The utility of the dehalogenation–deetherification sequence for the proof of structure of methoxyhalocyclohexanols and methoxyhalocyclopentanols. Synthesis of the *cis*- and *trans*-2- and -3-methoxycyclohexanols and -cyclopentanols[1]

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An unequivocal proof of structure for the methoxychlorocyclopentanols (I′*c*–IV′*c*) was obtained by deetherification with 68% hydrobromic acid at 65–70°, followed by hydrogenolysis with Raney nickel and hydrogen, to the 1,2- and 1,3-cyclopentanediols, in the same manner as the methoxybromocyclohexanols (I–IV) were converted into the 1,2- and 1,3-cyclohexanediols. Hydrogenolysis of the methoxybromocyclohexanols and the methoxychlorocyclopentanols provided stereospecific syntheses for the *cis*- and *trans*-2- and -3-methoxy-cyclohexanols and -cyclopentanols in 80–97% yields. Deetherification of the latter compounds with 68% hydrobromic acid gave the corresponding 1,2- and 1,3-cyclohexanediols and 1,2-cyclopentanediols in 70–90% yields, but only 5–7% yields of the 1,3-cyclopentanediols. For the proof of structure of methoxyhalocyclanols, deetherification should therefore precede, rather than follow, dehalogenation.

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For several years we have conducted studies of the factors which govern the rates of formation of alicyclic epoxides from their halohydrins and the distribution of products obtained on scission of these oxides with various nucleophiles (1–6). Recently (7) it became a matter of prime importance to establish unequivocally the structures of the methoxychlorocyclopentanols which are formed by scission of the stereoisomeric 3-methoxycyclopentene oxides with hydrogen chloride and by the action of hypochlorous acid on 3-methoxycyclopentene. Earlier (5, 6), in connection with the proof of structure of the stereoisomeric 3-methoxy-2-hydroxy-1-bromocyclohexanes (I and II) and 3-methoxy-2-bromo-1-hydroxycyclohexanes (III and IV), we described a useful deetherification and debromination reaction sequence for the conversion of these compounds in high yields into the corresponding 1-bromo-2,3-cyclohexanediols (V and VI), 2-bromo-1,3-cyclohexanediols (VII and VIII), and the *cis*- and *trans*-1,2- and -1,3-cyclohexanediols (IX–XII) as shown in Scheme 1.[2] It seemed reasonable to use the same reactions for the proof of structure of the methoxychlorocyclopentanols, but it occurred to us that the direct dehalogenation of I–IV and their cyclopentane chloro analogues (I′*c*–IV′*c*)[3] would provide stereospecific syntheses for the *cis*- and *trans*-2- and -3-methoxy-cyclohexanols (XIII–XVI) and -cyclopentanols (XIII′–XVI′). These compounds are of intrinsic interest because they can serve as useful reference substances for structural determination of the cyclitols formed by the degradation of more complex molecules. Furthermore, it appeared worthwhile to establish whether the efficiency of the

