9.3 g. (0.1 mole) of *t*-butyl chloride and heating to reflux for 10 min., the reaction mass was allowed to cool to ambient temperature and transferred under nitrogen to a dropping funnel on a second vessel under nitrogen.

2. **General Procedure Used in the Reaction of Lithium Diphenylphosphide with Aryl Halides. Method A. Normal Addition.**—The red reaction solution from 1 was allowed to run rapidly into the vessel leaving unchanged metal in the funnel. After the dropping funnel was replaced, the solution was heated to reflux and a solution of the aryl halide in tetrahydrofuran was added dropwise with rapid stirring under nitrogen.

Method B. Inverse Addition.—The red reaction solution was allowed to drop slowly into a rapidly stirred, refluxing solution of the aryl halide in tetrahydrofuran under nitrogen.

After addition was complete the reaction mixture was refluxed for 2 hr. and then allowed to return to ambient temperature. The flask was opened to air, most of the tetrahydrofuran distilled, and the residual mass steam distilled. After cooling the residue, the supernatant aqueous layer was separated from the bottom oily layer by extraction with chloroform. Acidification of the basic aqueous layer precipitated most of the phosphinic acid in it. This accounted for most of the phosphinic acid produced with little additional acid being isolated after treatment with 3% hydrogen peroxide at a later stage in the work-up.

The chloroform layer was then subjected to gas chromatographic analysis. The instrument was a Research Specialties Model 60-1A gas chromatograph with a flame ionization detector operating at 240–290°, which contained a 3-ft. column of 5% silicone oil DC-200 on 80–100-mesh Chromasorb (W-AW). In all cases a small amount of triphenylphosphine and its oxide were present. These materials presumably arose from uncleaved triphenylphosphine in the initial step. The per cent of uncleaved triphenylphosphine (calculated from chromatographic curve areas and conversion ratios arrived at from mixtures of known compositions) was usually between 10 and 15%.

The chromatographs of this chloroform solution showed peaks due to triphenylphosphine, triphenylphosphine oxide, small peaks of short retention times (due to unknown components and diphenylphosphine), and only two other peaks. These two were shown to be due to the phosphine and phosphine oxide expected from direct substitution of halide by the diphenylphosphide group.

Evaporation of the chloroform solution and dissolution of the remaining semisolid in acetone followed by addition of 3% hydrogen peroxide solution gave a clear solution which was allowed to stand overnight. The addition of peroxide was accompanied by heat evolution in most cases. Concentration of this solution, followed by addition of water and reconcentration, removed the acetone and produced a precipitate of semisolid. The supernatant aqueous layer was acidified after decantation and any precipitating phosphinic acid was isolated. Acetone trituration of water-insoluble material separated any remaining phosphinic acid as insoluble solid. The acetone filtrate solution was subjected to gas chromatographic analysis which, in most cases, disclosed peaks representing solvent, a small amount of triphenylphosphine, an even smaller amount of triphenylphosphine oxide, and a very large peak due to the diphenylarylphosphine oxide produced. Curve areas, conversion factors, and the weight of solid obtained on evaporation of acetone were used to calculate crude yields. Isolation of product in pure form was accomplished by crystallization.

3. **Preparation of Diphenyl(*m*-tolyl)- and Diphenyl(*p*-tolyl)-phosphines.**—The infrared spectra of the tolylphosphine oxides was that expected for *meta* and *para* isomers, respectively. The melting points of the isolated materials were identical with those reported in the literature.[12]

4. **Preparation of Diphenyl-*p*-biphenylphosphine Oxide.**—Diphenyl-*p*-biphenylphosphine oxide (m.p. 143–144°), previously unreported, showed no depression of mixture melting points with material prepared from the corresponding organometallic and diphenylphosphinous chloride, followed by oxidation. The two materials also had identical retention times under the conditions mentioned in connection with gas chromatographic separation of the isomeric tolyl oxides; their infrared spectra were identical.

Anal. Calcd. for $C_{24}H_{19}PO$: C, 81.4; H, 5.37; P, 8.75. Found: C, 81.71; H, 5.45; P, 8.28.

5. **Preparation of *p*-Bis(diphenylphosphino)benzene Dioxide.**—*p*-Dibromobenzene led, on normal addition, to *p*-bis(diphenylphosphino)benzene dioxide as shown by analysis, mixture melting points and infrared spectral comparison with the known material.[13,14] Gas–liquid partion chromatography at 320° employing very rapid carrier gas flow indicated that the crude reaction mixture contained only one diphosphine, the corresponding monoxide, and dioxide.

