[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Haloallenes[1a,b]

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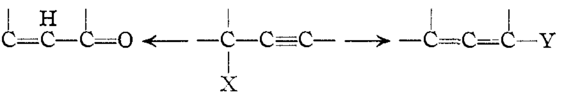
Bromopropadiene and chloropropadiene were prepared by isomerization of 3-bromo- and 3-chloropropyne in the presence of the corresponding cuprous halide. These haloallenes were identified by their composition, infrared spectra and low reactivity. Rate constants were determined for their reaction with potassium iodide at 25° and they were found to react at rates comparable with vinyl halides. 3-Bromopropyne reacts slightly faster than allyl bromide and over 50000 times faster than bromopropadiene. 3-Iodopropyne was the principal product from 3-bromopropyne and potassium iodide when the reaction and product isolation took place below 20°, but it isomerized readily to a mixture containing iodopropadiene. The product reported in the literature as 3-iodopropyne is such a mixture, and the reaction of bromopropadiene with potassium iodide is so slow that a mixture of about the same proportions is the only product.

The rearrangement of three-carbon acetylenic systems, I, to allenic systems, II, was first recognized in 1935,[2,3] although it was suggested earlier[4] that II (Y = OH) is the intermediate in the rearrangement of I (X = OH) to the unsaturated ketone III.



$$-\overset{|}{C}=\overset{H}{\overset{|}{C}}-\overset{|}{C}=O \longleftarrow -\underset{X}{\underset{|}{\overset{|}{C}}}-C\equiv C- \longrightarrow -\overset{|}{C}=C=\overset{|}{C}-Y$$

III I II

The rearrangement of *t*-chlorides or alcohols, I (X = Cl or OH) to allenic chlorides, II (Y = Cl) has been accomplished in several cases[2,5–10] by the action of concd. hydrochloric acid in the presence of cuprous chloride and ammonium chloride. No allenic bromides are known with certainty, although the compound prepared from *t*-butyl-*t*-butylethynylphenylcarbinol and phosphorus tribromide probably has such a structure (1-bromo-1,3-di-*t*-butyl-3-phenylpropadiene)[3,11] and similar bromides reported to have the acetylenic structure may also be allenes. With tertiary carbinols such as dimethylethynylcarbinol, hydrobromic acid yielded conjugated dienes (*e.g.*, 3-methyl-1-bromo-1,3-butadiene) by further rearrangement.[12,13] Hydriodic acid gave a mixture of the allenic iodide and the conjugated diene.[12]

In all previous studies of replacement reactions involving the acetylene–allene rearrangement the acetylenic compound, I, has had X attached to a tertiary carbon. It was of interest to obtain a simpler system in which X was primary or secondary and which would be incapable of some of the side reactions observed with the compounds already examined. This paper reports the preparation of the halopropadienes which, together with the previously-known propargyl halides, makes available a unique primary system: $XCH_2C\equiv CH$ and $CH_2=C=CHX$.

Bromopropadiene was prepared from 3-bromopropyne by rearrangement in the presence of cuprous salts. When the starting acetylene was shaken for six days with a catalyst containing cuprous bromide, ammonium bromide, concentrated hydrobromic acid and a little copper bronze, the organic layer gave on distillation a mixture of bromopropadiene and 3-bromopropyne. The ratio of these products sometimes reached 65 to 35, but more frequently the rearrangement proceeded less completely and the bromopropadiene content was between 35 and 60%. The recovery of pure separated isomers was only 40 to 60% and some higher boiling material, as yet unidentified, was obtained. The rearrangement is reversible; bromopropadiene gave a mixture containing up to 35% 3-bromopropyne by long shaking with the same catalyst.

A superior preparative method for the allene consisted of stirring 3-bromopropyne with solid cuprous bromide while it was slowly distilled through a good fractionating column. The allene boils 9° below the acetylene and was obtained in 55–65% yield.

These isomeric bromides show no tendency to isomerize at temperatures up to 110° in the absence of cuprous bromide, which is in marked contrast to the behavior of allylic bromides such as crotyl and methylvinylcarbinyl bromides,[14] but may not be different from that of allyl bromide itself.

