

centrated and the residue treated with semicarbazide hydrochloride and sodium acetate in aqueous ethanol. The yellow crystals (0.174 g.) were removed by filtration; m.p. 210°. After three recrystallizations from aqueous ethanol the semicarbazone melted at 217–219°. A mixed melting point with the semicarbazone of cyclooctatetraenyl

methyl ketone showed no depression and the infrared spectra were identical.

Anal. Calcd. for $C_{11}H_{13}N_3O$: C, 65.00; H, 6.40; N, 20.69. Found: C, 64.86; H, 6.39; N, 20.56.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY AND THE DIVISION OF PURE CHEMISTRY OF THE NATIONAL RESEARCH COUNCIL OF CANADA]

A Relationship between Conformation and Infrared Absorption in 1,2-Halohydrins

BY ALEX NICKON

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In dilute CS_2 solutions of alicyclic alcohols the degree of perturbation of the O–H and C–OH stretching frequencies by a neighboring halogen depends upon the steric arrangement of the two functional groups. In those molecules where intramolecular hydrogen bonding is geometrically favorable the O–H stretching frequency is lowered significantly (-25 to -48 cm^{-1}), and the C–OH stretching frequency is appreciably raised ($+13$ to $+25$ cm^{-1}). When internal chelation between halogen and hydroxyl is sterically impossible (or improbable) the displacements of these two bands are markedly less and sometimes negligible. Other things being equal the halogens appear to follow the sequence $I > Br > Cl$ in their ability to decrease the frequency of the O–H stretching vibration, but they adopt the reverse order ($Cl > Br > I$) in their power to increase the C–OH stretching frequency.

Knowledge of the relationships between vibrational spectra and molecular conformation has advanced in recent years. The discovery that the carbonyl band displacements observed on α -bromination of steroid ketones are directly related to the conformation of the C–Br bond,^{1a} and the further developments of this finding^{1b} have greatly facilitated structural studies of these and related compounds. In addition, for cyclohexane ring systems, correlations have been worked out that permit assignment of axial and equatorial conformations to epimeric pairs of compounds carrying the following individual functional groups: OH^2 ; OCH_3 , OAc^{3a} ; Br , Cl^{3b} ; D .⁴ When two functions are on adjacent carbons, mutual perturbation of their group frequencies often occurs and the extent of this perturbation might be expected to depend upon molecular geometry. We have therefore carried out a spectral investigation of 1,2-halohydrins, and in the present paper report the effects on the C–OH and O–H stretching frequencies in cyclic, secondary alcohols when a halogen is substituted on an adjacent carbon.

Results

The compounds examined and the results are presented in Table I. All spectra were taken in dilute CS_2 , in which solvent both the O–H and C–OH regions could be recorded in a single run. Spectral shifts to higher frequencies are recorded as $+\Delta\gamma$ values and those to lower frequencies as $-\Delta\gamma$ values. Repetition of some of the runs at later dates indicated that the $\Delta\gamma$ (O–H) values were

reproducible to ± 5 cm^{-1} , and the $\Delta\gamma$ (C–OH) values to ± 2 cm^{-1} .

O–H Stretching Bands.—The data in Table I show that the introduction of a halogen next to a secondary alcohol grouping produces a decrease in the O–H stretching frequency. According to the extent of this spectral displacement the halohydrins can be divided into two discrete categories.

One comprises those compounds that exhibit a small or negligible shift, which prevails when the 1,2-functional groups are in antiparallel arrangement (diaxial on a six-membered ring), or when they are in a *trans* relationship on a five-membered ring. In these steric situations the magnitudes of $\Delta\gamma$ (O–H) are of the order: 0 to -6 cm^{-1} for Cl (nos. 2, 8, 18, 28); -3 to -7 cm^{-1} for Br (nos. 3, 9, 29); and -7 cm^{-1} for I (no. 30).