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Aluminum Chloride-Induced Halogen Exchange of Alkyl Halides

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Halide exchange between *n*-propyl bromide or *n*-propyl iodide and aluminum chloride yields, initially, an exchange product containing a high per cent of *n*-propyl chloride. Interchange of halogen between ethyl and *n*-propyl halides, catalyzed by aluminum chloride, also gives initial exchange products rich in the *n*-propyl halide. An equilibrium constant for the exchange of propyl bromide with aluminum chloride is estimated and mechanistic implications of the results are considered.

Although much work has been done on aromatic substitution by means of the Friedel–Crafts, aluminum trichloride-catalyzed reaction, relatively little attention has been given to halogen exchange between alkyl halides and aluminum trichloride.

Isotopic studies reveal that alkyl and acyl halides will exchange halogen atoms with the corresponding aluminum trihalides,[1,2] and interchange of methyl halides with aluminum halides has been studied.[3] Aluminum trihalide also may catalyze exchange of halogen between one alkyl halide and another[4]; thus a mixture of carbon tetrachloride, ethyl iodide, and aluminum chloride affords carbon tetraiodide.[5] Recent

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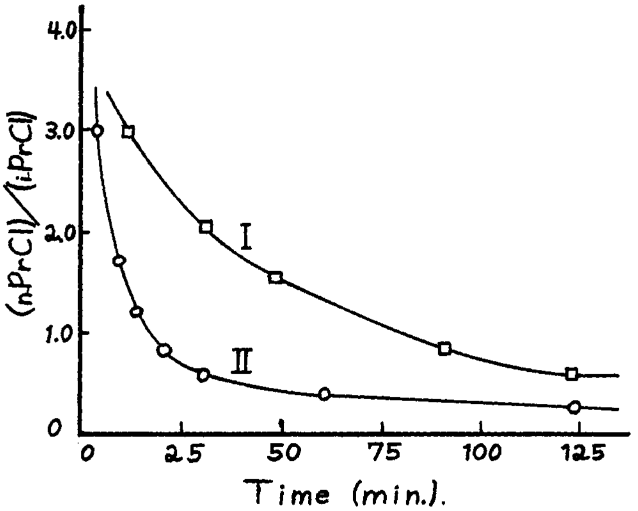

Fig. 1.—*n*-Propyl chloride to isopropyl chloride mole ratios in the aluminum chloride exchange reactions: I, *n*-propyl iodide plus aluminum chloride exchange reaction; II, *n*-propyl bromide plus aluminum chloride exchange reaction.

work demonstrates halide exchange of halobenzenes effected by aluminum halides.[6]

One possible mechanism for the exchange of AlX_3 with RX includes ionization of the alkyl halide.

$$RX, AlX_3 \rightleftharpoons R^+AlX_4^- \rightleftharpoons R^+ + AlX_4^{-\ 1,2,7}$$

If the reaction involves a carbonium ion (R^+), as in this mechanism, then one would expect products of an exchange reaction between *n*-propyl bromide or *n*-propyl iodide and aluminum chloride to consist predominantly of isopropyl chloride isomer formed by rearrangement of the primary carbonium ion.

This paper presents results of *n*-propyl bromide and *n*-propyl iodide interchange with aluminum chloride. The initial product of this exchange reaction contains a higher per cent of *n*-propyl chloride than of isopropyl chloride. The fact that exchange occurs readily without concomitant rearrangement is thought to indicate that halide interchange probably occurs through a mechanism not involving a carbonium ion. We also examined aluminum chloride-induced halogen exchange between propyl and ethyl halides and found that these reactions yield *n*-propyl halide as the predominant first product of interchange.

Experimental

Materials.—Aluminum chloride (Fisher Co., anhydrous sublimed) was used without further purification; it was transferred to small, screw-cap vials in a dry box and the vials were stored in a desiccator until used. Ethyl chloride was obtained from the Ohio Chemical Co. *n*-Propyl chloride, bromide, and iodide were from Eastman Organic Chemicals. Ethyl bromide and iodide were purchased from the Fisher Co. The ethyl iodide and *n*-propyl chloride used were shown by vapor phase chromatography to contain no more than 1.5 mole % of impurities. All other organic reagents used were shown by v.p.c. to be 99.5 mole % pure or better. All organic reagents were dried over anhydrous magnesium sulfate prior to use. The *n*-propyl bromides and iodides used were found, by injecting a large quantity (*ca.* 40 µl.) into the v.p.c. apparatus, to be free of detectable amounts of *n*- and isopropyl chlorides.

