macrocyclic polyether sulfides.[2] The hydrogen atoms located on the ethylene groups between oxygen atoms were observed as singlets at δ 3.56 ± 0.04 while those between sulfur atoms were at δ 2.77 ± 0.00. The hydrogen atoms on methylene groups α to oxygen and β to sulfur were observed as triplets at δ 3.62 ± 0.04. The hydrogen atoms on methylene groups α to sulfur and β to oxygen were observed as triplets at δ 2.70 ± 0.02. The methyl hydrogen atoms adjacent to sulfur and oxygen were observed at δ 2.14 ± 0.01 and 3.32 ± 0.01, respectively. The physical properties of the thiatetraglymes also were similar to those of the macrocyclic polyether sulfides in that the melting point increased as the number of sulfur atoms was increased.[3,4]

Experimental Section

All infrared (ir) spectra were obtained on a Perkin-Elmer 457 spectrophotometer. A Varian A-60A spectrometer was used to record the proton nuclear magnetic resonance (NMR) spectra. Elemental analyses and molecular weight determinations were performed by M-H-W Laboratories, Garden City, Mich. Melting points were determined on a Thomas-Hoover capillary type melting point apparatus and are uncorrected.

Preparation of 2,5,11,14-Tetraoxa-8-thiapentadecane (1). A mixture of 46.2 g (0.33 mol) of 1-(2-chloroethoxy)-2-methoxyethane (Eastman) and 350 ml of reagent ethanol were placed in a flask fitted with a stirrer, reflux condenser, and addition funnel. After the mixture was brought to reflux, an aqueous solution of 40.0 g of sodium sulfide nonahydrate, 0.5 g of sodium hydroxide, and 75 ml of water was slowly added over a 60-min period. The reaction mixture was then cooled and filtered and the ethanol was removed under vacuum. The aqueous residue was extracted three times with 150-ml portions of ether. The ether was removed and the crude product was distilled to give 26.6 g (67%) of product: bp 120–121° (0.1 mm); NMR δ 3.64 (t, 4, OCH$_2$CH$_2$S), 3.54 (s, 8, OCH$_2$CH$_2$O), 3.33 (s, 6, OCH$_3$), 2.72 (t, 4, SC H$_2$CH$_2$O).

Anal. Calcd for C$_{10}$H$_{22}$O$_4$S: C, 50.39; H, 9.30; S, 13.45; mol wt, 238.4. Found: C, 50.60; H, 9.05; S, 13.22; mol wt, 239.

Preparation of 5,8,11-Trioxa-2,14-dithiapentadecane (2). A mixture of 25 g of sodium hydroxide in 500 ml of reagent ethanol was cooled to −15°. Methanethiol (26.0 g, 0.54 mol, Eastman) at −15° was added to the above solution. A solid formed which dissolved when the mixture was allowed to warm to room temperature. The solution was then refluxed while 62.4 g (0.27 mol) of tetraethylene glycol dichloride[2] was slowly added. The resulting mixture was cooled and treated as in the previous example to yield 51.6 g (75%) of product: bp 133–134° (0.1 mm); NMR δ 3.68 (t, 4, OCH$_2$CH$_2$S), 3.62 (s, 8, OCH$_2$CH$_2$O) 2.68 (t, 4, SCH$_2$CH$_2$O), 2.13 (s, 6, SCH$_3$).

Anal. Calcd for C$_{10}$H$_{22}$O$_3$S$_2$: C, 47.21; H, 8.72; S, 25.21; mol wt, 254.4. Found: C, 47.20; H, 8.81; S, 25.16; mol wt, 253.

