracted with ether (50 mL), washed with water (1 × 15 mL), dried (Na_2SO_4), and evaporated under reduced pressure to produce **6** (13 mg, 74%) as a colorless crystalline solid after recrystallization from ether, mp 88–89 °C: ^1H NMR (270 MHz, $CDCl_3$) δ 1.83 (m, 1 H), 2.54–2.86 (m, 3 H), 3.88 (m, H_8), 4.02 (d, H_7), 7.37–7.72 (m, H_3, H_5, H_6), 8.15 (dd, H_4), 8.94 (dd, H_2), $J_{2,3}$ = 1.6, $J_{2,4}$ = 4.0, $J_{3,4}$ = 8.2, $J_{7,8}$ = 4.3 Hz; high resolution mass spectrum, exact mass calcd for $C_{13}H_{11}NO$ 197.0840, obsd 197.0840.

7,8,9,10-Tetrahydro-9,10-epoxybenzo[*h*]quinoline (7). The reaction of bromohydrin **16** (30 mg) in acetone (5 mL) containing 10% NaOH (0.4 mL) was affected as described for **5**. Workup gave crystalline **7** (15 mg, 71%) after recrystallization from petroleum ether: mp 128–129 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.87 (m, 1 H), 2.54–3.10 (m, 3 H), 3.91 (m, H_9), 5.46 (d, H_{10}), 7.20–7.75 (m, H_3, H_5, H_7), 8.13 (dd, H_4), 8.94 (m, H_2), $J_{2,4}$ = 1.2, $J_{3,4}$ = 8.5, $J_{9,10}$ = 4.3 Hz; high-resolution mass spectrum, exact mass calcd for $C_{13}H_{11}NO$ 197.0840, obsd 197.0821.

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Homogeneous Nucleophile Exchange. 1. Simple, High-Yield Synthesis of Some Heterodihalides

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Chemoselectivity holds a central position in organic synthesis.[1] To achieve this, differentiated di(poly)functional synthons often are used; heterodihalides would appear to be eminently employable to this end. However, although the halides are one of the most versatile sets of functions with which to create carbon–carbon bonds and introduce functional variations, the only readily and cheaply available heterodihalides, prior to this work, were the C_1–C_3 α,ω-bromochlorides; the C_4–C_6 bromochlorides and the C_1–C_6 chloroiodides are quite expensive. Higher homologues are prepared by methods so inconvenient and inefficient that they seldom are used in synthesis. This paper describes rapid, simple, inexpensive preparations of a range of bromochlorides and chloroiodides from readily available starting materials.

Our interest in this area arose initially because of a desire to rapidly convert an alkyl bromide to the corresponding chloride; we discovered that this could be accomplished nearly quantitatively by heating a neat mixture of the bromide with a large excess of 1-chlorobutane for 2–3 h in the presence of a catalytic amount of quaternary ammonium halide. A literature search for halide interconversion methodology yielded only two comparable examples. In 1981, Sasson and Yonovich-Weiss[2] reported homogeneously catalyzed exchange between primary alkyl bromides and chlorides. In 1984, Bidd and Whiting,[3] apparently unaware of the previous work, published a similar report; they also converted an iodide to the corresponding bromide or chloride but used more than an equivalent of the corresponding quaternary halide. The most cited work on halide interconversions, aside from Finkelstein (1910),[4] is the 1976 paper of Willy et al.[5] However, they employed metal halide catalyzed equilibrations, and although they usually achieved very high conversions, reactions often required 10 or more days, and the product had to be washed free of salts and solvent prior to distillation. They did not apply their method to synthesis of heterodihalides, although they discussed and demonstrated useful chemoselectivity of such reagents. Since then, most papers on bromide–chloride exchange,[6] citing Willy, have used metal halides, either as catalysts or as stoichiometric reagents in phase transfer catalyzed processes. It thus became clear that homogeneously catalyzed halide exchange is largely unappreciated and that its scope and limitations never have been systematically explored.

