mmoles) of 21.2% sodium hydroxide and 12.63 ml. of 6 *N* sodium bromide-82 in a 100-ml. flask equipped with stirrer, downward condenser, and receiver. (The large molar excess of base is to correct for the yield of *gem*-dihalide.) The reaction flask was gently heated until the *gem*-dihalide co-distilled with water. The work-up was the same except the oil was washed ten times with distilled water and the sulfuric acid wash was omitted. For counting, 0.0810 g. (0.375 mmole) was used *vs.* 0.4020 g. (1.86 mmoles) of original *gem*-dihalide and products were essentially identical. The average value of the *gem*-dihalide recovered was 335 c.p.m./mmole compared to 340 c.p.m./mmole for the starting *gem*-dihalide. The results indicate no exchange in the limits of experimental error. (Note: Nonradioactive *gem*-dihalide would have been employed, preferably, except that none was available at the time.)

Alkaline Stability of 1,1-Dibromo-2-methylpropane.—*gem*-Dihalide (66.7 mg., 0.209 mmole) was weighed into a 50-ml. flask equipped with stirrer and downward condenser and covered with 17.9 g. (74.5 mmoles) of 16.7% sodium hydroxide. The flask was slowly and carefully heated until the *gem*-dihalide had completely co-distilled with water. The hydrolysate was drained and rinsed into a 250-ml. beaker and bromide determined gravimetrically in the usual manner. The silver bromide weighed 1.9 mg., equivalent to 1.67% hydrolysis to aldehyde. A comparative experiment with 1,1-dibromopropane gave 0.44% hydrolysis, calculated to the aldehyde.

Rearrangement of α-Bromobutyramide and α-Bromoisovalerylamide. Standard Hot Procedure.—The standard hot procedure follows that described by Stevens, *et al.*, and designated by them as Procedure B.[2] This is essentially the procedure described above for the radiobromine studies except that the earlier work prepared the N-bromoamide *in situ*. This method was used for exploratory studies with α-bromoisovalerylamide. Two runs were made with α-bromobutyramide, repeating earlier work,[2] to acquire the comparative data reported in Table I.

Bromine balance data were obtained for two runs using Procedure B. An aliquot of the alkaline liquors was neutralized with nitric acid, filtered, a slight excess of nitric acid was added, and the solution boiled to destroy cyanate. Bromide ion, 83 mmoles, was found in the alkaline liquors out of a total of 85 mmoles, including the α-bromo atom. The *gem*-dihalide accounted for *ca.* 0.8 mmole leaving 1.2 mmoles unaccounted for. In a repeat run, 146.1 mmoles out of a possible 150.0 mmoles was found, 145.8 mmoles in the alkaline mother liquors.

α-Bromoisovalerylamide. Hot "Drop-In" Method.—In a typical run, 8.8 g. of bromine was added to 66 g. of 10% sodium hydroxide at 3–8° followed by 9.0 g. of α-bromoisovalerylamide. The cold solution was added dropwise to a boiling solution of 100 g. of 10% sodium hydroxide which was distilling, prior to addition, through a downward condenser. The addition was complete in 18 min. with heating continued for 3 more minutes; 68 g. of water plus oil was collected. The separated oil weighed 1.2 g., $n^{25}D$ 1.4425. Infrared analysis and subsequent work-up of the distillate indicated that the product was predominantly isobutyraldehyde, 26% isolated, and high-boiling polymers. (No *gem*-dihalide was found in a combined work-up and fractional distillation of 2.55 g. of oil from 0.23 mole of α-bromoamide.) Aliquots of the filtered mother liquor were analyzed for cyanate ion[5] and α-hydroxyisovaleric acid by usual means. Results are reported in Table I.