Chloropropadiene was not obtained by distillation of 3-chloropropyne from cuprous chloride even when dry hydrogen chloride and ammonium chloride were added. It was obtained in low yield by shaking the acetylene with a mixture of cuprous chloride, ammonium chloride and hydrochloric acid.

The allenes were identified by their composition, reactivity and infrared spectra. Neither bromo- nor chloropropadiene gave a positive test with ammoniacal silver nitrate, ammoniacal cuprous chloride or alkaline mercuric iodide[15] but both produced a slight turbidity with alcoholic silver nitrate. 3-

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(1) (a) This work was carried out under a contract with the Office of Naval Research. (b) To obtain spectra order Document 3838 from American Documentation Institute, c/o Library of Congress, Washington 25, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(2) A. Favorskii and T. A. Favorskaya, *Compt. rend.*, **200**, 839 (1935).

(3) J. H. Ford, C. D. Thompson and C. S. Marvel, THIS JOURNAL, **57**, 2619 (1935).

(4) K. H. Meyer and K. Schuster, *Ber.*, **55**, 819 (1922).

(5) T. A. Favorskaya, *Zhur. Obshchei Khim.*, **9**, 386, 1237 (1939); **12**, 638 (1942); **18**, 52 (1948).

(6) T. A. Favorskaya and A. I. Favorskaya, *ibid.*, **10**, 451 (1940).

(7) T. A. Favorskaya and A. I. Zakharova, *ibid.*, **10**, 446 (1940).

(8) T. O. Nagibina, *ibid.*, **10**, 427 (1940).

(9) G. F. Hennion, J. J. Sheehan and D. E. Maloney, THIS JOURNAL, **72**, 3542 (1950).

(10) G. F. Hennion and D. E. Maloney, *ibid.*, **73**, 4735 (1951).

(11) The hydrolysis of this compound to the starting carbinol does not prove that it has the acetylenic structure, I (X = Br) because allenic halides are now known to rearrange during replacement reactions.

(12) T. A. Favorskaya, *Zhur. Obshchei Khim.*, **10**, 461 (1940).

(13) I. N. Nazarov and Ya. M. Yanbikov, *Bull. acad. sci., U.R.S.S., Classe sci. chim.*, 566 (1941).

(14) S. Winstein and W. G. Young, THIS JOURNAL, **58**, 104 (1936).

(15) J. R. Johnson and W. L. McEwen, *ibid.*, **48**, 469 (1926).

Bromopropyne reacted far more rapidly with diethylamine than did bromopropadiene as shown by the fact that the latter was obtained in a pure state and in good yield by treating a mixture of the isomers with the amine and washing out the amine salts with water.

An attempt to prepare a 2,4-dinitrobenzenesulfenyl chloride of bromopropadiene was unsuccessful.

Table I summarizes the rates of reaction of the haloallenes and propargyl halides with sodium iodide in acetone, and presents a comparison of these with rates for the corresponding allyl and vinyl halides as far as these are known. There is a general similarity between the low reactivity of the vinyl and allenyl halides on the one hand and the high reactivity of the allyl and propargyl compounds on the other. No attempt was made to examine this parallel more closely by determining rates at different temperatures because 3-iodopropyne and iodopropadiene rearrange readily to an equilibrium mixture and the primary products of the reaction of the propargyl and allenyl chlorides and bromides with sodium iodide were difficult or impossible to determine.

TABLE I

RATE CONSTANTS AT 25° FOR THE REACTION OF UNSATURATED HALIDES WITH SODIUM IODIDE OR POTASSIUM IODIDE IN ACETONE

Halide	k(l.m.$^{-1}$ hr.$^{-1}$)^{a}
$HC\equiv CCH_2Cl$	$1.087^{a,b}$
$H_2C{=}C{=}CHCl$	$0.000076^{a,c}$
$HC\equiv CCH_2Br$	612
$H_2C{=}C{=}CHBr$	0.0112
$H_2C{=}CHCH_2Cl$	0.663^{d}
$H_2C{=}CHCH_2Br$	438^{e}
$CH_3CH{=}CHBr$	0.0005^{f}
$H_2C{=}CHBr$	0.014^{f}