Preparation of 2,8,14-Trioxa-5,11-dithiapentadecane (3). A mixture of 12.4 g (0.09 mol) of bis(2-mercaptoethyl) ether (Aldrich) and 12 g of potassium hydroxide in 500 ml of reagent ethanol was heated to reflux. To this solution was slowly added 25.0 g (0.18 mol) of 2-bromoethyl methyl ether (Eastman) in 50 ml of reagent ethanol. The resulting mixture was refluxed for 30 min, allowed to cool, and treated as for compound 1 to give 16.1 g (70%) of product, bp 137–138° (0.1 nm); NMR δ 3.65 (t, 4, OCH$_2$CH$_2$S), 3.56 (t, 4, OCH$_2$CH$_2$S), 3.32 (s, 6, OCH$_3$) 2.72 (t, 8, SCH$_2$CH$_2$O).

Anal. Calcd for C$_{10}$H$_{22}$O$_3$S$_2$: C, 47.21; H, 8.72; S, 25.21; mol wt, 254.4. Found: C, 47.14; H, 9.01; S, 25.06; mol wt, 254.

Preparation of 2,14-Dioxa-5,8,11-trithiapentadecane (4). A mixture of 13.9 g (0.09 mol) of bis(2-mercaptoethyl) sulfide (Pfaltz and Bauer), 25.0 g (0.18 mol) of 2-bromoethyl methyl ether (Eastman), and 12.0 g of potassium hydroxide in 500 ml of ethanol was treated as above for compound 3. The product was distilled to give 18.3 g (75.3%): bp 154–155° (0.1 mm); NMR δ 3.56 (t, 4, OCH$_2$CH$_2$S), 3.34 (s, 6, OCH$_3$), 2.77 (s, 8, SCH$_2$CH$_2$S), 2.68 (t, 4, SCH$_2$CH$_2$O).

Anal. Calcd for C$_{10}$H$_{22}$O$_2$S$_3$: C, 44.41; H, 8.20; S, 35.56; mol wt, 270.48. Found: C, 44.62, H, 8.34; S, 35.40; mol wt, 268.

Preparation of 8-Oxa-2,5,11,14-tetrathiapentadecane (5). A mixture of 8.5 g (0.06 mol) of bis(2-mercaptoethyl) ether (Aldrich), 13.5 g (0.12 mol) of 2-chloroethyl methyl sulfide (City Chemical) (vesicant, use caution) and 5.5 g of sodium hydroxide in 300 ml of ethanol was refluxed and the product was isolated as described for

3. The product (13.6 g, 78%) was a white solid which was recrystallized from benzene–hexane: mp 36–37°; NMR δ 3.66 (t, 4, OCH$_2$CH$_2$S), 2.77 (s, 8, SCH$_2$CH$_2$S), 2.72 (t, 4, SCH$_2$CH$_2$O), 2.13 (s, 6, SCH$_3$).

Anal. Calcd for C$_{10}$H$_{22}$OS$_4$: C, 41.92; H, 7.74; S, 44.76; mol wt, 286.54. Found: C, 41.99; H, 7.83; S, 45.01; mol wt, 284.

Preparation of 2,5,8,11,14-Pentathiapentadecane (6). This compound was prepared from 8.4 g (0.054 mol) of bis(2-mercaptoethyl) sulfide, 12.0 g (0.108 mol) of 2-chloroethyl methyl sulfide, 5.0 g of sodium metal and 300 ml of ethanol as above for compound 3. The product (14.5 g, 89%) was a white solid which was recrystallized from benzene–hexane: mp 87–88°; NMR δ 2.77 (s, 16, SCH$_2$CH$_2$S), 2.15 (s, 6, SCH$_3$).

Anal. Calcd for C$_{10}$H$_{22}$S$_5$: C, 39.69; H, 7.33; S, 52.98; mol wt, 302.61. Found: C, 39.49; H, 7.22; S, 53.69; mol wt, 301.