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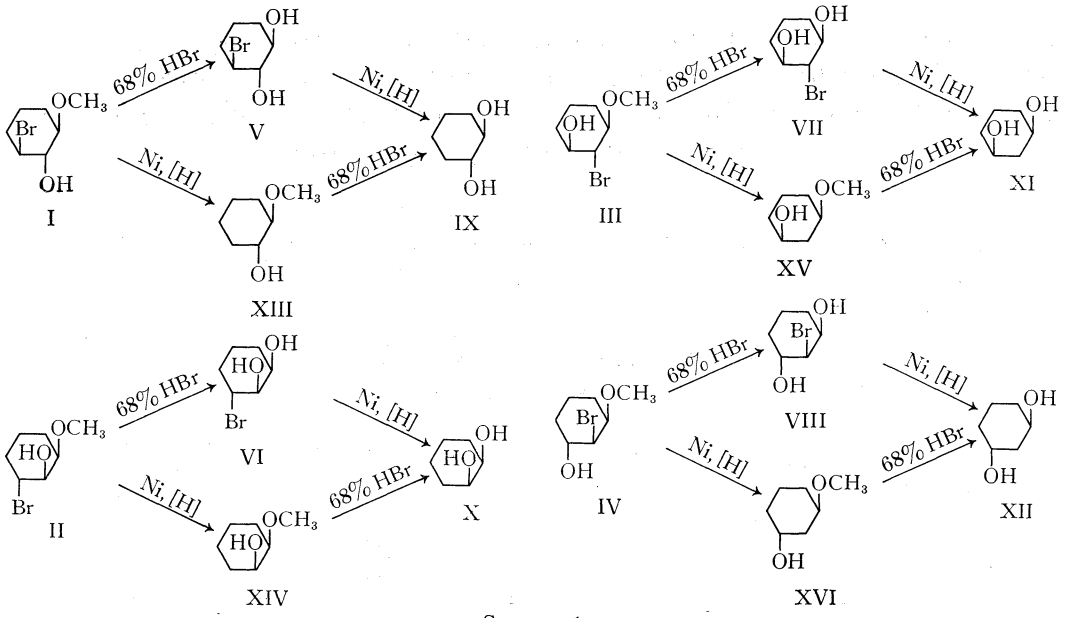
[2]It has been reported that the deetherification of *trans*-2-methoxycyclohexanol proceeds with retention of configuration at the oxygenated function (5), and it was assumed (5, 6) that the stereochemical integrity of all such groups would be preserved during the deetherification of the methoxybromocyclohexanols (I–IV). Since the structures of the latter compounds have recently been verified by nuclear magnetic resonance spectroscopy (8), the validity of the above assumption is firmly established.

[3]The prime indicates the cyclopentane analogue with the identical configuration; the *c* indicates substitution of chlorine for bromine.



SCHEME 1.

conversion of the alkoxyhalocyclanols into the cyclohexane- and cyclopentane-diols could be improved by performing the dehalogenation before the deetherification.

The dehalogenations were performed according to the general method of McCasland and Horswill (9) with Raney nickel and hydrogen in the presence of an anion-exchange resin, but the conditions were optimized with respect to the catalyst, making it possible to use a much smaller catalyst to substrate ratio than had been used previously (5, 6). The results shown in Tables I and III clearly establish the general utility of the method for the stereospecific synthesis of the *cis*- and *trans*-2- and -3-methoxy-cyclohexanols (XIII–XVI) and -cyclopentanols (XIII′–XVI′) in yields which generally exceed 85%. Although the procedure can also be used to produce 2- and 3-methoxyacetoxycyclohexanes (XIII*a*–XVI*a*)[4] from the corresponding methoxybromocyclohexyl acetates (I*a*–IV*a*), the usefulness of the method is somewhat marred by the concomitant formation of the corresponding alcohols, necessitating re-acetylation before final purification. Thus the methoxyacetoxycyclohexanes are best prepared by the dehalogenation of I–IV, followed by acetylation of the resultant methoxycyclohexanols.

Although *trans*-2-methoxy-cyclohexanol and -cyclopentanol have been known for many years (10, 11), the preparation of *cis*-2-methoxy-cyclopentanol and -cyclohexanol by benzoate "exchange" of the corresponding *trans*-methoxycycloalkanol methanesulfonates, in a considerably lower yield than by the method reported herein, has only recently been described by Foster and his co-workers (12). Eliel and Brett (13) have reported the separation of *cis*- and *trans*-3-methoxycyclohexanol formed during the catalytic reduction of *m*-methoxyphenol, by virtue of chelate formation between the *cis* isomer and the lithium aluminium hydride – aluminium chloride reagent. The *trans* isomer was obtained in a 99% pure form, but the *cis* compound was contaminated with 10% of its stereoisomer. The *cis*- and *trans*-3-methoxycyclopentanols (XV′ and XVI′) have not been reported previously.