Rearrangement of α-Bromoisovalerylamide. Cold Studies.—Bromine (16 g., 0.1 mole) was added at −5° to 120 g. (0.3 mole) of 10% sodium hydroxide, followed by 16.2 g. (0.09 mole) of α-bromoisovalerylamide. The batch was split and one portion (0.044 mole) was placed in the refrigerator for 21 days. After neutralization, approximately 7.0 g., 60%, of crude N-bromoamide was isolated. No *gem*-dihalide and no cyanate ion was found. The second portion was held at room temperature for 4 days and filtered to recover, after washing with cold water, 5.1 g., 61%, of pure α-bromoisovalerylamide, m.p. 129–130.5°. No *gem*-dihalide and no cyanate were found. A second experiment gave similar results.

Vapor Chromatography.—The column was prepared with Dow 702 silicone, 20% on 42–60 mesh firebrick. Studies with 1,1-dibromo-2-methyl-propane and the comparison with 1,2-dibromo-2-methylpropane and 2,3-dibromobutane all were carried out under the conditions: helium pressure 7.8 p.s.i., preheater temperature 150°, and column temperature 135–136°. Symmetrical peaks and excellent separations were achieved. The pentane solvent showed six components (peaks) and two of these were the apparent contaminants in the 1,1-dibromo-2-methylpropane isolated from the rearrangement experiments.

Cyanate Ion.—Aliquots of the alkaline mother liquor were filtered, if necessary, neutralized with 25–50% acetic acid to methyl red end point, and filtered again, if necessary. Sodium acetate, 2 g., was added, followed by 1 g. of semicarbazide hydrochloride.[3] The solution was shaken vigorously and placed in the refrigerator overnight. The filtered hydrazodicarboxamide was washed with cold water and dried at 105° for 2 hr. The melting points were within 3 to 6 degrees of the pure compound, 249° (252°).[5] Cyanate recovery was measured at 90–95%, but further study and refinement of the method is desirable.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY, DETROIT 2, MICH.]

gem-Dihalides from α-Haloamides. III. Rearrangement of Optically Active α-Chlorohydrocinnamamides[1]

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RECEIVED JANUARY 25, 1963

Additional evidence for the stereospecific nature of the conversion of α-haloamides to *gem*-dihalides was gained by the isolation of an optically active *gem*-dihalide from an optically active α-haloamide. D-α-Chlorohydrocinnamamide, $[\alpha]^{25}D$ +11.0°, was dissolved in alkaline sodium hypobromite and steam distilled to yield D-*gem*-dihalide, $\alpha^{25}D$ −0.065°, determined as a neat liquid with DL-*gem*-dihalide as reference. Similarly, L-α-chlorohydrocinnamamide, $[\alpha]^{25}D$ −10.7°, gave L-*gem*-dihalide, $\alpha^{25}D$ +0.066°, the reading of which was essentially doubled in a 2-dm. tube. A maximum racemization of 40% due to hydrogen exchange at the α-carbon atom was established by rearrangement of DL-α-chlorohydrocinnamamide in the presence of heavy water and determining the deuterium content of the isolated *gem*-dihalide. The signs of rotation of the *gem*-dihalides agree with prediction and the values are of the expected order of magnitude.

Work in this Laboratory has continued to provide additional insight into the conversion of α-haloamides to *gem*-dihalides[2,3] in the presence of alkaline hypobromite. The previous paper[2] in this series reviewed the progress of this program and provided additional evidence that the reaction proceeds almost exclusively by an intramolecular mechanism. The mechanism[2] predicts retention of configuration and additional evidence for the stereospecific character of the rearrangement forms the subject matter of this paper.

The objective of the present program was to utilize the optical center at the α-carbon atom of D- and L-α-chlorohydrocinnamamides and subject the enantiomers to the rearrangement reaction. Isolation of the resulting *gem*-dihalides and measurement of their optical rotation should provide evidence relative to the stereospecificity of the reaction. The preparation of the desired starting amides followed generally the methods of Greenstein and co-workers in the alanine series.[4]

D-, L-, and DL-phenylalanine were dissolved in hydrochloric acid at 5° and treated with sodium nitrite to form the corresponding α-chloro-hydrocinnamic acids. The latter were treated with excess thionyl chloride at

(1) This work was supported by the National Science Foundation, Research Grant G14630.