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Pyrolysis of Some Methyl- and Benzylindoles

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Under drastic pyrolytic conditions, alkylpyrroles exhibit competitive alkyl group migrations, alkyl group cleavage, and ring expansion reactions to pyridines.[1] The benzo analogs, methylindoles, likewise have been reported to undergo the ring expansion and dealkylation reactions. Thus, 2-methylindole is converted into quinoline[2] (17% yield) and 3-methylindole is converted into indole[3] when their vapors are passed through a glowing tube. The observation that allyl groups undergo competitive [3,3] and [1,5] sigmatropic shifts on the pyrolysis of allylindoles[4] prompted this investigation of the migratory behavior of alkyl groups in alkylindoles.

Results and Discussion

The pyrolysis of *N*-, 2-, and 3-methylindole and of *N*- and 3-benzylindole resulted in the formation of products arising from alkyl group migrations in addition to those arising from cleavage (dealkylation) and from ring expansion reactions (see Tables I and II). As was observed in the pyrrole series[5] and in contrast to the Claisen migrations of crotylindole,[4] the N to C isomerizations of the alkylindoles were irreversible processes. On the other hand, the 2- and

Table I
Pyrolyzate Composition[a] of the Methylindoles as a Function of Temperature

Methylindole	Temp, °C	Methylindoles			Indole	Quinoline
		N-	2-	3-		
2-	550	0	99	1	0	0
3-	550	0	3	97	0	0
N-	600	93	1	0	3	3
2-	600	0	92	8	0	0
3-	600	0	10	89	1	0
N-	650	71	5	2	10	12
2-	650	0	75	23	0.5	1.5
3-	650	0	45	52	2	1
N-[b]	700	21 ± 2	15 ± 1	8 ± 1	26 ± 1	30 ± 1
N-[c,d]	700	16 ± 1	16 ± 2	7 ± 1	23 ± 1	19 ± 1
2-	700	0	58	26	10	6
3-	700	0	49	28	13	10
N-	750	6	7	4	41	43
2-	750	0	16	9	39	36
2-[c,e]	750	0	20 ± 2	7 ± 1	27 ± 4	18 ± 1
3-	750	0	20	11	35	34

[a] Area percent of component in pyrolyzate. [b] Averages and average deviations of area percents from triplicate pyrolyses. [c] Weight percent yields (weight of component per 100 g of substance pyrolyzed) and two-standard-deviation ranges were determined by GLC (triplicate analyses) using 2,3,6-trimethylnaphthalene as internal standard and correcting for detector response. [d] Weight recovery, 81%. [e] Weight recovery, 73%.

Table II
Pyrolyzate Composition[a,b] of the Benzylindoles as a Function of Temperature

Benzyl-indole	Temp, °C	Benzylindoles			Indole	Phenylquinolines			Quinoline	Bibenzyl	Others
		N-	2-	3-		2-	3-	4-			
N-[c]	500	92	1	2	2	1	0	0	0	2	0
N-[d]	550	47 ± 2	4	10 ± 1	18 ± 2	3 ± 1	1	0.5	5 ± 1	10	1
3-	550	0	15	73	9	0	0	0	0	2	0
N-[d]	600	2 ± 1	11 ± 1	12 ± 1	40 ± 1	4 ± 1	2	2	5 ± 2	12 ± 2	7 ± 1
3-	600	0	46	24	20	0	2	2	3	1	1
3-	650	0	10	7	55	0	5	5	11	0	5

[a] Pyrolyses of melted solid. [b] Compositions reported as area percent. [c] Pyrolyzed as a 20% solution in benzene. [d] Averages and average deviations of area percents from duplicate pyrolyses.

3-methylindoles interconverted under all the reaction conditions used. These interconversions are first observed at temperatures (550°) at which the N isomer is not isomerized. The 2 to 3 isomer ratio, which becomes ca. 2:1 at higher temperatures regardless of the isomer pyrolyzed (N, 2, or 3), suggests that the 2 and 3 isomers have equilibrated under the higher temperature conditions.

