added and the mixture was warmed to gentle reflux. The suspended solid dissolved completely at the end of 20 minutes and the solution was diluted with 100 ml. of dry benzene. The solvent was removed (aspirator, room temperature) and the residue was flushed with benzene. A solution of the residue in 10 ml. of benzene was washed with 5 ml. of 5% sodium bicarbonate solution followed by 5 ml. of water, and then was lyophilized. The light yellow residue from the lyophilization was dissolved in 5 ml. of benzene and chromatographed over 12 g. of Brockman activity III ethyl acetate neutralized alumina, with benzene as the eluent. Residue from the first 50 ml. of eluate was crystallized from benzene–petroleum ether to afford 0.46 g. (47%) of needles, m.p. 123–7°. A sample recrystallized from acetone–petroleum ether had m.p. 128.1–129.8°.

Anal. Calcd. for $C_{22}H_{24}N_2O_5S_2$: C, 57.37; H, 5.25; N, 6.08. Found: C, 57.56; H, 5.46; N, 6.02.

6-(α-Toluenesulfonamido)-penicillanic Acid (IId).—A suspension of 140 mg. of 30% palladium on charcoal in a solution of 0.25 ml. of glacial acetic acid in 5 ml. of purified dioxane was prereduced at room temperature and atmospheric pressure. Benzyl ester IIb (45.7 mg.) was added and hydrogenation was continued. The theoretical quantity of hydrogen had been absorbed at the end of six minutes, but the reduction was continued for one hour. Catalyst was removed by filtration and the filtrate was lyophilized. The residue was taken up in 5 ml. of methylene chloride, N-(3,3-diphenylpropyl)-piperidine (Bristol Laboratories "Aspasan") (29.4 mg., 0.105 mmole) was added and the methylene chloride was removed by evaporation under reduced pressure. Lyophilization of the residue from benzene yielded the salt as a colorless amorphous solid which crystallized immediately upon solution in 0.5 ml. of benzene. A second crop was obtained by the addition of ethyl ether. The total yield was 48.4 mg., 74%, m.p. 112–115° dec.

Anal. Calcd. for $C_{35}H_{43}N_3O_5S_2$: C, 64.68; H, 6.67; N, 6.47. Found: C, 64.73; H, 6.98; N, 6.31.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Cyclic Polyolefins. XLI. Reaction of Acetyl Bromide and Propionyl Chloride with Cyclooctatetraene

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RECEIVED AUGUST 3, 1956

Acetyl bromide and propionyl chloride react with cycloöctatetraene in the presence of aluminum chloride in nitrobenzene solution to form *o*-methylcinnamaldehyde and *o*-ethylcinnamaldehyde, respectively, in low yield.

This paper describes the results of initial attempts to prepare acyl derivatives of cycloöctatetraene, now available by other routes,[3,4] by the Friedel–Crafts acylation of cycloöctatetraene. It appeared possible that cycloöctatetraene would react with acid halides in the manner characteristic of many olefins,[5] forming adducts that could be converted to acyl cycloöctatetraenes by dehydrohalogenation. The reaction was investigated under various conditions with acetyl chloride, acetyl bromide, benzoyl chloride and acetic anhydride as acylating agents, employing zinc chloride, acetylsulfoacetic acid,[6] stannic chloride and aluminum chloride as catalysts. Only with aluminum chloride in dilute nitrobenzene solution at 0–5° was any isolable product obtained, and then only in low yield. The reaction was accompanied by extensive polymerization, presumably caused by the strong Lewis acid catalyst. The product was isolated by steam distillation, followed by repeated distillation.