[a] Values marked with this superscript were calculated to 25° from the temperature indicated by using the average value of $A = 4000$ given by Conant, Kirner and Hussey, THIS JOURNAL, **47**, 488 (1925), in the equation $\log (k_{t_1}/k_{t_2}) = A(1/T_2 - 1/T_1)$. [b] Hatch and Chiola, *ibid*, **73**, 360 (1950). Calculated from 20°. The results given were multiplied by 2.303 because $\log_{10}$ was used. [c] Calculated from 50° where the value is 0.00081. [d] From ref. (a) corrected by multiplying by 2.303. Other values, suitably corrected, are 0.850, Tamele, Ott, Marple and Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941), and 0.882, Hatch, Gordon and Russ, THIS JOURNAL, **70**, 1093 (1948). [e] Bartlett and Rosen, *ibid.*, **64**, 543 (1942). [f] Juvala, *Ber.*, **63B**, 1989 (1950). Calculated from 15°. A mixture of *cis*- and *trans*-1-bromo-1-propene was used.

Both 3-bromopropyne and bromopropadiene were allowed to react with sodium iodide in acetone on a scale which permitted isolation of products, and the reaction of 3-bromopropyne with sodium iodide in alcohol, the method reported in the literature for the synthesis of 3-iodopropyne[16,17] was also examined. When the products were distilled at 50–70°, approximately the same mixture was obtained from all of these experiments as indicated by refractive index and infrared spectrum. An instantaneous test for acetylenic hydrogen was obtained with each product, and a weak band at 4.7 μ, the characteristic stretching frequency for the terminal acetylenic group, was observed in the infrared spectra. However, a far stronger band was observed at 5.1 μ which is characteristic of allenes. When the preparation from 3-bromopropyne and the distillation of the iodide were carried out entirely at room temperature or below, the product at first showed almost no infrared absorption at 5.1 μ, but this band gradually increased while the spectrum was being measured. The band at 4.7 μ was of no more than medium strength in this sample, but it was stronger than in the preparation which had been at higher temperature. These observations indicate that the primary product of the reaction between 3-bromopropyne and inorganic iodides is 3-iodopropyne, at least in large part, but that this compound rearranges readily to an equilibrium mixture containing large amounts of iodopropadiene. The poor photographs reported[17] in electron diffraction work on supposed 3-iodopropyne must have resulted at least in part from this fact. It is possible that under the conditions of the electron diffraction experiments some rearrangement of the chloride and bromide may also have occurred.

It has recently been pointed out that the infrared spectra of many propargyl alcohols and halides exhibit an unexplained band near 5.85 μ. In the present work this band[18,19] was not observed in the spectrum of 3-chloropropyne and was present in the spectrum of 3-bromopropyne as a very small peak (94% transmission) at 5.7 μ. Otherwise the spectra[19] of the bromide are very similar except that we obtained a broad, incompletely resolved doublet between 12.5 and 13.2 μ (transmission 2%). The spectrum of 3-chloropropyne is somewhat simpler than that of the bromide but quite similar. Both of these acetylenic compounds show the $C\equiv C$ stretching frequency as a sharp band at 4.65 μ and the band characteristic of acetylenic hydrogen at 3.0 μ.

The haloallenes are characterized by the usual sharp allene band at 5.1 μ. There is also a band of equal strength at 5.7 μ which is similar in appearance to that at 5.85 μ reported earlier[19] in the 3-bromopropyne spectrum but absent in our work on this compound. It is unlikely that this 5.85 μ band was caused by the presence of bromopropadiene because the 5.1 μ band should be equally in evidence if that were true. A sample of 3-bromopropyne prepared as usual but purified by simple distillation only (b.p. 36–60° (120 mm.)) gave absorption very like the purest samples at 3.0 and 4.65 μ; it also gave a very weak peak (91% transmission) at 5.7 μ.

The spectrum of the equilibrium mixture of 3-iodopropyne and iodopropadiene shows this new band at 5.85 μ (45% transmission compared with 25% transmission for the 5.15 μ band). In the sample containing the least iodopropadiene these two bands corresponded to 90 and 93% transmission, respectively, which suggests that either an impurity or 3-iodopropyne would have given a small absorption at 5.85 μ even if iodopropadiene were completely absent.