In the pyrolyses of N-methylindole, the yield of the 2-methyl isomer always exceeds that of the 3 isomer and at 600° the 2 isomer was the only alkyl migration product. Also, since at 650° the pyrolysis of N-methylindole produced a 2 to 3 isomer ratio of ca. 2.5:1 and under the same conditions only half of a sample of 3-methylindole was converted to 2 isomer, it is concluded that the 2 isomer is a primary pyrolysis product. By similar reasoning, the appearance of the 3 isomer in the N-methylindole pyrolysis is very likely the result of a secondary reaction of the initially formed 2 isomer.

The extent to which the primary reactions, isomerization, cleavage, or ring expansion, occur depends upon the position of methyl substitution in the indole. Over the temperature range 600–700° N-methylindole reacted approximately equally among the three paths while 2- and 3-methylindole reacted predominantly by alkyl group migration. The 3 isomer exhibited about twice the reactivity of the 2 isomer in the isomerization. At 750°, cleavage and

ring expansion became the predominant processes followed by all isomers.

The benzylindoles were pyrolyzed to provide information about the effect of phenyl substitution on the alkyl migration path as well as other competitive reaction paths and about the position occupied by the alkyl substituent in the ring expansion product.

Generally, the benzylindoles were more reactive than the methylindoles in each of the reaction paths—isomerization, cleavage, and ring expansion. This is consistent with expected radical character or partially developed radical character associated with each of the transition states of these processes.

As was observed with the methylindoles, the C-substituted indole (3-benzyl) was more reactive in the migration reaction than the N-substituted indole. Somewhat unexpected, however, was the observation that the yield of 3 isomer was greater than that of the 2 isomer in the N-benzylindoles pyrolyses. This suggests that the 3 isomer is either a primary product from N isomer or that it is formed from 2 isomer at a rate faster than the N to 2 isomerization.

In the pyrolysis of N-benzylindole, the majority of the cleavage product arises from N isomer rather than from 3 isomer as secondary product. For example, at 550° a 20% yield of indole is obtained from N isomer while under the same conditions only a 9% yield is produced from 3 isomer.

Chart I
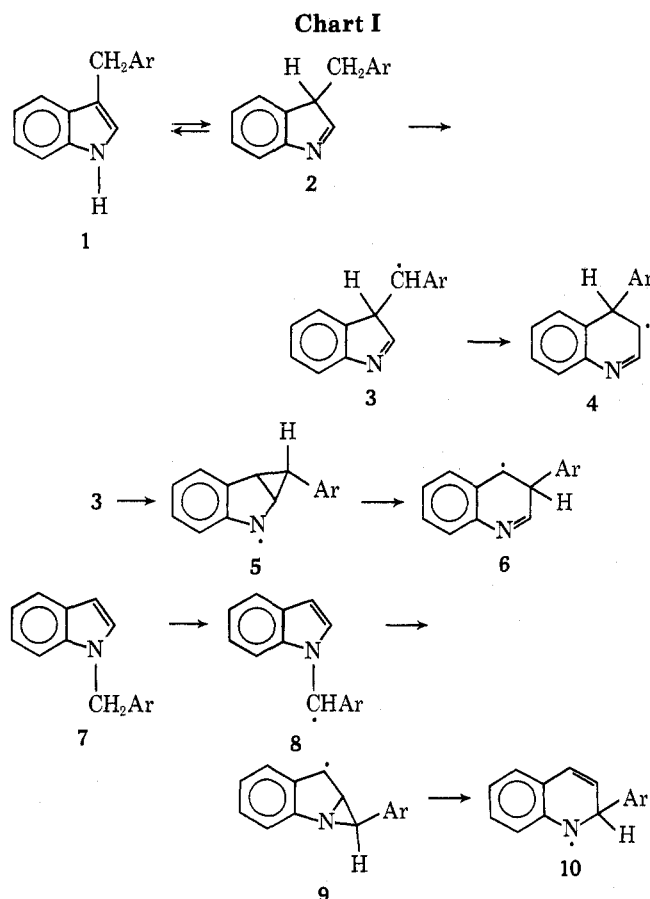
The relative amounts of cleavage and ring expansion appear to parallel the relative magnitudes of the ArC–C, ArC–H, and ArC–N bond energies. (The ring expansion reactions are presumed to be initiated by a C–H bond cleavage in the alkyl substituent.) Cleavage was found to be the more facile reaction of the two.