Comparison of the data on the dehalogenation of the bromocyclohexanediols (V–VIII) and chlorocyclopentanediols (V′*c*–VIII′*c*) contained in Table II with those given in Table I for the methoxybromocyclohexanols (I–IV) and the methoxychlorocyclopentanols (I′*c*–IV′*c*) shows that

[4]The *a* indicates acetylation of the hydroxyl group.

TABLE I

Dehalogenation–deetherification of methoxyhalocyclanols

Compound	Methoxycyclanol produced by dehalogenation	% yield*	Cyclanediol produced by deetherification	% yield†	Melting point (°C)	Overall % conversion of methoxyhalocyclanol into cyclanediol
dl-(1,3/2)-1-Bromo-2-hydroxy-3-methoxycyclohexane (I)	XIII	92.6	*trans*-1,2-Cyclohexanediol (IX)	90.2	103–104‡	83.6
dl-(1/2,3)-1-Bromo-2-hydroxy-3-methoxycyclohexane (II)	XIV	85.1	*cis*-1,2-Cyclohexanediol (X)	87.2	98§	74.3
dl-(1,3/2)-1-Hydroxy-2-bromo-3-methoxycyclohexane (III)	XV	97.0	*cis*-1,3-Cyclohexanediol (XI)	77.8	85.5–86.0‖	75.5
dl-(1/2,3)-1-Hydroxy-2-bromo-3-methoxycyclohexane (IV)	XVI	94.0	*trans*-1,3-Cyclohexanediol (XII)	69.3	117–118¶	65.2
dl-(1,3/2)-1-Chloro-2-hydroxy-3-methoxycyclohexane (I*c*)	XIII	94.1	—			
dl-(1,3/2)-1-Chloro-2-hydroxy-3-methoxycyclopentane (I′*c*)	XIII′	95.4	*trans*-1,2-Cyclopentanediol (IX′)	84.5**	143.5–144.5††	80.5
dl-(1/2,3)-1-Chloro-2-hydroxy-3-methoxycyclopentane (II′*c*)	XIV′	79.2	*cis*-1,2-Cyclopentanediol (X′)	68.4**	117–118‡‡	54.1
dl-(1,3/2)-1-Hydroxy-2-chloro-3-methoxycyclopentane (III′*c*)	XV′	93.2	*cis*-1,3-Cyclopentanediol (XI′)	4.7**	154–155§§	4.4
dl-(1/2,3)-1-Hydroxy-2-chloro-3-methoxycyclopentane (IV′*c*)	XVI′	95.5	*trans*-1,3-Cyclopentanediol (XII′)	6.8**	190.5–191.5‖‖	6.5
dl-(1,3/2)-1-Bromo-2-acetoxy-3-methoxycyclohexane (I*a*)	XIII*a*	84.9	—			
dl-(1,3/2)-1-Acetoxy-2-bromo-3-methoxycyclohexane (III*a*)	XV*a*	85.6	—			
dl-(1/2,3)-1-Acetoxy-2-bromo-3-methoxycyclohexane (IV*a*)	XVI*a*	86.2	—			

*See Table III for the physical constants and analyses.
†The identities were established by mixture melting point determinations.
‡Winstein and Buckles (24) report m.p. 104°.
§Criegee and Stanger (25) report m.p. 96–98°.
‖Rigby (26) reports m.p. 85–85.5°.
¶Rigby (26) reports m.p. 118–118.5°.
**Isolated as the bis(*p*-nitrobenzoyl) derivative.
††Owen and Smith (27) report m.p. 143°.
‡‡Owen and Smith (27) report m.p. 117°.
§§Darby *et al.* (28) report m.p. 149–152°.
‖‖Darby *et al.* (28) report m.p. 184–185°.

the efficiency of the reaction is virtually independent of the halogen atom removed, the presence of the methoxyl group, and the size of the alicyclic ring within the limits of examination of these variables.