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(16) L. Henry, *Ber.*, **17**, 1132 (1884).

(17) L. Pauling, W. Gordy and J. H. Saylor, THIS JOURNAL, **64**, 1753 (1942).

(18) J. H. Wotiz and F. A. Miller, *ibid.*, **71**, 3441 (1949).

(19) J. H. Wotiz, F. A. Miller and R. J. Palchak, *ibid.*, **72**, 5055 (1950).

Experimental Part

The distilling column used in this work was of the "Trubore" concentric-tube type 9.5 mm. i.d. and 85 cm. long. It was capable of giving 92 theoretical plates when 0.15 ml. of distillate was collected per hour and had a holdup of less than 1 ml.

Propargyl alcohol was obtained from the General Aniline and Film Corp. It was dried over anhydrous potassium carbonate and distilled under reduced pressure in the presence of about 1% of succinic acid[20] through a 3 ft. column packed with glass helices.

3-Bromopropyne was prepared from propargyl alcohol and phosphorus tribromide in the presence of pyridine[21] in 79% crude yield. The crude bromide was fractionated through the concentric-tube column, b.p. 46° at 200 mm., $n^{20}\text{D}$ 1.4929, d^{20}_4 1.571, 55% over-all yield. The boiling point at 750 mm. was 81.8°.

3-Chloropropyne was prepared similarly.[22] If distillation of the reaction mixture was carried on until the distillate corresponded to much beyond a 55% crude yield, a vigorous decomposition of the reaction residue sometimes occurred. The product was dried over anhydrous potassium carbonate and distilled through the concentric-tube column at atmospheric pressure, b.p. 56°, $n^{20}\text{D}$ 1.4344.

Bromopropadiene was prepared by stirring (magnetically) and heating 29 g. of 3-bromopropyne with 2.5 g. of dry cuprous bromide under the concentric-tube column, maintaining the temperature and controlling the take-off so that the head temperature remained between 72.8 and 73.5°. It was possible to keep the head temperature at 72.8° which gave bromopropadiene of better than 98% purity, but this required a distillation lasting several days and more material was lost by polymerization. The temperature range indicated a product of 75 to 85% purity in 84% yield in 24 hours. With this distillation rate the column had 25 to 30 theoretical plates on a test mixture.

Pure bromopropadiene was obtained with no more than 10–15% loss by slowly adding the product of the rearrangement to a 40% aqueous solution of diethylamine. Three to four moles of diethylamine were used for each mole of propargyl bromide remaining in the product, as calculated from the refractive index. The reaction mixture was swirled occasionally during one-half hour, acidified with 15% hydrochloric acid, the layers separated and the bromopropadiene washed thoroughly with water and dried over anhydrous potassium carbonate. Simple distillation under reduced pressure into a receiver cooled in Dry Ice gave pure bromopropadiene, b.p. 72.8° at atmospheric pressure, $n^{20}\text{D}$ 1.5212, d^{20}_4 1.5508; *MR*D obs. 23.37, *MR*D calcd. 22.89.[23]

Anal. Calcd. for C_3H_3Br: C, 30.27; H, 2.54. Found: C, 30.13; H, 2.52.

After shaking 114 g. of 3-bromopropyne with 10 g. of cuprous bromide, 10 g. of ammonium bromide, 15 ml. of concd. hydrobromic acid and 0.2 g. of copper bronze in a glass-stoppered flask for six days, the organic layer, 85 g., was separated and dried over anhydrous potassium carbonate. Careful fractionation at 200 mm. gave 32.5 g. of bromopropadiene (28% yield) and 18.5 g.of 3-bromopropyne. By reusing a catalyst solution much better recovery was realized, but the rearrangement was far slower and even after 19 days the ratio of bromopropadiene to 3-bromopropyne was only 56 to 44. Attempts to recover more of either bromide from the catalyst mixture by dilution, steam distillation or extraction were unsuccessful. Propargyl alcohol was identified by odor in the aqueous solutions from these operations.