In the ring-expansion reaction, the major products arise from an insertion of the benzyl–methylene carbon between the atom to which it is attached and an adjacent ring carbon. 3-Benzylindole produced only 3- and 4-phenylquinoline but no 2-phenylquinoline. Similarly, only 2-phenylquinoline was produced from N-benzylindole at 500°, and at higher temperatures the 2-phenylquinoline remained as the major ring-expansion product. The appearance of 3- and 4-phenylquinoline at higher temperatures in the N-benzylindole pyrolyzate is probably due in part to secondary decomposition of the primary product, 3-benzylindole. Quinoline formation accompanied the isomeric phenylquuoline formation, the yield of quinoline and the sum of yields of the phenylquinolines being approximately equivalent. It is postulated that the ring expansion reaction involves an initial C–H bond cleavage followed by isomerization to a quinolinyl radical which then loses either Ar · or H · with equal facility to form the quinoline or phenylquinoline, respectively. A possible scheme for the process is outlined in Chart I.

The conversion of **3** to **4** involves a 1,2-phenyl shift while conversions **3** to **6** and **8** to **10** involve either a vinyl-type shift or its equivalent. The equivalent process consists of a radical addition to a double bond followed by ring opening to the quinolinyl radical.

Experimental Section

Melting points are corrected. Infrared spectra were measured on a Beckman IR-8 spectrophotometer; ultraviolet spectra were measured on a Perkin-Elmer Model 202 spectrophotometer; and NMR spectra were measured on a Varian T-60 spectrometer in carbon tetrachloride or chloroform using Me$_4$Si as internal standard. Gas chromatographic analyses and separations were made on a Hewlett-Packard Model 5750 or an F & M Model 810 gas chromatograph.

The methylindoles were obtained from commercial sources. N-,[6,7] 2-,[8,9] and 3-benzylindole,[10] 2-,[11] 3-,[12] and 4-phenylquinoline[13,14] were synthesized by methods described in the literature.

Pyrolyses. The pyrolyses were carried out in the apparatus previously described[15] using a nitrogen flow of 100 ml/min. Berl saddles, filling a 12.5-cm length of the pyrolysis tube 1 cm from the top of the furnace, were used to volatilize the sample. The pyrolysis temperature quoted refers to the temperature in the empty region of the pyrolysis tube below the Berl saddles.

Samples were introduced into the reaction tube from a syringe (heated when melts were added) at a constant rate as neat liquids or molten solids (1 ml/40 min) or as 20% (w/v) benzene solutions (1 ml/15 min). Pyrolyzates obtained from the pyrolysis of benzene solutions contained biphenyl while those obtained from the pyrolysis of neat samples did not.

Analysis and Identification of Products. A. Methylindole Pyrolyses. Pyrolyzates were analyzed by GLC using a 12 ft × 0.125 in. Hewlett-Packard Hi-Pak Carbowax 20M column at 170 and 200° and a 12 ft × 0.125 in. 2% polyphenyl ether (six-ring) 90/100 Anakrom ABS column at 170°. The former column separated quinoline, N-methylindole, biphenyl, and indole but not 2- and 3-methylindole, while the latter column separated indole, biphenyl, and 2- and 3-methylindole but not N-methylindole and quinoline. The 2- and 3-methylindole ratio obtained from the polyphenyl ether column was used to calculate the yields of these indoles from the combined peak exhibited by the Carbowax column.