On the other hand, in those halogeno-alcohols where the groups are configurationally *cis*, or where they are diequatorially *trans*, the O–H band shifts are distinctly greater and fall in the range -25 to -48 cm^{-1} . The only 1,3-halohydrin inspected was no. 20. This compound, which has the OH and Br in a *cis*, diaxial arrangement, exhibits a $\Delta\nu$ (O–H) value of -37 cm^{-1} and so belongs to this second category.

C–OH Stretching Bands.—The strong peak in the region around 990–1065 cm^{-1} displayed by cyclohexanols has been assigned to the C–OH stretching motion, and it has been shown that an equatorial hydroxyl group displays this band at a higher frequency than does its axial partner.² We now find that the effect of a neighboring halogen is to displace this band to higher frequencies. The extent of these shifts can be more conveniently correlated with steric structure by separate consideration of the five- and six-membered ring compounds.

(a) **6-Membered Rings.**—For the *trans*, diaxial (*i.e.*, antiparallel) arrangements in chloro- and bromohydrins the $\Delta\nu$ (C–OH) increments are small and fall in the range $+2$ to $+6$ cm^{-1} (nos. 2, 3, 8, 9, 16). In contrast the chloro- and bromohydrins with the *cis* configurations (nos. 10, 12, 22) or with

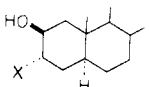
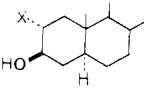
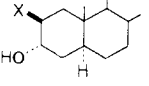
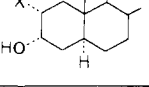
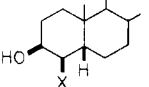
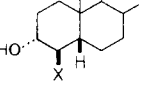
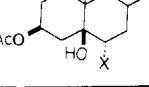
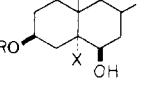
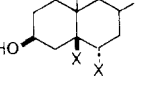
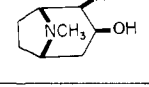
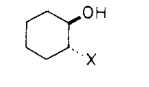
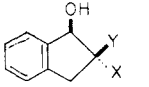
(1) (a) R. N. Jones, D. A. Ramsay, F. Herling and K. Dobriner, *THIS JOURNAL*, **74**, 2828 (1952); (b) E. J. Corey and H. J. Burke, *ibid.*, **77**, 5418 (1955); references are available there to earlier papers in their series.

(2) (a) A. R. H. Cole, R. N. Jones and K. Dobriner, *ibid.*, **74**, 5571 (1952); (b) H. Rosenkrantz, A. T. Milhorat and M. Farber, *J. Biol. Chem.*, **195**, 509 (1952); (c) A. Fürst, H. H. Kuhn, R. Scotini, Jr., and H. H. Günthard, *Helv. Chim. Acta*, **35**, 951 (1952); (d) W. G. Dauben, E. Hoerger and N. K. Freeman, *THIS JOURNAL*, **74**, 5206 (1952); (e) H. Rosenkrantz and L. Zablou, *ibid.*, **75**, 903 (1953).

(3) (a) J. E. Page, *J. Chem. Soc.*, 2017 (1955); (b) D. H. R. Barton, J. E. Page and C. W. Shoppee, *ibid.*, 331 (1956).

(4) E. J. Corey, R. A. Sreen, M. G. Danaher, R. L. Young and R. I. Rutledge, *Chemistry & Industry*, 1294 (1954).