After shaking 48 g. of bromoallene (containing 6% 3-bromopropyne) with the same amount of the same catalyst as above for 12 days, 17.6 g. of a mixture containing 32% 3-bromopropyne and 68% bromopropadiene was obtained. This mixture was treated with fresh catalyst with shaking for 17 days more. The final mixture contained 35% 3-bromopropyne. In each case the organic layer after drying was distilled completely without fractionation into a Dry Ice trap, and the mixture analyzed by refractive index determination. Known mixtures of pure bromides disclosed a practically linear relationship between composition and refractive index for these isomers.

Shaking 56 g. of propargyl alcohol with 333 g. of 48% hydrobromic acid, 20 g. of cuprous bromide, 10 g. of ammonium bromide and 0.3 g. of copper bronze for 24 hours gave a dark homogeneous solution. After 50 ml. of water was added the solution was steam distilled and the organic layer that resulted was dried over anhydrous potassium carbonate. This crude product, 116 g., $n^{20}\text{D}$ 1.4970, was fractionated to give 5.5 g. of bromopropadiene and 8 g. of 3-bromopropyne. The major portion of the distillate consisted of higher boiling fractions which have not been identified. Several of them appear to be azeotropic mixtures.

Attempted Thermal Rearrangement.—Twenty-four hour refluxing of 3-bromopropyne in the concentric-tube column at atmospheric pressure gave no drop in head temperature from the boiling point of the acetylene. A 5-g. sample held at 105–110° for 24 hours and distilled completely under reduced pressure was found to have $n^{20}\text{D}$ 1.4934 instead of 1.4929. This corresponds to no more than 2% isomerization to bromopropadiene. Polymerization and mechanical losses allowed only 85% recovery during the experiment. Bromopropadiene was heated in a sealed tube at 75° for a day. No more than 1.5% isomerization occurred and losses were 15–20%.

The reaction of bromopropadiene with 2,4-dinitrobenzenesulfenyl chloride[24] in gl. acetic acid gave yellow crystals when the reaction mixture was poured on ice. These were recrystallized twice from large volumes of acetone. They gave no sharp m.p., but darkened at 180° and slowly decomposed over a wide range above this temperature.

Anal. Calcd. for $C_9H_6BrClN_2O_4S$: C, 30.54; H, 1.71. Calcd. for $C_9H_7ClN_2O_5S$: C, 37.15; H, 2.43. Found: C, 37.90; H, 2.65.

The formula $C_9H_7ClN_2O_5S$ corresponds to a 1:1 derivative in which the bromine has been replaced by hydroxyl. No proof of the structure of this compound was attempted.

Chloropropadiene.—After shaking 37.2 g. (0.5 mole) of 3-chloropropyne with 5 g. of cuprous chloride, 4 g. of ammonium chloride, 4 ml. of concd. hydrochloric acid and 12 ml. of water for five days the organic layer, 31 g., was separated and dried with anhydrous potassium carbonate. Careful fractionation at atmospheric pressure gave 5.5 g. of product (14.5% yield) and 18.4 g. of 3-chloropropyne (49.5% recovery). The remainder was higher boiling material, mostly polymeric. Chloropropadiene has the following constants: b.p. 44°, $n^{20}\text{D}$ 1.4617, d^{20}_4 0.996; *MR*D obsd. 20.56, *MR*D calcd. 19.99.[23]

Anal. Calcd. for C_3H_3Cl: C, 48.35; H, 4.06. Found: C, 48.32; H, 4.21.

A mass spectrogram showed a strong peak at 74 and a peak one-third as strong at 76 representing the Cl^{35} and Cl^{37} isotopes.[25]

Kinetic Measurements.—The reactions of 3-bromopropyne and bromopropadiene with potassium iodide in acetone were followed by the titration method of Andrews[26] and

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[20] J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publ. Corp., New York, N. Y., 1949, p. 106.

[21] A. Kirrmann, *Bull. soc. chim.*, [4] **39**, 698 (1926).

[22] L. F. Hatch and V. Chiola, THIS JOURNAL, **73**, 360 (1951).