Pyrolyzate constituents were isolated by preparative GLC using a 15 ft × 0.375 in. 20% SE-30 50/60 Anakrom U column (isolation of quinoline, N-methylindole, and indole) and a 20 ft × 0.375 in. 20% polyphenyl ether (six-ring) 50/60 Anakrom U column (isolation of biphenyl, 2-, and 3-methylindole). Constituents were identified by comparisons of GLC retention times and ultraviolet spectra with those obtained from authentic samples.

B. Benzylindole Pyrolyses. The pyrolyzates were analyzed on an 8 ft × 0.375 in. 25% SE-30 column heated isothermally at 100° for 7 min and then programmed at 2°/min to 250° and on a 12 ft × 0.125 in. 2% polyphenyl ether (six-ring) column at 250°. The SE-30 column separated quinoline, indole, bibenzyl, 4-phenylquinoline, 3-benzylindole, and an additional peak consisting of 2-benzylindole, 2-, and 3-phenylquinoline. The polyphenyl ether column separated N-, 2-, and 3-benzylindole as well as the 2-, 3-, and 4-phenylquinolines.

Components of the pyrolyzate were isolated by preparative GLC using the SE-30 column. Identifications of all components, except the mixture of 2-benzylindole, 2-, and 3-phenylquinoline, are based on comparisons of GLC retention times and ultraviolet spectra with those of authentic compounds. Extraction of crude pyrolyzate with 1 M HCl removed only those components corresponding to quinoline, 2-, 3-, and 4-phenylquinoline and 2-benzylindole was isolated from the neutral fraction using a 15 ft × 0.375 in. 20% SE-30 column. The GLC retention time, infrared, and NMR spectra were identical with those obtained from an authentic sample.

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A Convenient Preparation of Optically Active 2-Halooctanes and Related Compounds[1]

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Optically active 2-haloalkanes have been of considerable utility in the elucidation of the mechanisms of many organic reactions and also serve as models for the theoretical study of optical activity.[2] The practical synthesis of these compounds is, therefore, a matter of some importance. We wish to report that 2-halooctanes can be conveniently prepared in good yields and in generally high optical purity by halide ion displacement on the tosylate formed from optically active 2-octanol.[3]

$$\overset{\cdots}{\underset{\diagup}{\text{C}}}\text{—OTs} \xrightarrow{\text{MX}} \text{X—}\overset{\cdots}{\underset{\diagdown}{\text{C}}} \qquad (1)$$
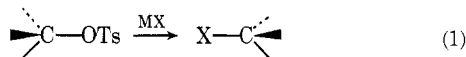
In a typical experiment, the tosylate (7.10 g, 25.0 mmol) of (+)-(S)-2-octanol, α^{20}_{589} +7.97°, optical purity 99.4%, was stirred vigorously with anhydrous potassium fluoride (7.25 g, 125 mmol) in 25.0 ml of triethylene glycol at 110° under a reduced pressure of 4.0 Torr. The volatile materials were allowed to distil from the reaction mixture and collected in a cold trap (−50°). Analysis of the crude distillate by GLC indicated a 52% yield of 2-fluorooctane (based on starting alcohol), accompanied by a 27% yield of octene(s). This crude distillate was treated with a slight excess of bromine in carbon disulfide, washed with aqueous sodium thiosulfate, dried (MgSO₄), and distilled to afford pure (−)-(R)-2-fluorooctane (1), α^{20}_{589} −9.99°.[4] The results of
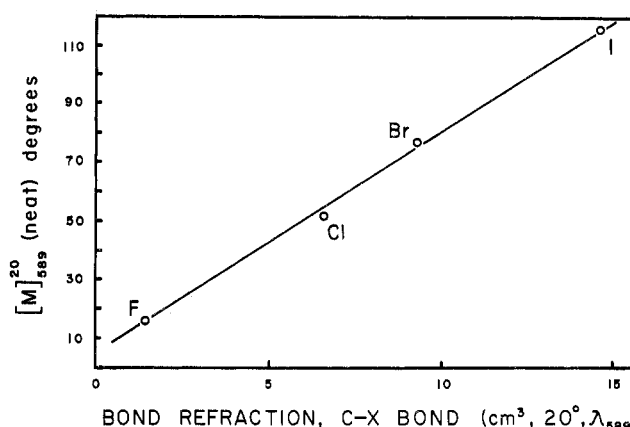
similar reactions employing lithium chloride, potassium bromide, and lithium iodide are listed in Table I.