Exchange Reactions.—All experiments were carried out in an ice bath at 0° and the reacting mixtures were magnetically stirred. Reactions were performed in a 125-ml. erlenmeyer flask with a two-hole rubber stopper fitted with a calcium chloride drying tube and a piece of 5-mm. glass tubing leading to a test tube containing 3 ml. of water into which samples of approximately 2 ml. each could be withdrawn by suction. Samples were quenched by shaking with water; the organic layer then was withdrawn, dried over magnesium sulfate, and analyzed by v.p.c. To prevent losses due to volatility, samples were kept cold in ice at all times and the syringe used for v.p.c. injections was kept in a refrigerator at about 4°. Time of sample withdrawal was recorded with a stopwatch, and zero time was taken as the moment at which aluminum chloride was added to the organic compounds.

Quantities of reagents used are listed in Tables I and II; 560 mmoles of each alkyl halide was used for the reactions so that the mixed alkyl halide starting material was equimolar. Approximately 1.1 g. (8.27 mmoles) of aluminum chloride was used for all reactions, so that aluminum trichloride comprised about 0.8 mole % of mixed alkyl halide systems and 1.6 mole % of the aluminum chloride exchange reaction mixtures. No solvent was used.

Analysis.—For analysis of product mixtures, an Aerograph A-90-P gas chromatograph was used with a Sargent Model SR recorder. A 50-ft. column of 0.25-in. copper tubing packed with 20% L.A.C.-446 (Wilkens Instrument and Research Inc., California) on 30–60-mesh firebrick was used. The column was maintained at 85° in an air bath, and a flow rate of 100 cc./min. was used with helium as the carrier gas. This column completely resolved all reaction products, which were identified by comparison of their relative retention ratios with those of known standard samples. Gas chromatographic analyses of weighed standard mixtures of the alkyl halides encountered in this study show that the per cents calculated from v.p.c. peak areas correspond to mole per cents of the mixtures within 2% error in all cases. Although the mole per cents of propyl chlorides present in samples from exchange reactions of *n*-propyl bromide or *n*-propyl iodide with aluminum chloride were difficult to determine accurately due to the small quantities present, relative amounts of *n*-propyl chloride and isopropyl chloride could be measured easily by the technique of injecting large samples (*ca.* 40 µl.) into the v.p.c. apparatus, recording propyl chloride peaks with the attenuator on ×1, and then attenuating to ×64 in order to record the propyl bromide or propyl iodide peaks.

Results

Aluminum chloride dissolved readily in the alkyl halide mixtures in two to three minutes to give homogeneous systems; it required seven minutes to dissolve in pure *n*-propyl bromide. The catalyst did not dissolve completely in pure *n*-propyl iodide and the *n*-propyl iodide–aluminum chloride system remained heterogeneous throughout the reaction.

Preliminary experiments on the mixed alkyl halide systems showed that the ice bath held reaction temperatures at 0 ± 1° at all times, and the reactions evolved less than 10 ml. of gas (STP)—dehydrohalogenation reactions were insignificant under the conditions used. We observed no appreciable polymerization in these reactions.

Table I lists chromatographic analyses of samples from the *n*-propyl bromide or *n*-propyl iodide plus aluminum chloride exchange reactions. Total mole per cent of propyl chlorides is given in the fourth column of Table I, and the fifth column contains the mole ratio of *n*-propyl chloride to isopropyl chloride. The aluminum chloride was only slightly soluble in *n*-propyl iodide whereas it dissolved completely in *n*-propyl bromide; the much slower rate for exchange of *n*-propyl iodide with aluminum chloride may be caused primarily by low solubility of aluminum chloride in the iodide.