The usefulness of 68% aqueous hydrobromic acid for the deetherification of the methoxybromocyclohexanols (I–IV) in 80–95% yields to the bromocyclohexanediols (V–VIII) was established earlier (5, 6). The method is most efficient when 3 moles of reagent are used per mole of ether. The data in Tables I and II show that the method is also very effective for the deetherification of the methoxychlorocyclopentanols (I′*c*–IV′*c*), the 2- and 3-methoxycyclohexanols (XIII–XVI), and the 2-methoxycyclopentanols (XIII′ and XIV′). It is, however, unsuitable for the deetherification of the 3-methoxycyclopentanols (XV′ and XVI′), and totally unsatisfactory for the proof of structure of III′*c* and IV′*c*, when deetherification is preceded by dehalogenation. Notwithstanding the latter results, 68% hydrobromic acid is, in our experience, a much more convenient reagent for the conversion of ethers into alcohols than are the boron halides. Numerous attempts to effect the deetherification of *trans*-2-methoxycyclohexanol with the latter reagents under a wide variety of experimental conditions proved unsuccessful in our hands, in spite of a report in the literature to the contrary (12).

It is clear from Table I that the 2-methoxycyclanols and (or) the 1,2-cyclanediols are more stable toward 68% hydrobromic acid than the 3-methoxycyclanols and (or) the corresponding diols. It is also evident that the cyclopentane derivatives are

TABLE II

Deetherification–dehalogenation of methoxyhalocyclanols

Compound	Halocyclanediol produced by deetherification	% yield	Literature reference	Cyclanediol produced by dehalogenation	% yield	Literature reference	Overall % conversion of methoxyhalocyclanol into cyclanediol
I	*dl*-(1,3/2)-1-Bromo-2,3-cyclohexanediol (V)	96.3	2*	IX	90.3	2	87.0
II	*dl*-(1/2,3)-1-Bromo-2,3-cyclohexanediol (VI)	79.6	2	X	85.0	*	67.7
III	*meso*-(1,3/2)-2-Bromo-1,3-cyclohexanediol (VII)	97.4	3	XI	87.4	3	85.0
IV	*dl*-(1/2,3)-2-Bromo-1,3-cyclohexanediol (VIII)	90.6	3	XII	92.6	3	84.0
I′*c*	*dl*-(1,3/2)-1-Chloro-2,3-cyclopentanediol (V′*c*)	95†	*	IX′	88‡	*	84.3
II′*c*	*dl*-(1/2,3)-1-Chloro-2,3-cyclopentanediol (VI′*c*)	74†	*	X′	90‡	*	66.5
III′*c*	*meso*-(1,3/2)-2-Chloro-1,3-cyclopentanediol (VII′*c*)	75†	*	XI′	91‡	*	68.6
IV′*c*	*dl*-(1/2,3)-2-Chloro-1,3-cyclopentanediol (VIII′*c*)	86†	*	XII′	88‡	*	74.5

*This investigation.
†Crude yield on a weight basis.
‡Product was isolated as the bis(*p*-nitrobenzoyl) derivative and identified as in Table I.

TABLE III

Physical constants and analytical data for methoxycyclanols and methoxycyclohexyl acetates