TABLE I

Configurational type	Cmpd. no.	X	Compound	Conformation ^a	Stretching frequency in Cm. ⁻¹				Ref.
					O-H	$\Delta\nu$ O-H	C-OH	$\Delta\nu$ C-OH	
	1	H	Cholestan-2 β -ol	HO-a	3622		1012		^b
	2	Cl	3 α -Chlorocholestan-2 β -ol	HO-a	3617	- 5	1018	+ 6	^b
	3	Br	3 α -Bromocholestan-2 β -ol	HO-a Br-a	3616	- 6	1017	+ 5	^b
	4	H	Cholestan-3 β -ol	HO-e	3615		1037		^c
	5	Cl	2 α -Chlorocholestan-3 β -ol	HO-e	3594	-21	1053	+16	^b
	6	Br	2 α -Bromocholestan-3 β -ol	HO-e Br-e	3590	-25	1051	+14	^d
	7	H	Cholestan-3 α -ol	HO-a	3623		1002		^c
	8	Cl	2 β -Chlorocholestan-3 α -ol	HO-a	3617	- 6	1008	+ 6	^b
	9	Br	2 β -Bromocholestan-3 α -ol	HO-a Br-a	3616	- 7	1007	+ 5	^b
	10	Br	2 α -Bromocholestan-3 α -ol	HO-a Br-e	3588	-35	1016	+14	^d
	11	H	Methyl 3 β -hydroxycholestanate	HO-a	3614		1028		^d
	12	Br	Methyl 3 β -hydroxy-4 β -bromocholestanate	HO-a Br-e	3580	-34	1052	+24	^d
	13	H	Methyl lithocholate	HO-e	3611		1033		^e
	14	Br	Methyl 4 β -bromolithocholate	HO-e Br-e	3582	-29	1049	+16	^d
	15	H	Coprostan-3 β ,5 β -diol 3-acetate	HO-e	3603		1040		^f
	16	Br	6 α -Bromocoprostan-3 β ,5 β -diol 3-acetate	HO-e Br-e	3598	- 5	1042	+ 2	^f
	17	H R = H	Cholestane-3 β ,6 β -diol	HO-a	3615 ^g		1020 ^h 1038		^d
	18	Cl R = Ac	5 α -Chlorocholestane-3 β ,6 β -diol 3-acetate	HO-a Cl-a	3615	0			^d
	19	H	Coprostan-3 β -ol	HO-a	3625		1033		^c
	20	Br	5 β ,6 α -Dibromocoprostan-3 β -ol ⁱ	HO-a Br-a	3588	-37	1058	+25	^e
	21	H	Pseudotropine	HO-e HO-e	3609		1057		^k
	22	Br	2 β -Bromopseudotropine	Br-a	3561	-48	1082	+25	^k
	23	H	Cyclohexanol	HO-e	3615		1065		
	24	Cl	<i>t</i> -2-Chlorocyclohexanol	HO-e	3594	-21	1079	+14	^e
	25	Br	<i>t</i> -2-Bromocyclohexanol	Cl-e HO-e Br-e	3586	-29	1078	+13	^e
	26	I	<i>t</i> -2-Iodocyclohexanol	HO-e I-e	3574	-41	1073	+ 8	^e
	27	H Y = H	Indanol-1	...	3608		1053		^e
	28	Cl Y = H	<i>t</i> -2-Chloroindanol-1	..	3608	0	1063	+10	^e
	29	Br Y = H	<i>t</i> -2-Bromoindanol-1	...	3605	- 3	1062	+ 9	^e
	30	I Y = H	<i>t</i> -2-Iodoindanol-1	...	3601	- 7	1060	+ 7	^e
	31	H Y = Cl	<i>c</i> -2-Chloroindanol-1	...	3575	-33	1070	+17	^e

^a Conformations (a = axial, e = equatorial) refer to the ring carrying both the OH and X groups. ^b Samples kindly provided by Professor D. H. R. Barton [G. H. Alt and D. H. R. Barton, *J. Chem. Soc.*, 4284 (1954)]. ^c Specimens purified