It was evident that the light-yellow liquid product obtained from the reaction of cycloöctatetraene with acetyl bromide was not an acetyl derivative, for it was readily oxidized by air to an acid, m.p. 176–176.5° (I). The acid I was characterized by oxidation to *o*-toluic acid and by quantitative reduction with the absorption of 98% of one molar equivalent of hydrogen forming β-*o*-tolylpropionic acid (II), which was oxidized to *o*-phthalic acid, isolated as the anhydride. Literature values for the melting point of *o*-methylcinnamic acid are 169°[7] and 174–175°.[8] That compound I was indeed *o*-methylcinnamic acid was shown by comparison with an authentic sample prepared from *o*-tolualdehyde and malonic acid. None of the reported preparations of I has been identified as the *cis* or *trans* isomer. The ultraviolet spectrum of the authentic acid I prepared as described above has a maximum at 274 mμ (log ε 4.18). The ultraviolet spectra of *cis*- and *trans*-cinnamic acid have maxima at 264 mμ (log ε 3.98) and 273 mμ (log ε 4.32), respectively.[9] Accordingly, the acid I probably is the *trans* isomer.

The above results indicated that the original Friedel–Crafts product is *o*-methylcinnamaldehyde (III). An authentic sample of III was prepared by condensation of *o*-tolualdehyde with acetaldehyde in the presence of sodium hydroxide. The identity of the two samples of III was established by their ultraviolet maxima at 283 mμ, comparison of their infrared spectra, and mixed melting points of the semicarbazones, which showed no depression.

In order to obtain information concerning the source of the methyl group in III, cycloöctatetraene was treated with propionyl chloride under the conditions used with acetyl bromide. The product proved to be *o*-ethylcinnamaldehyde (IV), which was purified by extraction with Girard reagent T and regeneration. An authentic sample of the aldehyde IV was synthesized by condensation of *o*-ethylbenzaldehyde with acetaldehyde. Both samples had ultraviolet maxima at 291 mμ and infrared spectra that were identical within experimental error, and contained bands at 2809 and 2747 $cm.^{-1}$

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(1) National Science Foundation Fellow, 1952–1955.

(2) Atomic Energy Commission Fellow, 1951–1952.

(3) A. C. Cope and D. J. Marshall, THIS JOURNAL, **75**, 3208 (1953).

(4) A. C. Cope and R. M. Pike, *ibid.*, **75**, 3220 (1953).

(5) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, p. 752 ff.

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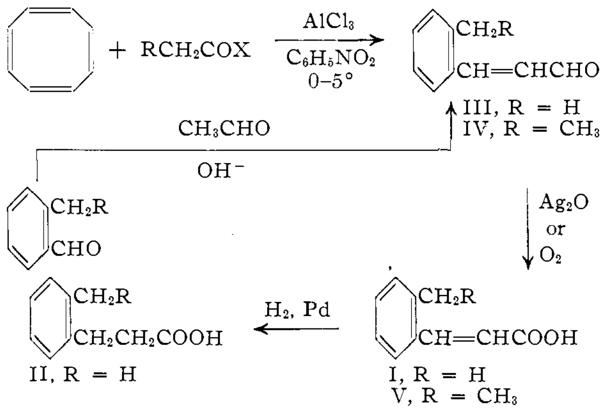
(7) J. F. J. Dippy and J. E. Page, *J. Chem. Soc.*, 357 (1938).

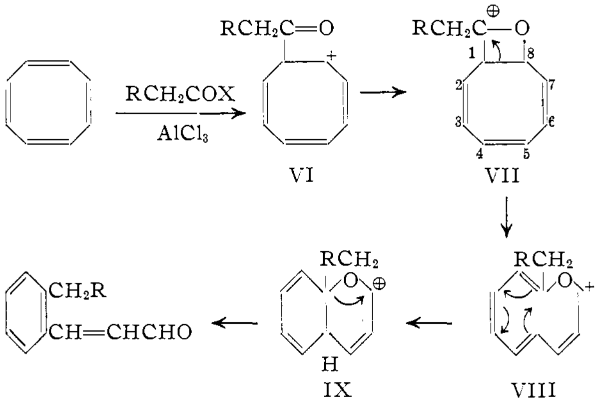
(8) K. v. Auwers, *Ann.*, **413**, 265 (1917).