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TABLE I

ALUMINUM CHLORIDE EXCHANGE REACTIONS

V.p.c. analysis of *n*-PrBr and AlCl$_3$ reaction
(1.1150 g. of AlCl$_3$; 51.0 ml. of *n*-PrBr)

Time, min.	Mole %			
	n-PrBr	*i*-PrBr	(*n*-PrCl + *i*-PrCl)	(*n*-PrCl)/(*i*-PrCl)[a]
0.0	100.0	0.0	0.0	. . .
4.5	92.1	6.9	1.0	3.00
8.5	84.1	14.8	1.1	1.71
12.5	78.5	20.4	1.1	1.19
20.5	70.7	28.2	1.1	0.85
30.0	65.3	33.6	1.1	.62
60.0	55.5	43.4	1.1	.39
123.5	46.1	52.8	1.1	.27
175.0	40.8	58.3	1.0	.23

V.p.c. analysis of *n*-PrI and AlCl$_3$ reaction
(1.3337 g. of AlCl$_3$; 54.1 ml. of *n*-PrI)

Time, min.	Mole %			
	n-PrI	*i*-PrI	(*n*-PrCl + *i*-PrCl)	(*n*-PrCl)/(*i*-PrCl)[a]
0.0	100.0	0.0	0.00	. . .
11.0	99.7	0.3	.02	3.0
30.5	99.3	0.7	.03	2.1
48.5	98.7	1.3	.04	1.6
91.0	97.3	2.6	.05	0.9
123.5	95.9	4.0	.08	.6
252.0	88.6	11.3	.15	.4
410.0	82.0	17.8	.18	.2

[a] Since a greater quantity of propyl chlorides was formed in the *n*-PrBr + AlCl$_3$ exchange reaction, the (*n*-PrCl)/(*i*-PrCl) ratio could be determined more accurately than that for the *n*-PrI + AlCl$_3$ reaction.

Figure 1 shows a plot of the *n*-propyl chloride to isopropyl chloride mole ratios for the two aluminum chloride interchange reactions of Table I.

Results of v.p.c. analyses of ethyl and propyl halide exchange catalyzed by aluminum chloride appear in Table II. A number of points are listed for the first reaction (*n*-PrCl + EtI), and a graph (Fig. 2) showing the mole per cents of the exchange products in this reaction is given. Data also are presented for the reverse reaction (*n*-PrI + EtCl).

TABLE II

ALKYL HALIDE EXCHANGE REACTIONS

V.p.c. analysis of *n*-PrCl and EtI reaction
(1.1256 g. of AlCl$_3$; 45.3 ml. of EtI; 49.4 ml. of *n*-PrCl)

Time, min.	Mole %					
	n-PrCl	EtI	*i*-PrCl	*n*-PrI	*i*-PrI	EtCl
0.0	49.2	50.8	0.0	0.0	0.0	0.0
12.0	39.5	41.7	0.3	9.2	.0	9.3
30.0	32.0	34.8	1.3	15.7	.0	16.2
60.5	26.5	32.0	3.2	19.3	.2	18.8
91.0	24.0	30.3	5.0	19.6	.3	20.8
125.5	22.6	31.3	6.6	19.5	.6	19.4

V.p.c. analysis of *n*-PrI and EtCl reaction
(1.0152 g. AlCl$_3$; 40.0 ml. EtCl; 54.1 ml. *n*-PrI)

Time, min.	Mole %					
	n-Pr I	EtCl	*i*-PrI	*n*-PrCl	*i*-PrCl	EtI
0.0	50.0	50.0	0.0	0.0	0.0	0.0
26.0	31.0	30.1	.0	15.9	2.9	20.2
64.5	25.6	25.6	.0	16.7	6.8	25.3
120.0	24.1	23.6	.6	14.2	10.3	27.2

The remaining four aluminum chloride-induced propyl–ethyl exchange reactions were also run at 0° and with the same catalyst concentration as those of Table II. They are represented as shown.

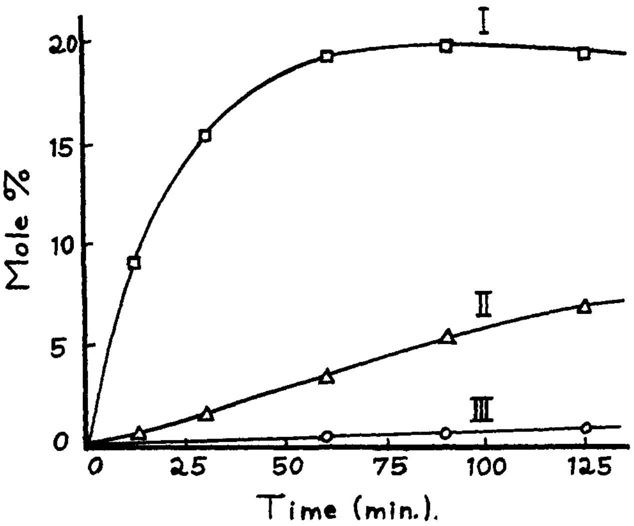

Fig. 2.—Product mole per cent in the *n*-propyl chloride plus ethyl iodide exchange reaction: I, *n*-propyl iodide; II, isopropyl chloride; III, isopropyl iodide.