by sublimation were kindly supplied by Dr. D. J. Whittingham through the courtesy of Dr. R. N. Jones. The uncorrected m.p.'s were: 143–144.5° (no. 4); 177–179° (no. 7); 100–102° (no. 19); 107–108° (cholestan-3 β -ol acetate); 88–89° (coprostan-3 β -ol acetate).^d Samples kindly donated by Professor L. F. Fieser [see L. F. Fieser and W. Y. Huang, *THIS JOURNAL*, **75**, 4837 (1953), for compounds no. 6, 10; and L. F. Fieser and R. Ettore, *ibid.*, **75**, 1700 (1953), for compounds no. 11, 12, 14]. The preparation of no. 17 is described by P. A. Plattner and W. Lang [*Helv. Chim. Acta*, **27**, 1872 (1944)] and that of no. 18 by R. A. Baxter and F. S. Spring [*J. Chem. Soc.*, 613 (1943)].^e See experimental, this paper. ^f The preparation of compound no. 15 (m.p. 80–81°) is reported by P. A. Plattner, H. Heusser and A. B. Kulkarni [*Helv. Chim. Acta*, **31**, 1885 (1948)], and that of no. 16 (m.p. 124–125°) is described in the Ph.D. dissertation of E. J. Tarlton, Harvard Univ., 1953. We are grateful to Professor L. F. Fieser and Dr. E. J. Tarlton for the samples. ^g Single peak, no splitting detected. ^h The 1038 cm.⁻¹ peak is assigned to the C-3 equatorial hydroxyl (*cf.* no. 4); and this peak exhibits a distinct shoulder at 1020 cm.⁻¹, which is attributed to the C-6 axial hydroxyl. ⁱ As a result of superposition with acetate bands the absorption here is broad and unresolved, and so a definite C–OH assignment cannot be made. ^j 5 α ,6 β -Dibromocholestan-3 β -ol showed the relevant bands at 3617 and 1034 cm.⁻¹. Comparison of these values with those of cholestan-3 β -ol (no. 4) indicates that the presence of a C-6 bromine has negligible effect on the infrared characteristics of the hydroxyl at C-3, and this justifies our choice of compound no. 19 as a reference model for no. 2.0. ^k Prepared as described by A. Nickon, *THIS JOURNAL*, **77**, 4094 (1955). The spectra of these two compounds (no. 21, 22) were also recorded in dilute CCl₄ solution. The essentially identical $\Delta\nu(\text{O–H})$ values obtained in both solvents (*cf.* –49 cm.⁻¹ in CCl₄; –48 cm.⁻¹ in CS₂) reassured us that even for these amines we could employ CS₂ solutions with impunity.

the *trans*, diequatorial dispositions (nos. 5, 6, 14, 24, 25) showed distinctly greater increments, +13 to +25 cm.⁻¹; the 1,3-*cis*, diaxial bromohydrin (no. 20) with $\Delta\nu(\text{C–OH})$ of +25 cm.⁻¹ is in this latter class. The single iodohydrin inspected (no. 26) is of borderline category with a $\Delta\nu(\text{C–OH})$ of +8 cm.⁻¹.

(b) **5-Membered Rings.**⁵—On the basis of the four compounds examined (nos. 28, 29, 30, 31) it appears that the *trans*-halohydrins give smaller shifts than do the corresponding *cis* compounds.

Discussion

Although the O–H and C–OH band displacements created by a neighboring halogen are undoubtedly due to several factors, the pronounced shifts in some cases and the minor shifts in others are best explained in terms of hydrogen bonding phenomena. Participation of the hydrogen in such bonding decreases the O–H stretching frequency; and these effects have been observed in *o*-halophenols⁶ and ethylene halohydrins⁷ and extensively studied in the cases of alcohols.⁸ The relationship between geometry and intramolecular bridging in glycols has been discussed by Kuhn.⁹

Our results indicate that in cyclic halohydrins, bridging between the hydroxyl and halogen occurs whenever the geometry is favorable.¹⁰ This bridging is attended not only by a decrease in the O–H stretching frequency but as well by an increase in the frequency of the C–OH vibration. Where intramolecular hydrogen bonding is sterically impossible (or improbable) these band shifts are minor.

In agreement with this interpretation are the large $\Delta\nu$ values shown by the 1,3-diaxial bromohydrin (no. 20), which is also ideally disposed for

(5) In view of the dearth of comparison cases available, our C–OH assignments in the 5-membered ring alcohols are vulnerable to criticism and so should be regarded as provisional.

(6) O. R. Wulf, U. Liddel and S. B. Hendricks, *THIS JOURNAL*, **58**, 2287 (1936).

(7) (a) L. R. Zumwalt and R. M. Badger, *ibid.*, **62**, 305 (1940); (b) S. I. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954, p. 61.