Compound	n_D^{25}	Air-bath distillation temperature (°C at 9–10 mm)	Vapor-phase chromatographic retention time (min)¶	Calculated (%) C	Calculated (%) H	Found (%) C	Found (%) H
trans-2-Methoxycyclohexanol (XIII)	1.4575*	70–80	5.0	64.58	10.84	64.59	10.94
cis-2-Methoxycyclohexanol (XIV)	1.4580†	60–65	3.5	64.58	10.84	64.65	10.69
cis-3-Methoxycyclohexanol (XV)	1.4618	70–80	8.0	64.58	10.84	64.49	10.90
trans-3-Methoxycyclohexanol (XVI)	1.4641‡	90–95	9.0	64.58	10.84	64.37	11.12
trans-2-Methoxycyclopentanol (XIII′)	1.4504§	80–90	5.5	62.04	10.41	61.83	10.38
cis-2-Methoxycyclopentanol (XIV′)	1.4460	50–60	3.0	62.04	10.41	62.05	10.30
cis-3-Methoxycyclopentanol (XV′)	1.4510	70–74	5.0	62.04	10.41	61.81	10.29
trans-3-Methoxycyclopentanol (XVI′)	1.4519	80–90	7.0	62.04	10.41	61.83	10.30
trans-2-Methoxyacetoxycyclohexane (XIII*a*)	1.4417‖	85–90	6.0	62.76	9.36	62.62	9.45
cis-3-Methoxyacetoxycyclohexane (XV*a*)	1.4450	90–95	7.0	62.76	9.36	62.67	9.27
trans-3-Methoxyacetoxycyclohexane (XVI*a*)	1.4445	85–90	6.5	62.76	9.36	62.96	9.51

*Winstein and Henderson (10) report n_D^{25} 1.4586.
†Buck *et al.* (12) report b.p. 75° at 20 mm.
‡Eliel and Brett (13) report b.p. 105–106° at 24 mm and n_D^{25} 1.4670.
§Mousseron and Granger (11) report b.p. 175° and n_D^{20} 1.4534.
‖Winstein and Henderson (10) report n_D^{25} 1.4410.
¶At 140° in the Aerograph model A-700 gas chromatograph (10 ft × ⅜ in. diameter aluminium column; packing, Anakrom 60/70 impregnated with 30% diethylene glycol succinate; helium flow rate, 300 ml/min).

generally less stable toward the reagent than their corresponding cyclohexane analogues. This difference in stability becomes extreme for the 3-methoxycyclopentanols, and is shown by the change in color of these reaction mixtures from clear and colorless or very pale yellow to black and opaque in less than 5 min at 65°. The data in Table II on the deetherification of the methoxyhalocyclanols demonstrate unequivocally that the presence of a halogen atom in the molecule generally improves the stability of the compounds toward the reagent. The improvement is marginal for

TABLE IV

Chlorocyclohexanediols and their bis(*p*-nitrobenzoyl) derivatives

Compound	% yield	Melting point (°C)	Calculated (%)				Found (%)			
			C	H	N	Cl	C	H	N	Cl
V*c*	97.2	87.7–89.0	47.83	7.37		23.55	47.85	7.31		23.42
							47.62	7.43		23.42
Derivative	88.7	206.0–207.0	53.50	3.82	6.25	7.90	53.52	3.92	6.33	7.94
VI*c*	87.2	81.0–81.8	47.83	7.37		23.55	47.31	7.06		23.40
							47.37	7.07		
Derivative	86.4	159.5–160.6	53.50	3.82	6.25	7.90	53.31	3.94	6.15	7.82
VII*c*	83.5	139.6–140.0	47.83	7.37		23.55	47.63	7.42		23.60
							47.74	7.24		23.23
Derivative	71.0	197.3–198.1	53.50	3.82	6.25	7.90	53.72	3.93	6.19	7.81
VIII*c*	51.0	79.2–79.5	47.83	7.37		23.55	48.03	7.34		23.64
Derivative	74.0	188.2–189.1	53.50	3.82	6.25	7.90	53.77	3.97	6.19	7.90