(2) Paper II of this series: C. L. Stevens, M. E. Munk, A. B. Ash, and R. D. Elliott, *J. Am. Chem. Soc.*, **85**, 3390 (1963).

(3) C. L. Stevens, T. K. Mukherjee, and V. J. Traynelis, *ibid.*, **78**, 2264 (1956).

(4) S. C. J. Fu, S. M. Birnbaum, and J. P. Greenstein, *ibid.*, **76**, 6054 (1954).

room temperature to form the corresponding acid chlorides. The acid chlorides were dissolved in benzene at 5° and treated with ammonia to form the corresponding α-chlorohydrocinnamamides. Each step in this sequence is presumed to be stereospecific and proceed with retention of configuration.[4,5] The properties of the α-chlorohydrocinnamamides used for the conversion to *gem*-dihalides are listed in Table I.

TABLE I
PROPERTIES OF α-CHLOROHYDROCINNAMAMIDES

α-Chlorohydrocinnamamides	M.p., °C.	$[\alpha]^{25}D$
DL-	90.5–91.5	.....
L-	103.4–104.5	−10.7°[a]
D-	103.4–104.5	+11.0°[b]

[a] *c* 1.79 in ethanol; highest value observed was −12.6°, *c* 1.86 in ethanol, m.p. 105°. [b] *c* 1.86 in ethanol.

Crystalline N-bromo-α-chlorohydrocinnamamides in the DL- and L-forms were obtained, but the poor yields and relative instability of the compounds led to the adoption of the simpler procedure of preparing these N-bromo derivatives *in situ*. The isomeric α-chlorohydrocinnamamides were dissolved in alkaline sodium hypobromite and the solution was then subjected to a 3-min. steam distillation. The *gem*-dihalides were then isolated and purified by two successive fractional distillations through a 30 cm. by 5 mm. unpacked column.

Vapor chromatographic analysis of the thus-purified DL-, L-, and D-1-bromo-1-chloro-2-phenylethanes revealed that two impurities persisted to essentially the same concentration in all three products. The impurities were identified as β-bromo- and β-chlorostyrene by direct comparison with authentic samples. The impurities were found to be present to the extent of *ca.* 2.4% and *ca.* 0.3%, respectively, by vapor chromatography. The infrared spectra of the three isomeric *gem*-dihalides were identical.

The optical rotations of the *gem*-dihalide were performed neat at room temperature, *ca.* 25°, using the DL-*gem*-dihalide as a reference blank. Measurements were made by two of us (J. Kovacs and Helmut Dittmer), as described in the Experimental part. For the D-*gem*-dihalide, there was obtained $\alpha^{25}D$ −0.061 ± 0.010° (J. K.) and −0.068 ± 0.015° (H. D.). For the L-isomer, there was obtained $\alpha^{25}D$ +0.077 ± 0.018° (J. K.) and +0.063° ± 0.014° (H. D.). These values for the L-isomer were essentially doubled in the 2-dm. tube as follows: $\alpha^{25}D$ +0.126 ± 0.015° (J. K.) and +0.123 ± 0.014° (H. D.). If these two average values for the D-isomer and the four average values for the L-isomer are again averaged, the data may be summarized as follows, the specific rotation being based on the measured density, d^{25}_4 1.472.

1-Bromo-1-chlorophenylethane	$\alpha^{25}D$	$[\alpha]^{25}D$
D-Isomer	−0.065°	−0.044°
L-Isomer	+0.066°	+0.045°

The maximum extent of racemization by α-hydrogen exchange was established by repeating the rearrangement with DL-α-chlorohydrocinnamamide in the same manner as before but utilizing deuterium oxide in place of water for the preparation of the sodium hypobromite solution and for the steam distillation step. The isolated *gem*-dihalide, purified in the same manner, was found to contain 5.0 excess atom per cent deuterium, indicating a maximum racemization of 40% due to hydrogen exchange at the active center.