(8) For compendia on spectroscopic studies of hydrogen bonding see: (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954; (b) R. N. Jones and C. Sandorfy, "The Application of Infrared and Raman Spectrometry to the Elucidation of Molecular Structure," in A. Weissberger's "Techniques of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, vol. 9, p. 247.

(9) L. P. Kuhn, *THIS JOURNAL*, **74**, 2492 (1952); **76**, 4323 (1954).

(10) This generalization applies strictly to dilute solutions in CS₂ (and very probably to dilute solutions in other non-polar solvents), but is not necessarily valid for polar media or for the solid phase.

chelation,¹¹ and so it appears that the infrared shifts occur not only in 1,2-halohydrins, but whenever the two groups can interact.

Badger has pointed out that as the force constant of a hydrogen bridge increases, so does the extent of the shift in the O–H absorption, and that this is true for association between two OH groups or between an OH and a halogen.¹² Thus for 1,2-halohydrins (see nos. 23, 24, 25, 26) the hydrogen bonding power of the halogens falls in the order I > Br > Cl. Since this relationship is the reverse of the electronegativity sequence, the perturbing action of a halogen on the O–H vibration must be governed not only by electronegativity effects, but as well by the proximity and polarizability of the electrons on the halogen.^{6,7} These three elements show the reverse order (Cl > Br > I) in their ability to increase the C–OH force constant (nos. 23, 24, 25, 26) but not enough is known to justify an explanation at the present time.

By analogy to Kuhn's spectral work on glycols we would expect a given halogen to chelate more strongly with an OH, the closer the two functions are held to each other.⁹ This expectation is borne out by our findings that the $\Delta\nu(\text{O–H})$ increments are slightly greater for the *cis* arrangements on a cyclohexane ring than for the corresponding *trans*, diequatorial ones (nos. 10, 12, 6, 14).¹³

In the case of coprostan-3 β ,5 β -diol 3-acetate (no. 15) the attachment of an equatorial bromine to C-6 of this molecule (no. 16) has little effect on the two relevant vibrations ($\Delta\nu(\text{O–H})$ –5 cm.⁻¹; $\Delta\nu(\text{C–OH})$ +2 cm.⁻¹). Since the OH and Br are suitably oriented for chelation, more pronounced displacements would be expected. A closer analysis, however, reveals that we are dealing not with an exception but with a situation where the OH is for the most part preferentially chelated to the ester grouping at C-3. The basis for this contention rests upon a comparison of the spectral characteristics of the acetoxy unit in the three re-

(11) L. P. Kuhn (ref. 9) has observed that in *cis*-cyclohexane-1,3-diol the hydroxyl groups are intramolecularly chelated in CCl₄ solution. Presumably, this bonding is sufficiently strong to hold the molecule in the chair form with the two OH groups in axial conformations.

(12) R. M. Badger, *J. Chem. Phys.*, **8**, 288 (1940).

(13) The geometry of a chair-shaped cyclohexane ring is such that the separation between two adjacent equatorial groups (*trans*) is identical to that between an axial and an equatorial group (*cis*). However, there is overwhelming chemical and physical evidence that less energy is required to effect partial eclipsing of *cis* bonds by ring distortion than of *trans* ones. For explanations of these phenomena see ref. 9 as well as C. J. Angyal and C. G. Macdonald, *J. Chem. Soc.*, 695 (1952).

lated molecules, nos. 15, 16 and coprostan-3 β -ol acetate (Table II).

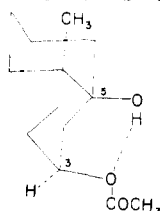
TABLE II

	STRETCHING FREQUENCY OF ACETOXY BONDS IN CM. ⁻¹		
	A C=O	B sp ² C-O	C sp ³ C-O
Coprostan-3 β -ol acetate	1736	1248 1236 1220	1021
Coprostane-3 β ,5 β -diol 3-acetate (no. 15)	1745	1224	1030
6 α -Bromocoprostan-3 β ,5 β -diol 3-acetate (no. 16)	1742	1223 1235 ^a	1032 ^b

^a This band appeared as a resolved shoulder on the 1223 cm.⁻¹ peak. ^b This band is superposed on the C-OH absorption at 1042 cm.⁻¹, but both show up as resolved maxima.