(9) A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," Edward Arnold, Ltd., London, 1954, p. 233.

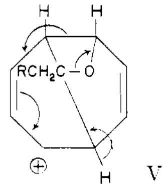
characteristic of the C–H stretching frequency of aldehydes.[10] The two samples also formed identical semicarbazones and 2,4-dinitrophenylhydrazones, as shown by mixed melting points, and both formed *o*-ethylcinnamic acid (V) on oxidation.



Because of the low yields of the aldehydes III and IV, the mechanisms of these unusual reactions were not studied further, and at present only speculative reaction schemes can be proposed. One possible mechanism is



In this sequence, the first step is the normal acylation to give the expected cation VI. Interaction of the oxygen atom of the acetyl group with the neighboring positively charged carbon atom then could form VII. Opening of the four-membered ring in VII in the manner shown would form VIII, which could then bridge to form IX.[11] IX would be expected to aromatize immediately to form an *o*-alkylcinnamaldehyde, the product that is isolated. Examination of models shows that in structure VII, atom 5 lies very close to the carbon atom shown bearing the positive charge, indicating that ring closure to form VIIIa may be possible.



VIIIa

By means of the electronic shifts indicated by the arrows, VIIIa could then form the aldehyde directly.

It appeared to be possible that the acyl cycloöctatetraene was first formed, which then underwent a reverse aldol condensation under the acidic conditions of the steam distillation to form 9-oxo-2,4,6-decatrienal, which in turn could tautomerize and undergo an aldol condensation to form the resonance-stabilized *o*-alkylcinnamaldehyde. In order to test this possibility a mixture of cycloöctatetraenyl methyl ketoxime and hydrochloric acid was steam distilled. The organic portion of the steam distillate was identified as unchanged cycloöctatetraenyl methyl ketone, isolated as the semicarbazone. Hence, this reaction path through the open-chain ketoaldehyde is eliminated.

Experimental[12]

Friedel–Crafts Reaction of Cycloöctatetraene with Acetyl Bromide.—A solution of 10 g. of cycloöctatetraene and 12 g. of acetyl bromide in 350 ml. of dry nitrobenzene[13] was cooled to 0–5° in an ice–water-bath stirred vigorously as a solution of 6.7 g. of aluminum chloride in 30 ml. of nitrobenzene was added dropwise over a period of 30 minutes. The mixture was stirred for an additional period of 2 hours at 0–5°, after which the reaction was quenched by adding 250 ml. of 3 *N* hydrochloric acid. The resulting mixture was steam distilled, and the nitrobenzene was distilled from the organic layer. The residue from this distillation was then purified by distillation through a semi-micro column. The resulting liquid was combined with similar material from a preparation in which 20.8 g. of cyclooctatetraene was employed, redistilled, washed with sodium bicarbonate solution, and redistilled to yield 0.91 g. (2.1%) of III, $n^{25}\mathrm{D}$ 1.6103, identical with authentic III in all respects.

In other preparations III was also isolated as the sodium bisulfite addition compound, obtained by shaking the organic layer from steam distillation with saturated sodium bisulfite solution and cooling.

The above product (III) formed a semicarbazone on heating with semicarbazide hydrochloride and sodium acetate in aqueous ethanol. After several recrystallizations from aqueous ethanol the yellow needles melted at 205.0–205.6°; the melting point was not depressed on admixture with the semicarbazone of an authentic sample of III described below.

***o*-Methylcinnamaldehyde (III).**—An authentic sample of III was prepared according to the procedure used by Scholtz and Wiedemann[14] for preparation of the *para* isomer by condensation of *o*-tolualdehyde with acetaldehyde. The crude product was distilled through a Vigreux column (40 × 1-cm.) and redistilled twice under nitrogen through a semi-micro column as a light-yellow liquid, b.p. 91° (0.4 mm.), $n^{25}\mathrm{D}$ 1.6098 (reported $n^{22}\mathrm{D}$ 1.5623),[15] $\lambda_{\max}$ 282 mμ, log ϵ 4.36, with characteristic infrared bands at 2825, 2755 and 1672 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.19; H, 6.85. Found: C, 81.94; H, 6.97.