We soon realized that such an exchange has at least one major advantage over the Finkelstein reaction or any phase

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transfer catalyzed process: It is not subject to solubility or transportability effects. This property ensures that the composition of a (di)halide mixture at equilibrium will depend only on the relative numbers of each kind of exchangeable covalent halide in the system. On this principle, we developed a two-stage process for preparation of α,ω-bromochloroalkanes. After one equilibration of (e.g.) a 1:1 mixture of 1,4-dibromo- and dichlorobutane to a 1:2:1 mixture of Br_2, BrCl, and Cl_2 compounds, the heterodihalide is separated by fractional distillation. In the second stage, all dihalide fractions (from the first stage) that are not acceptably pure heterodihalide are recombined with starting materials equivalent to the removed product and reequilibrated. The isolated yield of heterodihalide from the second equilibration, based on new stock, is theoretically quantitative; in principle, the second stage can be repeated indefinitely.

A limitation on the applicability of the bromo chloride synthesis is imposed by the boiling point differences among the components of the final equilibrated mixture. For the 1,4-C_4 system, these differences are about 24 °C at 1 atm; they decrease with increasing molecular size. To minimize decomposition during fractionation (appreciable for bromides above 200 °C), pressure must be reduced, but this lowers boiling point differences and fractionation efficiency as well as boiling points. Thus, obtention of usably pure bromochlorides containing more than six carbons by the process described herein, to be economical, appears to require a large-scale operation and/or very efficient fractionation apparatus. However, the C_4–C_6 compounds should find wide application in synthesis. The bromochlorobutane is the smallest bromochloride capable of forming a usably stable mono-Grignard reagent;[7,8] efficient monocoupling[8,9] of this reagent with the inexpensive C_3–C_6 α,ω-dibromides now should be a superior route to pure C_7–C_{10} α,ω-bromochlorides.[10]

In developing the above process, we made two observations particularly pertinent to expanding its scope. First, one can make a bromochloride from a dichloride and a *mono*bromide (usually cheaper than the necessary dibromide), by distilling out monochloride as it is formed. Second, the catalyst (usually $Bu_4N^+Br^-$) remains active over 100 °C. We attribute this stability to the absence of strongly basic anions in the equilibrating system (contrast the behavior of onium salts as phase-transfer catalysts).[11]

Extension to chloroiodides next was sought. While the Finkelstein reaction has been used to convert dichlorides to chloroiodides,[12] long reflux (in solvent) usually is required, and yields *based on dichloride* normally cannot exceed 50% because chloroiodide is converted to diiodide as rapidly as it is formed. Also, once formed in this system, diiodide cannot revert back to chloroiodide. Selective Finkelstein conversion of some bromochlorides to chloroiodides is possible[13] but is not practical unless the bromochlorides are readily available. It was thought that homogeneously catalyzed chloride–iodide exchange could be achieved if (1) R'Cl (eq 1) was removed as formed and (2) Cl–I exchange could be made to occur at a practical rate. In a second-stage experiment, a mixture of 1-iodo-

$$\mathrm{RCl} + \mathrm{R'I} \xrightarrow[\text{heat}]{} \mathrm{RI} + \mathrm{R'Cl}\uparrow \qquad (1)$$

butane, 1,4-dichlorobutane, and residues from a previous equilibration was heated to 163 °C, giving a >95% isolated yield of >98% pure chloroiodobutane. We note that chloro iodides are more easily separated from the corresponding homodihalides than are bromochlorides, because of greater boiling point differences (30–35 °C at ca. 80 mm.)

As the foregoing syntheses were being developed, it came to our attention that the smallest member of the chloroiodoalkane family, chloroiodomethane (CIM), is an extremely versatile synthon. In little more than a decade, several dozen patents[14] have appeared in which penicillins, cephalosporins, and similar antibiotics have been linked by a simple bridge (e.g., $(CH_2)_n$) to a second molecular unit functioning as an inactivator of body enzymes that otherwise would weaken or destroy the effect of the antibiotic. In most cases, the bridging carbons are obtained from heterodihalides, quite commonly $BrCH_2Cl$ (BCM) and CIM. The latter has played a significant role also in (e.g.) (a) homologation of boronic esters as part of a general synthesis of enantiomerically pure chiral compounds,[15,16] (b) a simple, one-carbon homologation of terminal alkenes,[17] (c) a highly efficient conversion of aldehydes or ketones to chlorohydrins or epoxides,[18] and (d) convenient conversion of enol silyl ethers to trimethylsilyloxycyclopropanes.[19] In view of its current high cost (>$110/mol), a cheap, facile synthesis of CIM should be well received.