Column A shows that introduction of a 5 β -OH creates a notable alteration of the carbonyl stretching frequency, whereas the further introduction of an α -Br at C-6 has little additional influence. From column B we see that the trio of peaks (attributed to the sp² C-O stretching¹⁴ and characteristic of axial acetates at C-3¹⁵) is modified to give a single sharp maximum at 1224 cm.⁻¹ in the hydroxy-acetate (no. 15). Finally, the sp³ C-O peak^{8a} at 1021 cm.⁻¹ progresses to 1030 cm.⁻¹ when OH is introduced, but is sensibly unchanged when Br is then affixed (column C). These spectral modifications point to a definite interaction between the C-5 β -OH and the C-3 β -acetoxy functions, most likely by hydrogen bonding. Similar chelation between β -oriented groups at C-5 and C-3 was noted earlier for compound 20. This example illustrates the caution to be exercised in spectral interpretation of halohydrins when complicating factors are present.

Interestingly enough, the *direction* of the band displacements recorded in Table II is consistent with bridging of the OH to the alkyl oxygen of the ester link rather than to the carbonyl oxygen,¹⁶ as shown in the accompanying figure.



Acknowledgment.—The author is deeply grateful to those persons cited in the text who made this study possible by contributing model compounds. Extra appreciation is extended to Dr. R. N. Jones

(14) Throughout this paper the term "C-O" stretching implies involvement of the sp³ hybridized carbon on the cyclohexane ring. In the discussion of acetoxy steroids a distinction is necessary between the two kinds of singly-bonded carbon-oxygen units present. This distinction is made by use of the terms sp² C-O and sp³ C-O, which identify the relevant carbon by reference to its state of hybridization.

(15) R. N. Jones, P. Humphries, F. Herling and K. Dobriner, *THIS JOURNAL*, **73**, 3215 (1951).

(16) Hydrogen bonding between a C-5 -OH and a C-3 -OAc (when the stereochemistry is favorable) has been discerned recently by H. B. Henbest and B. J. Lovell (*Chemistry & Industry*, 278 (1956)). These authors used CCl₄ as solvent and their spectral interpretations agree with ours.

for helpful advice on many aspects, and to Mr. R. Lauzon and Mr. P. Alisea for technical assistance. This work was initiated while the author was the holder of a National Research Council of Canada Post-doctorate Fellowship (1954-1955); it is published as N. R. C. Publication No. 4104.

Experimental

Unless otherwise stated, all temperatures recorded here are uncorrected. The physical constants of compounds that were provided by other investigators are not quoted when the values are essentially the same as those given in the original publications, which are listed in the footnotes to Table I. The parenthesized number after each compound refers to its listing in that table.

Measurement of Infrared Spectra.—Spectra were taken at room temperature on a Perkin-Elmer double-beam recording spectrophotometer, model 21, equipped with a sodium chloride prism. All compounds were examined in 5-mm. matched cells (NaCl) in CS₂ solution at concentrations between 1 \times 10⁻³ and 2 \times 10⁻³ molar. This high dilution was employed to eliminate intermolecular effects; however, separate runs revealed that many of the sterols were substantially devoid of such effects at higher concentrations (*ca.* 10⁻² molar) where 1-mm. cells could be used.

In each case the atmospheric water vapor band at 3740 cm.⁻¹ was used as a calibration standard,¹⁷ and the O-H stretching frequencies given are the corrected values. In most instances the spectra of a set of halohydrins and their corresponding parent alcohol were run consecutively to minimize instrumental fluctuations.