the 2-methoxyhalocyclanols (I, II, I′*c*, and II′*c*), but striking for the 3-methoxy-2-bromocyclohexanols (III and IV) and particularly striking for the 3-methoxy-2-chlorocyclopentanols (III′*c* and IV′*c*). The results given in Tables I and II demonstrate conclusively that the most efficient method for the conversion of a methoxyhalocyclanol into the corresponding cyclanediol is by deetherification followed by dehalogenation, rather than the reverse. They also provide an unequivocal proof of structure for the methoxychlorocyclopentanols (I′*c*–IV′*c*), since the structures of the 1,2- and 1,3-cyclopentanediols were assigned previously by Owen and Smith (27) and by Darby *et al.* (28), respectively. In addition to its utility for the proof of structure of methoxyhalocyclanols, the method of deetherification described herein can be adapted readily for the synthesis of halocyclanediols on a preparative scale, as indicated in Table IV for the chlorocyclohexanediols (V*c*–VIII*c*).

It is well known that cyclohexane- and cyclopentane-diols are dehydrated by heating them in the presence of acids (14, 15). The results summarized in the preceding paragraph regarding the stability of the methoxy-cyclohexanols and -cyclopentanols and (or) the corresponding diols toward the reagent can be rationalized qualitatively if the reasonable assumption is made that the main pathways leading to the formation of by-products are probably via E1 elimination and S_N1 substitution (16, 17). It should be emphasized that it is impossible to differentiate between these pathways on the basis of product analysis. In the 1,2-disubstituted compounds, pinacol rearrangement can also intervene (18), but there is no basis (19, 20) for assuming that the 1,3-diol cleavage reaction (21), which proceeds with comparative ease in acyclic compounds, is a factor in the loss of the 1,3-cyclanediol derivatives. The generally lower yields of diols for the cyclopentane derivatives may be ascribed to the considerably greater ease with which cyclopentane compounds undergo S_N1 (and hence also E1) reactions in relation to the cyclohexane derivatives (22). The lower yields of 1,3-diols in relation to their 1,2-analogues are probably due to the greater ease of carbonium ion formation in the former because of the greater distance between the second electronegative group and the reaction site. The stabilizing influence of introducing a halogen atom, which is particularly noticeable in the 1,3-cyclopentanediol derivatives, can be ascribed to its inhibitory effect upon carbonium ion formation by virtue of its proximity to the reaction site. The only experiments in which the isolation of by-products was attempted, namely, the deetherification of *cis*- and *trans*-3-methoxycyclohexanol, yielded, after vapor-phase chromatographic purification, colorless oils which gave analytical figures and infrared spectra consistent with a bromocyclohexanol (not identical with *trans*-2-bromocyclohexanol), but insufficient for complete characterization. A by-product with identical vapor-phase chromatographic characteristics, infrared spectrum, and elemental composition was also isolated in a single

experiment in which only 58% of *cis*-1,3-cyclohexanediol was recovered after it had been heated at 65–70° for 35 min with 3 moles of 68% hydrobromic acid. This result demonstrates that loss of product can readily occur after deetherification, and emphasizes the desirability of keeping the heating period as short as possible, consistent with completion of the deetherification. It does not, however, preclude loss of methoxycyclanol before ether cleavage. Further experiments to elaborate the nature of the products arising from the action of 68% hydrobromic acid on the 1,2- and 1,3-cyclopentanediols and -cyclohexanediols and the mechanism of their formation are planned.

EXPERIMENTAL[5]