The semicarbazone of the authentic sample of III, after several recrystallizations from aqueous ethanol, melted at 204.8–205.8° (reported m.p. 217°[15] and 216°[16]).

Anal. Calcd. for $C_{11}H_{13}N_3O$: C, 64.97; H, 6.40; N, 20.69. Found: C, 64.86; H, 6.45; N, 20.71.

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(10) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 136.

(11) *Cf.*, for example, the bridging of cycloöctatriene to bicyclo-[4.2.0]octa-2,4-diene; A. C. Cope, A. C. Haven, F. L. Ramp and E. R. Trumbull, THIS JOURNAL, **74**, 4867 (1952).

(12) We are indebted to Dr. S. M. Nagy and his associates for analyses. Melting points are corrected and boiling points are uncorrected. Ultraviolet absorption spectra were determined in 95% ethanol with a Cary ultraviolet recording spectrophotometer, model 11 MS.

(13) If the product III is to be purified solely by distillation, the nitrobenzene should be purified carefully by fractional distillation, because otherwise the small amount of *m*-dinitrobenzene that is apt to be present will contaminate the product.

(14) M. Scholtz and A. Wiedemann, *Ber.*, **36**, 850 (1903).

(15) L. Bert and P. Dorier, *Compt. rend.*, **191**, 332 (1930).

(16) R. Delaby, *ibid.*, **194**, 1248 (1932).

Oxidation of III.—A sample of III prepared from cyclooctatetraene was oxidized to I by exposing the liquid to air at room temperature. The acid was isolated by extraction with sodium bicarbonate solution, acidification of the aqueous extracts, and extraction with ether. Evaporation of the ether and two recrystallizations of the residue from 95% ethanol followed by sublimation at 0.3 mm. gave pure I, m.p. 176.0–176.5°,[7,8] which did not depress the melting point of authentic I, the preparation of which is described below.

Oxidation of I.—A solution of 50 mg. of I and 163 mg. of potassium permanganate plus a small amount of magnesium sulfate in aqueous acetone was heated at 60° for 1 hour, and then allowed to stand for 16 hours at room temperature. After the acetone was removed by distillation the mixture was acidified, treated with sodium bisulfite, and extracted with ether. Evaporation of the ether gave an oil which was dissolved in dilute sodium hydroxide; this solution was extracted with ether, and acidified. The precipitate was recrystallized from aqueous ethanol to give 5 mg. of pure *o*-toluic acid, m.p. 103.2–103.9°; mixed melt with an authentic sample was not depressed.

A mixture of 76 mg. of I and 440 mg. of potassium permanganate in 10 ml. of water was heated at 100° for 17 hours. The product was isolated as above except that basic extraction was unnecessary. Sublimation at 0.6 mm., followed by crystallization from benzene–carbon tetrachloride, gave 34 mg. of pure phthalic anhydride, m.p. 130.1–131.7°.

β-*o*-Tolylpropionic Acid (II).—Hydrogenation of a solution of 0.19 g. of I in 5 ml. of methanol in the presence of 0.2 g. of 10% palladium-on-Norit was complete in 25 minutes with the absorption of 98% of one molar equivalent of hydrogen. The solution was filtered, the filtrate was concentrated, and the residue was crystallized from 95% ethanol to give analytically pure II, m.p. 103.1–103.6° (reported 102°).[7]

***o*-Methylcinnamic Acid** (I).—A solution of 6.0 g. of *o*-tolualdehyde and 9.9 g. of malonic acid in 20 ml. of dry pyridine and 0.5 ml. of piperidine was heated at 100° for 2 hours. The solution was then poured into a mixture of 30 ml. of concentrated hydrochloric acid and 50 g. of cracked ice. The precipitate was washed with 10% hydrochloric acid and water and crystallized from 95% ethanol, yielding 5.5 g. (68%) of I, m.p. 175.7–177.6°. Recrystallization from 95% ethanol gave pure I, m.p. 176.6–177.2°.