Methyl Lithocholate (13).—Crude commercial (Gane and Ingram) lithocholic acid (180 g.) in 500 cc. of methanol containing 12 g. of dissolved hydrogen chloride gas was refluxed 4 hr. An additional 150 cc. of methanol containing 12 g. of hydrogen chloride gas was added and the reflux continued 2 hr. during which time some solid impurities gradually precipitated. The hot mixture was cooled a little under the water tap and filtered rapidly by gravity. The plaster-like solid was washed with warm methanol. The combined filtrates (800-900 cc.) when cold, deposited 143 g. (m.p. 128-132°) of the methyl ester. Concentration of the mother liquor to 150-200 cc. gave an additional 14 g. with m.p. 129-131°. The material used for the infrared work had m.p. 127-128° (cor.) and was crystallized from methanol.¹⁸

5 α ,6 β -Dibromocholestan-3 β -ol.—This dibromide was prepared by Fieser's method¹⁹ and was purified by crystallization from ethyl acetate-methanol as described by Barton and Miller²⁰; m.p. 112-113° (cor.); ν 3617, 1034 cm.⁻¹

5 β ,6 α -Dibromocoprostan-3 β -ol (20).—This compound was obtained by rearrangement of the 5 α ,6 β -isomer in chloroform as reported²⁰; m.p. 139-140° when crystallized from ethyl acetate-methanol.

trans-2-Bromocyclohexanol (25).—This bromohydrin (*n*_D²⁰ 1.5183) was prepared by the action of N-bromosuccinimide on cyclohexene. It was converted to cyclohexene oxide (b.p. 130-131°) by the action of aqueous sodium hydroxide.²¹

trans-2-Chlorocyclohexanol (24).—Treatment of cyclohexene oxide with cold concentrated hydrochloric acid as reported gave the *trans*-chlorohydrin, b.p. 71° (7 mm.), *n*_D²⁰ 1.4882.²²

trans-2-Iodocyclohexanol (26).—This iodohydrin was prepared by treatment of cyclohexene oxide with hydriodic acid as reported,²³ m.p. 39-40.5°, crystallized from petroleum ether (b.p. 30-60°).

Indanol-1 (27).—Obtained in two steps from indene by action of dry hydrogen chloride followed by aqueous alkali as described,²⁴ this alcohol was crystallized from petroleum ether (b.p. 30-60°) and had m.p. 53-54°.

(17) A. R. Downie, M. C. Magoon, T. Purcell and B. Crawford, Jr., *J. Opt. Soc. Am.*, **43**, 941 (1953).

(18) L. F. Fieser and S. Rajagopalan, *THIS JOURNAL*, **72**, 5530 (1950).

(19) L. F. Fieser, *ibid.*, **76**, 5421 (1953).

(20) D. H. R. Barton and E. Miller, *ibid.*, **72**, 1066 (1950).

(21) C. O. Guss and R. Rosenthal, *ibid.*, **77**, 2549 (1955).

(22) S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

(23) S. Winstein, E. Grunwald, R. E. Buckles and C. Hanson, *ibid.*, **70**, 816 (1948).

(24) R. Weissgerber, *Ber.*, **44**, 1436 (1911).

trans-2-Chloroindanol-1 (28) and *cis*-2-Chloroindanol-1 (31).—These chlorohydrins were prepared according to the procedure of Suter and Lutz²⁵ by addition of chlorine to indene, treatment with aqueous ethanol and fractional crystallization of the resulting mixture. Deposited from ether the *cis* isomer had m.p. 112–113°, and the *trans* isomer (from benzene) had m.p. 124–126°. Both of these m.p.'s are corrected.

trans-2-Bromoindanol-1 (29).—The action of aqueous N-bromosuccinimide on indene gave this bromohydrin, m.p.

(25) C. M. Suter and G. A. Lutz, *THIS JOURNAL*, **60**, 1360 (1938).

130–131° (cor.), when crystallized from benzene–petroleum ether (b.p. 60–75°).²¹

trans-2-Iodoindanol-1 (30).—The literature procedure²⁸ was duplicated to give the iodohydrin, which was purified from benzene–petroleum ether (b.p. 60–75°); m.p. 124–126° dec.

(26) M. Tiffeneau and O. Orekhoff, *Bull. soc. chim.*, **27**, 782 (1920).