Dehalogenation of Halomethoxycyclanols and Halocyclanediols

Amberlite IR-45 (OH) resin (13.5 ml), which was prepared in the usual manner and solvent exchanged with absolute methanol, was transferred to a 250 ml centrifuge bottle in absolute methanol (10 ml). Raney nickel W-7 (23) (2.5 g, wet with methanol) was added and the catalyst was activated by shaking it at 50 p.s.i. hydrogen pressure for 10 min. The halomethoxycyclanol or halocyclanediol (0.006 mole) was added and the mixture was shaken at 50 p.s.i. hydrogen pressure for 17 h. The mixture was centrifuged at 1 200 r.p.m. for 5 min, and the almost clear supernatant liquid was decanted and filtered through a medium-porosity fritted-glass funnel containing a $\frac{1}{4}$ in. pad of acid-washed Celite 545. The residue in the centrifuge bottle was triturated three times with absolute methanol (15 ml), with centrifugation before each decantation. The combined filtrates were fractionated at atmospheric pressure on an 18 in. Stedman column until the pot residue was reduced to *ca.* 25 ml. The residual methanol was removed by distillation at 10 mm pressure and room temperature, and the resultant oil was transferred in anhydrous ether to a Späth tube and distilled at 9 mm pressure in an electrically heated air bath. The homogeneity of the various fractions was checked by vapor-phase chromatographic analysis on an Anakrom 60/70 column which had been impregnated with 30% diethylene glycol succinate. The methoxycyclanols and methoxyacetoxycyclohexanes were all liquids, and their refractive indices and vapor-phase chromatographic retention times are recorded in Table III, together with the analytical data. It should be noted that the removal of all of the methanol *in vacuo* in the above procedure results in greatly reduced yields because of co-distillation of the dehalogenated products with the methanol. Also, recovery of the methoxyacetoxycyclohexanes as described above was accompanied by appreciable conversion into the methoxycyclohexanols, presumably as a result of transesterification during removal of the methanol. The yields reported in Table I for these compounds are therefore those which resulted after re-acetylation of the primary product. The yields after dehalogenation of the halocycloalkanediols are given in Table II.[6]

Deetherification of Methoxycyclanols and Halomethoxycyclanols

The methoxycyclanol or halomethoxycyclanol (2.5×10^{-3} mole) was placed in a 13 mm diameter Carius tube and cooled to −80° in a dry ice – carbon tetrachloride – chloroform bath. Aqueous hydrogen bromide (68%, 0.5 ml, 7.5×10^{-3} mole), which was kept at −20°, was introduced into the Carius tube by means of a long-stemmed precooled (0°) funnel, using a similarly precooled pipette. The aqueous hydrogen bromide froze immediately on addition to the tube, and was kept in this condition until the latter had been sealed. The tube was kept at 65–70° for 15–35 min depending on the extent of darkening of the solution, cooled to −80°, and opened, and the contents were transferred quantitatively in water (30 ml) to a round-bottomed flask. The excess hydrogen bromide was neutralized by the addition of solid sodium bicarbonate (1.5 g), and the solution was evaporated to dryness *in vacuo*. The residue was extracted with anhydrous ether in a Soxhlet extractor for 16 h, after which the product was isolated by crystallization, distillation *in vacuo*, or conversion into the bis(*p*-nitrobenzoyl) derivative after removal of the solvent. The yields are given in Tables I and II.

For the preparation of chlorocyclohexanediols on a larger scale, the methoxychlorocyclohexanol (16.4 g, 0.100 mole) was placed in a spring-topped glass pressure vessel together with 68% hydrobromic acid (40 ml), and the solution was heated at 75° for 1.5–3 h. After the vessel was cooled to −80°, it was opened, the contents were transferred to a flask and neutralized with sodium bicarbonate, and the resultant solution was evaporated to dryness on the rotary evaporator. The product was isolated by extraction with ether or acetone in a Soxhlet apparatus and recrystallized from the solvent used for extraction. The yields, melting points, and analytical data for these compounds and their bis(*p*-nitrobenzoyl) derivatives are given in Table IV.

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We are indebted to Dr. L. N. Owen for providing us with authentic samples of the bis(*p*-nitrobenzoyl) derivatives of the 1,2-cyclopentanediols, to Prof. H. B. Henbest

[5]Melting points are uncorrected. Microanalyses were performed by J. G. Helie, Defence Chemical, Biological and Radiation Laboratories, Ottawa.

[6]The method can be used for the synthesis of halomethoxycyclanols and halocyclanediols on a preparative scale by employing 10 times the quantities of reactants indicated above.

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