CIM has been made from reaction of dichloromethane and sodium iodide, in solvent; published processes are lengthy, and the best reported isolated yield is 63%.[20] Hine[21] has reported that, in sodium iodide–acetone at 50 °C, BCM reacted over 1000 times faster (to replace Br) than did CIM (to replace Cl). While a selective Finkelstein BCM to CIM conversion thus appeared feasible, catalytic bromide–iodide exchange is more convenient (much smaller volume, no solvent handling) and we wanted to evaluate the selectivity of a catalytic process. When BCM and iodomethane were heated together to 70 °C, selective iodide–bromide exchange occurred (eq 2) to give a 92% yield of >99% pure CIM. In this particular case, a re-

$$\underset{\text{bp 68 °C}}{\mathrm{BrCH_2Cl}} + \underset{\text{bp 42 °C}}{\mathrm{CH_3I}} \xrightarrow[(\mathrm{Cl^-\ form})]{\text{Amberlyst A-26}} \underset{\text{bp 108 °C}}{\mathrm{ClCH_2I}} + \underset{\text{bp 4 °C}}{\mathrm{CH_3Br}}\uparrow \qquad (2)$$

sin-anchored catalyst,[22] not used previously because of

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thermal sensitivity, was found to be more easily separated from the product mixture.

In summary, homogeneous nucleophile exchange, applied to heterodihalide synthesis as described herein, is faster, simpler, and cheaper and gives better yields than any previously reported process. Also, it should not be overlooked that primary monohalides (except fluorides) now can be interchanged almost at will, under mild, neutral conditions. One consequence is that the heretofore rare use of chloride as a protecting function[3,5,23] should find application in a wider range of synthetic schemes. We continue to explore the scope of this method.

Experimental Section

All chemicals in this work are known compounds; starting materials (97% or higher purity, from Aldrich, Columbia, Lancaster) usually were used without further purification; some iodides were decolorized with dilute aqueous sodium bisulfite. **Warning**: *Many of these compounds, particularly iodides, are known or suspected to be toxic and/or carcinogenic.* Products were identified by comparison of boiling points and ^{1}H NMR spectra with the literature data. NMR spectra were recorded for $CDCl_3$ solutions on a GE QE-300 spectrometer. Fractional distillations of product mixtures and selective removal of volatile components during mixture equilibrations were done with tape-heated, insulated, glass helices packed fractionating columns. The tallest column used was 30 in. high. Iodide-containing mixtures/products were shielded from direct light during and after distillations. Reaction mixtures (before, during, and after) and distillation fractions were analyzed by analytical gas chromatography, using a Hewlett-Packard (HP) 5780 instrument equipped with a 0.2-mm i.d. 25-m cross-linked 5% phenyl methyl silicone fused silica capillary column, a 0.2-mm i.d. 25-m methyl silicone capillary column, flame ionization detectors, and HP 3390A and 3392A reporting integrators.

1-Bromo-4-chlorobutane (BrC_4Cl). This experiment was done on an analytical scale to assess the utility of the method. A stock mixture was prepared from ClC_4Cl (6.36 g, 50 mmol) and BrC_4Br (10.80 g, 50 mmol). A 1.0-g aliquot (5.9 mmol) from stock was brought to ca. 100 °C in a test tube in a thermostated oil bath; Bu_4NBr (19 mg, 0.059 mmol, 1%) was added and rapidly dissolved with stirring. After 60 min, the mol % of BrC_4Cl (GC analysis) was >47%; after 19.5 h, it was 49.7%.

1-Bromo-6-chlorohexane (BrC_6Cl). A mixture of *n*-BuBr (274 g, 2.0 mol), ClC_6Cl (233 g, 1.5 mol), and Bu_4NBr (22.5 g, 70 mmol, 2%) was heated in a system fitted with a fractionating column and pot and head thermometers. The pot temperature rose to 99 °C and then dropped to 92 °C; distillate (bp 78 °C) evolved as rapidly as 1 mL/min. After 5 h of heating (pot temperature 110 °C), the cooled, orange-yellow solution (nearly 50% BrC_6Cl) was washed with water (2 × 250 mL) and filtered through a 6-in. column of flash-grade silica gel, which was flushed with hexane (20 mL). Fractionation (first at 1 atm and then at ca. 100 mm) gave no fractions greater than 80% pure. The entire mixture of dihalides later was converted to a chloro iodo system by a selective Finkelstein reaction and then successfully fractionated.