The synthesis of (−)-(R)-2-fluorooctane (1) is particularly noteworthy. Its preparation provides the first completed series of configurationally related 2-haloalkanes. The resulting relationship can be used to estimate the optical purity of this compound based on the empirically observed linear correlation between the optical rotation and bond refraction developed by Davis and Jensen.[5] Figure 1 shows this relationship plotted for values of optically pure 2-chloro-, 2-bromo-, and 2-iodooctane of the same configuration. The extension of this line to include 2-fluorooctane leads to predicted molecular rotation for (−)-(R)-2-fluorooctane of $[M]^{20}_{589}$ −16.6°.[6] The agreement between this value and the observed molecular rotation of $[M]^{20}_{589}$ −16.4° suggests that displacement has proceeded with essentially complete *inversion* of configuration, to produce optically pure 1.

Of the existing procedures for the preparation of optically active 2-chloro- and 2-bromooctane, the reaction of an optically active alcohol with phosphorous trihalides and related reagents provides products of highest optical purity,[7] although overall yields are sometimes poor and conditions frequently critical. It is clear that the reaction of 2-octyl tosylate with halide ion as described above provides a significantly improved procedure for the synthesis of optically

Figure 1. A plot of the molecular rotation, [M], vs. the common bond refraction, [R] (C–X bond), for 2-halooctanes.

Table I
Reaction of (+)-(S)-2-Octyl Tosylate with Potassium Fluoride, Lithium Chloride, Potassium Bromide, and Lithium Iodide (Eq 1)

MX (concn, M)	Solvent[a]	Temp, °C (Torr)	Reaction time, hr	2-Halooctane (%)[b]	α^{20}_{589}	Optical purity, %	C–X bond refraction,[c] cm³, 20° (λ = 589)	Oc-tene (s), %[b,d]
KF (5.0)	Triethylene glycol	110 (4.0)	3	2-Fluorooctane (52)	−9.99[e]	~100[f]	1.44	27
LiCl (5.0)	Triethylene glycol	110 (1.0)	2	2-Chlorooctane (80)	−30.72[e]	97.2[g]	6.74	16
KBr (1.2)	Triethylene glycol	65 (0.1)	2	2-Bromooctane (75)	−41.56[e]	95.4[g]	9.80	8.0
LiI (1.2)	Tetraethylene glycol	90 (0.1)	1.5	2-Iodooctane (83)	−19.32[e]	30.6[g,h]	14.08	8.0

[a] All solvents were vacuum distilled under nitrogen immediately prior to use. [b] These values represent GLC yields based on starting alcohol; isolated halocarbon yields were somewhat lower. [c] The specific value for 2-fluoro-, 2-chloro-, 2-bromo-, and 2-iodooctane are unavailable. This number represents the common bond refraction of a number of fluoro-, chloro-, bromo-, and iodo-substituted alkanes. A tabulation of these values is given in ref 5. [d] No attempt was made to distinguish possible octene isomers. [e] GLC analysis indicated minimum sample purity >99%. [f] See text for discussion of this value. [g] Calculated for optically pure (+)-(S)-2-halooctane: α^{20}_{589} +31.6° (Cl), α^{20}_{589} +43.6° (Br), α^{20}_{589} +63.2° (I), taken from ref 7, Table V, footnote c. [h] The considerable racemization observed in this instance is presumably a result of iodide exchange; see ref 12.