$$n\text{-PrCl} + \text{EtBr} \rightleftharpoons n\text{-PrBr} + i\text{-PrBr} + \text{EtCl} + i\text{-PrCl} \quad (1)$$

$$n\text{-PrBr} + \text{EtCl} \rightleftharpoons n\text{-PrCl} + i\text{-PrCl} + \text{EtBr} + i\text{-PrBr} \quad (2)$$

$$n\text{-PrBr} + \text{EtI} \rightleftharpoons n\text{-PrI} + i\text{-PrI} + \text{EtBr} + i\text{-PrBr} + \frac{\text{EtCl} + n\text{-PrCl} + i\text{-PrCl}}{(\text{Total} = 0.6\%)} \quad (3)$$

$$n\text{-PrI} + \text{EtBr} \rightleftharpoons n\text{-BrBr} + i\text{-PrBr} + \text{EtI} + i\text{-PrI} + \frac{\text{EtCl} + n\text{-PrCl} + i\text{-PrCl}}{(\text{Total} = 0.4\%)} \quad (4)$$

These reactions proceed in essentially the same manner as the *n*-propyl chloride system of Fig. 2; exchange, which is more rapid than rearrangement, gives *n*-propyl halide as the predominant first product. (For example, reaction 1 yields an exchange product containing more *n*-propyl bromide than isopropyl bromide.) As indicated, reactions 3 and 4 exhibit exchange with the aluminum chloride present to give a total alkyl chloride concentration of about 0.5 mole %.

It also has been found in this study that, under the influence of aluminum trichloride, methyl iodide will exchange readily with ethyl chloride and *n*-propyl chloride and that butyl halides undergo halogen interchange with propyl, ethyl, and methyl halides.

Discussion

The results of these experiments show clearly that halogen interchange of *n*-propyl halides, with both aluminum chloride and ethyl halides, proceeds more rapidly than rearrangement of exchange products. Thus, it is possible to prepare unrearranged RY from RX by means of aluminum chloride-catalyzed exchange.

Constancy of (*n*-PrCl + *i*-PrCl) total concentration in the *n*-propyl bromide plus aluminum chloride exchange reaction (*cf.* Table I) suggests that exchange equilibrium was reached during the first four and one-half minutes of reaction. On this basis, an equilibrium constant can be estimated for the interchange of propyl bromides with aluminum chloride. Ignoring the presence of AlCl$_2$Br and AlClBr$_2$, we may write the reaction as shown.

$$\begin{array}{ccccccc} 3\mathrm{PrBr} & + & \mathrm{AlCl_3} & \rightleftharpoons & 3\mathrm{PrCl} & + & \mathrm{AlBr_3} \\ (554) & & (6.2) & & (6.2) & & (2.1) \end{array}$$

$$K_{\mathrm{eq}} \approx \frac{(6.2)^3(2.1)}{(554)^3(6.2)} = 4.7 \times 10^{-7}$$

The symbols PrBr and PrCl represent sums of the propyl halides, (n-PrBr + i-PrBr) and (n-PrCl + i-PrCl), respectively. The number of mmoles of each species present at equilibrium, calculated from the data of Table I, is shown in parentheses under the reaction. In view of small equilibrium constant for the previous reaction, it is not surprising that the following analogous reactions were found to be essentially irreversible.[3]

$$\mathrm{MeCl} + \mathrm{AlBr_3} \longrightarrow \mathrm{MeBr} + \mathrm{AlCl_3}$$

$$\mathrm{MeCl} + \mathrm{AlI_3} \longrightarrow \mathrm{MeI} + \mathrm{AlCl_3}$$

Both $\mathrm{AlY_3}$ + n-PrX and EtY + n-PrX exchange reactions proceed rapidly, and both interchanges yield initial products rich in the n-PrY isomer. These similarities suggest that the two exchange processes occur *via* the same mechanism and exchange of halogen between two alkyl halides may result from successive exchanges of alkyl halide with aluminum halide.

Unrearranged interchange products point to a noncarbonium ion mechanism for the exchange reaction, since carbonium ion intermediates would be expected to yield predominantly rearranged products.