1-Chloro-4-iodobutane (ClC_4I; First Stage). In an unoptimized first experiment, decolorized *n*-BuI (368 g, 2.00 mol), ClC_4Cl (190.5 g, 1.50 mol), and Bu_4NI (5.5 g, 15 mmol) were heated together (apparatus as for BrC_6Cl) to 105 °C; little distillate appeared. Addition of Bu_4NBr (4.9 g, 15 mmol) and heating from 105 to 141 °C over 6 h gave 49 mL of nearly pure *n*-BuCl (NMR), bp 75–76 °C. The product mixture, on washing with very dilute aqueous $NaHSO_3$ (2 × 250 mL), went from dark red to yellow-orange; pressure filtration through flash grade silica gel (6 in.) decolorized it. Fractionation as for BrC_6Cl yielded, as a middle fraction, 109 g (0.50 mol, 75% of theory) of >97% pure ClC_4I, bp 115–116 °C. Early fractions and pot material were recombined for use in the next experiment.

1-Chloro-4-iodobutane (ClC_4I; Second Stage). Leftovers from the above experiment were mixed with decolorized *n*-BuI (92 g, 0.5 mol), ClC_4Cl (63.5 g, 0.5 mol), and Bu_4NI (7.5 g, 20 mmol). Heating from 25 to 163 °C over 1.5 h (apparatus as before) gave 58 mL of distillate, maximum bp 74 °C. Workup of the pot material as before gave a colorless filtrate containing ClC_4Cl, ClC_4I, and IC_4I, nearly 1:4:4, which afforded 104.5 g (0.48 mol, >95%) of >98% pure ClC_4I on fractionation. Other fractions and pot material (all nearly colorless) were saved for further equilibration.

Chloroiodomethane. Beads of Amberlyst A-26 (chloride form) on a column were washed sequentially with methanol and acetone and vacuum-dried overnight. Material so obtained effectively catalyzed bromide–iodide exchange between $BrCH_2Cl$ and EtI, on an analytical scale. In a preparative experiment, the catalyst (20 g, >80 mequiv of reactive sites) was heated with MeI (246 g, 1.75 mol) to 35 °C until the vigorous evolution of MeCl ceased. $BrCH_2Cl$ (131 g, 1.01 mol) was added; the system was fitted with a reflux condenser connected to a gas collection setup. Heating from 25 to 70 °C over 9 h (gas evolution up to 25 mL/min) gave a pot mixture containing $BrCH_2Cl$, CIM, and CH_2I_2 (14:84:2), plus MeI and a small amount of MeBr. Catalyst beads and broken particles were separated by pressure filtration through coarse sintered glass, rinsed with a small amount of MeI, and stored for reuse. The pale yellow-green filtrate was fractionated at 1 atm; three fractions were collected: fraction 1 (11.0 g), bp 43–65 °C, 73% MeI, 30% $BrCH_2Cl$; fraction 2 (19.7 g), bp 65–104 °C, 58% $BrCH_2Cl$, 38% CIM, 4% ClC_2Cl [^{1}H NMR δ 4.35 (s; impurity in starting $BrCH_2Cl$)]; fraction 3 (149 g), bp 104–105 °C, 99+% CIM (92% yield, based on unrecovered starting material). The pot was empty (no CH_2I_2 recovered).

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Registry No. ClC_4Cl, 110-56-5; BrC_4Br, 110-52-1; ClC_6Cl, 2163-00-0; BuBr, 109-65-9; BuI, 542-69-8; $BrCH_2Cl$, 74-97-5; MeI, 74-88-4; BrC_4Cl, 6940-78-9; BrC_6Cl, 6294-17-3; ClC_4I, 10297-05-9; $ClCH_2I$, 593-71-5; Bu_4NBr, 1643-19-2; Bu_4NI, 311-28-4; BuCl, 109-69-3; IC_4I, 628-21-7.

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