Friedel–Crafts Reaction of Cycloöctatetraene with Propionyl Chloride.—The general procedure followed was similar to the one described above for the reaction with acetyl bromide. To a solution of 20.8 g. of cycloöctatetraene in 630 ml. of redistilled nitrobenzene was added over a period of 70 minutes a solution of 13.4 g. of aluminum chloride and 17.4 g. of propionyl chloride in 100 ml. of nitrobenzene. The reaction was quenched, after an additional 2 hours of stirring at 0–5°, by adding 500 ml. of 3 *N* hydrochloric acid. The aqueous layer from subsequent steam distillation was extracted with ether, and the combined ethereal extracts and organic layer were distilled until no more nitrobenzene collected. The small black residue was distilled through a semi-micro column, yielding 2.9 g. of recovered cyclooctatetraene and 2.2 g. of a chlorine-containing liquid product.

This impure product was refluxed for 70 minutes with 5 g. of Girard reagent T in 100 ml. of absolute ethanol and 10 ml. of glacial acetic acid. This mixture was then poured into a mixture of 550 ml. of water, 200 g. of ice, 11.2 g. of sodium carbonate and 200 ml. of petroleum ether. The aqueous layer was extracted with another portion of petroleum ether, after which it was stirred for 24 hours with 200 ml. of petroleum ether and 70 ml. of concentrated hydrochloric acid. After separation of the layers, the aqueous layer was stirred overnight with an additional 30 ml. of concentrated hydrochloric acid and 200 ml. of diethyl ether. The combined ether and petroleum ether extracts were dried over magnesium sulfate, concentrated, and the residue was distilled through a semi-micro column, yielding 0.65 g. (2.0%) of IV, b.p. 78° (0.3 mm.), n^{25}_{D} 1.5909.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.15; H, 7.79.

The 2,4-dinitrophenylhydrazone of IV was recrystallized several times from a mixture of ethanol and ethyl acetate. The bright red crystals melted at 243.6–244.6° (dec., sample inserted at 238°). A mixed melting point with the 2,4-dinitrophenylhydrazone of authentic IV, prepared as described below, showed no depression.

Anal. Calcd. for $C_{17}H_{16}N_4O_4$: C, 60.01; H, 4.74; N, 16.46. Found: C, 59.79; H, 4.93; N, 16.21.

The semicarbazone of IV was recrystallized from aqueous ethanol, and melted at 190.8–191.8°; a mixed melting point determination with an authentic sample showed no depression.

Silver Oxide Oxidation of IV.—To a solution of 370 mg. of silver nitrate in 2 ml. of water and 1 ml. of ethyl alcohol was added 99 mg. of IV prepared from cycloöctatetraene. To this mixture was then added dropwise, with stirring, over a period of about 60 minutes, a solution of 120 mg. of sodium hydroxide in 3 ml. of water. The mixture was stirred for an additional 60 minutes and then allowed to stand overnight. The silver oxide was removed by filtration and washed with hot water; the filtrate was concentrated to about 5 ml., and then acidified to yield 82 mg. (75%) of crude V. Four recrystallizations from aqueous ethanol afforded 61 mg. of V, m.p. 151.0–152.0°; on admixture with an authentic sample of V, described below, the melting point showed no depression.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87; neut. equiv., 176. Found: C, 74.65; H, 6.93; neut. equiv., 178.