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COMMUNICATIONS TO THE EDITOR

THE SYNTHESIS OF FLUOROCARBON PHOSPHORUS IODIDES¹

Sir:

A news report² of our work on fluorocarbon-phosphorus compounds produced from CF_3PI_2 or $(\text{CF}_3)_2\text{PI}$ led to inquiries concerning the synthesis of these iodides by the $\text{CF}_3\text{I}-\text{P}_4$ reaction. Hence it appears timely to describe the conditions under which we obtained them in yields as good as originally reported,³ and with far higher utilization of CF_3I per single run. A convenient short-cut method also is described.

In the work at Corona (Table I) most of the runs were done in a liter-size stainless-steel bomb, which had been thoroughly cleaned, and dried at 200°, before loading with the thoroughly-dried reagents in a dry argon atmosphere. In all cases the CF_3I had been made from iodine and silver trifluoroacetate⁴ and purified by distillation. Each heating was for 48 hr. at 200°. For comparison, the first line of Table I summarizes one of the experiments by the earlier workers,³ showing their results after twice-repeated heatings of the non-volatile part with the $(\text{CF}_3)_3\text{P}$ and the recovered CF_3I .

From this table it appears that equally good results can be obtained with red or white phosphorus, except that the presence of iodine seems to be more important for the latter. The improvement over previously reported results is attributed to the rigorous exclusion of atmospheric contaminants.

For the work at the University it was considered that the reaction $\text{AgCO}_2\text{CF}_3 + \text{I}_2 \rightarrow \text{CO}_2 + \text{AgI} + \text{CF}_3\text{I}$ might well occur in the presence of phosphorus, which then could react to form the $\text{CF}_3\text{-P-I}$ compounds. Thus a convenient one-step procedure was devised: the three well-dried solid reagents were loaded into a one-liter mild-steel bomb

in such a way that the silver trifluoroacetate formed a layer between the red phosphorus and the iodine; or in another case the premature I_2-P_x reaction was avoided by cooling the bomb to -78° for the loading process. A heating of 88 g. of AgCO_2CF_3 , 50 g. of P_x , and 100 g. of I_2 , for 120 hr. at 195°, produced 9 g. of $(\text{CF}_3)_3\text{P}$, 13 g. of $(\text{CF}_3)_2\text{PI}$,

TABLE I

Run	Reactants, g.	$(\text{CF}_3)_3\text{P}$	% Conversion to $(\text{CF}_3)_2\text{PI}$	CF_3PI_2	% CF_3I utilized
(BEH)	60 CF_3I ; 50 P_4 ; 50 I_2	13	19	18	50
1	50 CF_3I ; 50 P_4 ; 50 I_2	22	60	11	93
2	342 CF_3I ; 175 P_x (red)	30	50	16	96
3	406 CF_3I ; P_x residue of 2	49	32	14	95
4	60 CF_3I ; 55 P_4	5		10	12

and 10 g. of CF_3PI_2 ; all representing 58% of the CF_3 groups. Other products included 4 g. of CF_3I , 3 g. of POF_3 , and 5 g. of a new compound of yet-uncertain composition (m.p. 0°; mol. wt. 196; vapor tension 19 mm. at 0°), which was separated from the $(\text{CF}_3)_2\text{PI}$ fraction (44 mm. at 0°) by a fairly tedious process of high-vacuum distillation. The presence of this new substance does no harm when the $(\text{CF}_3)_2\text{PI}$ is used for making $\text{P}_2(\text{CF}_3)_4$ ³ or $(\text{CF}_3)_2\text{PCI}$, for the former can be purified by treatment with water and the latter by distillation. If pure $(\text{CF}_3)_3\text{P}$ is desired, most of the POF_3 can be removed by distillation at atmospheric pressure, and the remainder by hydrolysis.

The use of the fluorocarbon-phosphorus iodides for making a considerable variety of new compounds will be reported in detail in later papers.

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(2) *Chem. and Eng. News*, **34**, 2124 (1956).

(3) F. W. Bennett, H. J. Emel us and R. N. Haszeldine, *J. Chem. Soc.*, 1568 (1953).

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