Without implying ionization, a pathway involving bimolecular nucleophilic substitution could explain the observed results. A displacement mechanism for alkyl halide–aluminum halide interchange is consistent with the finding that the exchange of ethyl bromide (labeled with radioactive bromine) and aluminum bromide is a third-order reaction. The reaction rate is proportional to the concentration of ethyl bromide and to the square of the concentration of aluminum bromide.[2] Conductivity and transport measurements of solutions containing aluminum bromide in ethyl bromide are compatible with the absence of carbonium ions in the exchange mechanism. Formation of $\mathrm{AlBr_4^-}$ and $\mathrm{RBrAlBr_2^+}$ ions best explains the findings of these experiments.[8]

In many cases, Friedel–Crafts alkylations can yield unrearranged alkyl benzenes.[9] It is possible that these alkylations and the observed interchange reactions proceed by analogous displacement mechanisms of the type proposed by Brown based on kinetic data.[10][11]

Acknowledgment.—This work was supported in part by the National Science Foundation. We also wish to thank Dr. Gerard V. Smith of this laboratory for valuable advice during the course of the work and for the use of v.p.c. equipment.

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[9] See, for example, S. H. Sharman, *J. Am. Chem. Soc.*, **84**, 2945 (1962).

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Synthesis of Eight New Halodeoxyinositols. Configurations of Chloro, Bromo, and Iodo Derivatives of Cyclohexanepentol[1,2]

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A 6-chloro, a 6-bromo, and a 6-iodo derivative of *cis*-quercitol, each of the *meso* configuration (12345/6), were prepared by reaction of 1,2-anhydro-*cis*-inositol (diketal) with the appropriate aqueous hydrohalic acid. Reaction of 1,2-anhydro-*allo*-inositol (diketal) with aqueous hydrochloric acid gave a mixture of two chloro quercitols, m.p. 215 and 236°, and with hydriodic acid, two iodoquercitols, m.p. 181 and 254°, the lower melting product predominating in each case. The predominant isomers were shown to have the configuration (125/346) corresponding to *gala*-quercitol, since the nonpredominant isomers on hydrogenolysis gave *talo*-quercitol and thus had the configuration (123/456). A bromoquercitol pentaacetate (m.p. 153°) prepared from *epi*-inositol in 1955 has for the first time been converted to the corresponding free bromoquercitol and by hydrogenolysis of the latter to *allo*-quercitol is now shown to have the configuration DL(1234/56), instead of the previously proposed (1235/46). New derivatives of *epi*-inositol and of pinitol are described.

The haloquercitols or halodeoxyinositols (6-halo-1,2,3,4,5-cyclohexanepentols, I) are of interest because of their possible inositol or anti-inositol activity in biological systems, as intermediates for synthesis of other cyclitols, and as model substances for the application to carbohydrates of such physical methods as nuclear magnetic resonance.[4]

Twenty diastereomers (eight *meso*, twelve active or racemic) are predicted for any such monosubstituted inositol, so that the stereochemistry of the haloquercitols is unusually complex and interesting. Previous work in our own and other laboratories has led to the synthesis of not less than ten of the twenty predicted bromoquercitols; not less than three of the chloroquercitols; but of only one of the iodoquercitols.[5]

We now wish to report the preparation and configurational characterization of three new chloroquercitols, two new bromoquercitols, and three new iodoquercitols. Crystalline pentaacetates have been obtained for all but two of these. The recently prepared haloquercitol diastereomers are summarized in Table I, which includes all known iodoquercitols. The previously known

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[1] Paper XV on Cyclitol Stereochemistry by G. E. McCasland and coworkers: for preceding publication, see *J. Org. Chem.*, **28**, 894 (1963).

[2] Presented in part by V. B. to the 13th Annual Convention of the Student Affiliates of the American Chemical Society, Reno, Nev., May 4, 1962.

[3] Aided by the National Science Foundation Undergraduate Participation Program at the Department of Chemistry, University of San Francisco, 1962.

[4] See G. E. McCasland, S. Furuta, L. F. Johnson, and J. N. Shoolery, *J. Am. Chem. Soc.*, (a) **83**, 4243 (1961); (b) **83**, 2335 (1961).

[5] The number of known chloro and bromo isomers is somewhat uncertain because of similarities in melting points, and the fact that some haloquercitol pentaacetates have not yet been correlated with their parent haloquercitol.