[23] Calculated using values of atomic refractions from Landolt-Börnstein, "Physikalisch-Chemische Tabellen," 5th ed., Vol. II, p. 985. The value for the allene bond was taken as 2 double bonds. It is noteworthy that the observed values of the molecular refraction as calculated from refractive indices and densities given in "Tables of Selected Values of Properties of Hydrocarbons," API Project 44, National Bureau of Standards for C_5- and C_6-allenes vary somewhat more than the molecular refractions of olefins. Thus 1,2-pentadiene, 2,3-pentadiene and 3-methyl-1,2-butadiene give values of 25.0, 24 and 24.8 (calcd. 24.36). For 1,2-hexadiene, 2,3-hexadiene, 3-methyl-1,2-pentadiene, 4-methyl-1,2-pentadiene and 2-methyl-2,3-pentadiene the observed values are 29.5, 29.0, 29.4, 29.6 and 29.6 (calcd. 28.97). If one omits the uncertain value for 2,3-pentadiene, the average value for the allene bond appears to be 0.44 more than for two isolated double bonds (3.466) or about 3.9. This gives a *MR*D calcd. of 23.32 for bromopropadiene and 20.42 for chloropropadiene in good agreement with observed values. The *MR*D obsd. or *MR*α obsd. for 3-methyl-1-chloro-1,2-butadiene[9,5] and similar chloroallenes[6,7] shows exaltations of 0.4 to 0.9 above the calculated even when the new value is used for the allene bond.

[24] N. Kharasch and C. M. Buess, THIS JOURNAL, **71**, 2724 (1949).

[25] A modified Westinghouse Model LV mass spectrometer was used. We wish to thank Mr. T. C. Hall, Jr., for this spectrogram.

[26] L. W. Andrews, THIS JOURNAL, **25**, 756 (1903).

Juvala.[27] With the first of these the concentration of organic bromide was 0.016 *M* and of potassium iodide 0.0077 *M*; with the second the concentrations were 0.2 and 0.035 respectively. Both reactions were carried out in a thermostat at 24.90 ± 0.05°. The data were plotted according to the form of the equation for a bimolecular reaction

$$kt = \frac{2.303}{(M - 1)b} \log_{10} \frac{M - Z}{M(1 - Z)}$$

where M is the initial molecular proportion of organic bromide to inorganic iodide, b is the initial concentration of iodide, and Z is the fraction of iodide which has reacted in time t. The values of the rate constants were obtained from linear plots of this equation. They were not reproducible to better than 10%, but the uncertainty in the product made it seem pointless to attempt refinement of the method. Earlier runs with bromopropadiene employed material containing a few per cent. of 3-bromopropyne and with these it was necessary to calculate the constant starting from 15 to 20% reaction as zero time.

The reaction with chloropropadiene was carried out at 49.7 ± 0.1° and concentrations of 0.2 *M* for organic chloride and 0.04 *M* for potassium iodide. The value is less reliable because the reaction has proceeded only to the extent of 43% in five months.

3-Bromopropyne and Sodium Iodide.—From half-mole quantities of sodium iodide and 3-bromopropyne in anhydrous ethanol was obtained on standing for three days approximately the theoretical amount of sodium bromide. The filtrate was poured into ice-water and the organic layer washed once with water and dried over calcium chloride. The yield of C_3H_3I, b.p. 52–52.6° (100 mm.), $n^{20}_{\rm D}$ 1.6077 to 1.6112 (several fractions), was only 31% of theoretical. A small amount of forerun and 16% of high boiling material were obtained, but the remaining material was lost in the wash water. The C_3H_3I fraction had a broad boiling point at atmospheric pressure (109–115° with slight decomposition).

The experiment was repeated with one-fourth mole amounts using acetone as a solvent and maintaining a temperature below 20° at all times. The yield of C_3H_3I, b.p. 13.0–13.2° (10 mm.), was 9.6 g. (23%), $n^{20}_{\rm D}$ 1.5889, d^{20}_4 2.0430, *MR* obsd. 27.38, $MR_{\rm D}$ calcd. for $HC{=}CCH_2I$ 26.85, $MR_{\rm D}$ calcd. for $H_2C{=}C{=}CHI$ 28.35 using 3.9 for the allene bond.[23]

Anal. Calcd. for C_3H_3I: C, 21.70; H, 1.82. Found: C, 22.36; H, 1.99.