***o*-Ethylcinnamaldehyde.**—*o*-Ethylaniline was purified by distillation just prior to use, n^{22}_{D} 1.5586 (reported n^{22}_{D} 1,5584 for the *ortho* isomer, n^{22}_{D} 1.5529 for the *para* isomer).[17] The N-acetyl derivative melted at 111.8–112.4° (reported melting points are 110–112° for the *ortho* isomer and 94° for the *para* isomer).[18] *o*-Ethylaniline was converted to the nitrile by the Sandmeyer reaction with cuprous cyanide according to the method used by Clarke and Read for *o*-methylaniline.[19] The nitrile was obtained in 53% yield as a colorless liquid, b.p. 87° (9 mm.), n^{20}_{D} 1.5228 (reported n^{20}_{D} 1.5232 for the *ortho* isomer, n^{20}_{D} 1.5274 for the *para* isomer).[20] The nitrile was hydrolyzed with 75% sulfuric acid[21] to *o*-ethylbenzoic acid (75% yield), which was converted *via* the acid chloride to *o*-ethylbenzaldehyde (61% yield based on the acid), b.p. 89° (11 mm.), n^{25}_{D} 1.5370, by the method used by Hershberg and Cason for β-naphthoic acid.[22]

The 2,4-dinitrophenylhydrazone was prepared by adding a solution of 2,4-dinitrophenylhydrazine in methanol and hydrochloric acid to the *o*-ethylbenzaldehyde; the orange crystals after two recrystallizations from a mixture of ethanol and ethyl acetate melted at 185.7–186.6°.

Anal. Calcd. for $C_{15}H_{14}N_4O_4$: C, 57.32; H, 4.49; N, 17.83. Found: C, 57.22; H, 4.69; N, 17.76.

o-Ethylbenzaldehyde was condensed with acetaldehyde, according to the method used by Bernhauer and Skudrzyk[23] to condense benzaldehyde with propionaldehyde, to form IV, b.p. 88° (0.2 mm.), n^{25}_{D} 1.5962, $\lambda_{\max}$ 291 mμ, log ε 4.32, with characteristic infrared bands at 2809, 2755 and 1672 cm.$^{-1}$. The 2,4-dinitrophenylhydrazone of authentic IV after three recrystallizations from a mixture of ethanol and ethyl acetate melted at 242.9–243.3° dec. The semicarbazone of authentic IV melted at 192.0-193.0°.

Anal. Calcd. for $C_{12}H_{15}N_3O$: C, 66.34; H, 6.96; N, 19.36. Found; C, 66.32; H, 7.09; N, 19.26.

An authentic sample of V, formed by oxidizing this sample of IV with silver oxide as above, melted at 150.8–152° after two recrystallizations from aqueous ethanol.

Stability of Cycloöctatetraenyl Methyl Ketone to Aqueous Acid.—Cycloöctatetraenyl methyl ketoxime[2] (0.200 g.) was added to 200 ml. of 3 *N* hydrochloric acid and the resulting mixture steam distilled until no more organic layer collected. The ethereal extracts of the distillate were con-

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(17) E. Schreiner, *J. prakt. Chem.*, **81**, 559 (1910).

(18) H. Paucksch, *Ber.*, **17**, 768 (1884).

(19) H. T. Clarke and R. R. Read, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 514.

(20) S. F. Birch, R. A. Dean, F. A. Fidler and R. A. Lowry, THIS JOURNAL, **71**, 1362 (1949).

(21) H. T. Clarke and E. R. Taylor, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 588.

(22) E. B. Hershberg and J. Cason, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 627.

(23) K. Bernhauer and I. Skudrzyk, *J. prakt. Chem.*, **155**, 310 (1940).

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 cycloöctatetraenyl 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.

CAMBRIDGE, MASSACHUSETTS

[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

RECEIVED JUNE 7, 1956

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 + Δγ values and those to lower frequencies as −Δγ values. Repetition of some of the runs at later dates indicated that the Δγ (O–H) values were reproducible to ±5 cm.$^{-1}$, and the Δγ (C–OH) values to ± 2 cm.$^{-1}$.

O–H Streching 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 Δγ(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 Δν(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 Δν(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

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[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. Zablow, *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. Sneen, M. G. Danaher, R. L. Young and R. L. Rutledge, *Chemistry & Industry*, 1294 (1954).