When a sample of this compound was left at 40.0° the refractive index changed regularly, reaching a final value of 1.6210 after 10 days.

Bromopropadiene and sodium iodide (0.15 mole of each) were refluxed for 20 hours in 150 ml. of anhydrous acetone. The precipitate of sodium bromide was removed by filtration, two-thirds of the acetone was distilled through a column packed with helices and the residue was thrown into ice-water. The organic layer was washed with ice-water, dried over calcium chloride and fractionated at 195 mm. A small amount of bromopropadiene was recovered and 8.5 g. of material, b.p. 68.9–69.5°, $n^{20}_{\rm D}$ 1.5858–1.6032, was obtained (34% calculated as C_3H_3I). All fractions gave slight tests with 2,4-dinitrophenylhydrazine. The best fraction (b.p. 69.5°, $n^{20}_{\rm D}$ 1.6032, 4.3 g.) was washed thoroughly with sodium bisulfite solution and with water, dried over potassium carbonate and distilled to give material with $n^{20}_{\rm D}$ 1.6118. The remaining fractions were combined and treated similarly, giving a $n^{20}_{\rm D}$ 1.5989.

Infrared spectra were obtained with a Beckman IR 2½ spectrophotometer using rock salt cells, liquid samples and a cell thickness of about 0.03 mm.

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[27] A. Juvala, *Ber.*, **63B**, 1995 (1930).

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ARKANSAS]

The Relative Configurations of the 2- and 3-Hydroxycyclohexanecarboxylic Acids and the Related Methylcyclohexanols; the Stereochemistry of the Catalytic Hydrogenation of Substituted Cyclohexanones

BY SAMUEL SIEGEL

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The configurations of the 2- and 3-hydroxycyclohexanecarboxylic acids have been related to the corresponding methylcyclohexanols by a series of chemical transformations which do not affect a center of assymmetry .Although the configurations of the 1,2-isomers are consistent with present designations, the configurations of the 3-methylcyclohexanols must be reversed. These results are consistent with current concepts of the stereochemistry of disubstituted cyclohexanes. An hypothesis is advanced to account for the predominance of the unstable isomer, and its configuration, in the catalytic hydrogenation of substituted cyclohexanones.

The assignment of configurations to isomeric disubstituted cyclohexanes has been unequivocal in the relatively few instances in which criteria of symmetry and/or the formation of cyclic compounds could be established.[1] Frequently the configurations are assigned by use of some empirical rule which is based upon differences in physical constants for geometrical isomers such as that of von Auwers.[2] The reassignment of the configurations of the 1,3-dimethylcyclohexanes by Beckett, Pitzer and Spitzer[3] as well as their able theoretical discussion of the energetics of disubstituted cyclohexanes excited our interest in the problem of obtaining chemical evidence for the configurational relationships among unsymmetrically disubstituted cyclohexanes. In particular, the configurations of 1,3-disubstituted cyclohexanes were suspect. In this paper chemical evidence for the relative configurations of the 2- and 3-hydroxycyclohexanecarboxylic acids and the corresponding 2- and 3-methylcyclohexanols is presented. The configuration of *trans*-4-hydroxycyclohexanecarboxylic acid has been related to *trans*-4-methylcyclohexanol by a method similar to the one used in this study.[4]

The configurations of the 2-hydroxycyclohexanecarboxylic acids are currently based upon their mode of formation and the physical properties of their derivatives,[5] and the 3-hydroxycyclohexanecarboxylic acids are assigned configurations upon

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[1] H. Gilman, "Organic Chemistry," Second Edition, Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 478–482; Chapter written by C. S. Marvel.

[2] K. von Auwers, *Ann.*, **420**, 91 (1920).

[3] C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947).

[4] L. N. Owens and P. A. Robins, *J. Chem. Soc.*, 326 (1949).

[5] J. Pascual, J. Sistare and A. Regas, *ibid.*, 1943 (1949).