(5) W. Klyne, "Progress in Stereochemistry," Vol. I, Butterworths Scientific Publications, London, 1954, pp. 194–195. Deamination of the amino acids proceeds with retention of configuration due to the participation of the carboxylate ion. Other steps in the sequence do not affect the optical center. The conclusion of this paper that the rearrangement of th α-chlorohydrocinnamamides to *gem*-dihalides is stereospecific is not dependent on the assignment of configuration to the amides, however.

Discussion

Although the observed rotations for the isomeric 1-bromo-1-chloro-2-phenylethanes are small in magnitude, the required accuracy and precision are well within the capability of the instrument and the observer. The difference between the average rotational values for the two enantiomers of 0.131° (−0.065 to +0.066°), and the essential doubling of the reading for the L-*gem*-dihalide in the 2-dm. tube *vs.* the 1-dm. tube, lend no doubt as to the validity of the data. The impurities, represented by the β-halostyrenes in a concentration of *ca.* 2.7% are, of course, optically inactive. Measurements of less pure fractions of the *gem*-dihalides gave only minor variations in the readings and impurities having large specific rotations were considered to be absent. Further, it is important to note that the observed value, $[\alpha]^{25}D$ +0.045°, for the L-1-bromo-1-chloro-2-phenylethane is in agreement with the value of +0.13° predicted by Brewster[6] with respect to sign and in relatively good agreement with respect to magnitude. The *gem*-dihalides cannot be optically pure since deuterium exchange established a maximum racemization of 40% due to enolization of the α-hydrogen, and some racemate is doubtless present in the starting α-chlorohydrocinnamamides.[7]

As discussed in the opening paragraph, our previously reported work with radiobromine had demonstrated that, in the case of two aliphatic N-bromo-α-haloamides, the rearrangement reaction occurs almost exclusively by an intramolecular process, leading to the thesis that the reaction occurs by a simple four-center process.[2] The present work is in agreement with this thesis and strongly supports the contention that the rearrangement is stereospecific with retention of configuration as demanded by the geometry of the transition state. Accordingly, the results are best represented by a concerted four-center process with a high degree of stereospecificity. Whether the driving force for the reaction is a nucleophilic attack by internal bromine on the α-carbon atom or by the incipient formation of cyanate ion, *i.e.*, whether the reaction is initiated by bond-making or breaking, will have to be settled by an alternate approach.

Experimental

DL-α-Chlorohydrocinnamic Acid.[8]—DL-Phenylalanine, 33.0 g., was suspended in 400 ml. of concentrated hydrochloric acid at 0° and 22 g. of sodium nitrite was added with stirring over a 3-hr. period. The reaction mixture was allowed to stand overnight, extracted with chloroform, and the chloroform was removed. Distillation of the viscous oil gave 29.4 g. (79%) of the α-chloroacid, b.p. 132–134° at 1.5 mm.,[8] $n^{25}D$ 1.5380.

DL-α-Chlorohydrocinnamamide.—The α-chloroacid, 18.4 g., was dissolved in chloroform and added gradually to 23.8 g. of refluxing thionyl chloride dissolved in chloroform. After 4 hr., the chloroform and excess thionyl chloride were removed and distillation of the resulting yellow oil gave 18.0 g. (89%) of the acid chloride, b.p. 74–75° at 1.4 mm., $n^{25}D$ 1.5365. The acid chloride, 4.1 g., was dissolved in 100 ml. of dry benzene and dry ammonia gas was passed over the surface of the stirred solution at 5 to 10°. The reaction mixture was warmed to 50–60°, filtered while hot, and the benzene was removed. Recrystallization of the yellow solid from ethanol–water gave 3.0 g. (82%) of the amide,

(6) J. H. Brewster, private communication. See J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5475 (1959). Dr. Brewster's prediction was suitably qualified for uncertainties in polarizability and steric factors.

(7) The optical purity of the isomeric α-chlorohydrocinnamamides is estimated at 80–90% based on the rotation of a sharp-melting purified sample of the L-isomer (see Table I) and a mixture m.p. study (see Experimental) of the L- and DL-amides.

(8) R. Gaudry, *Laval Med.*, **9**, 412 (1944); *Chem. Abstr.*, **38**, 4928 (1944).

white needles, m.p. 89–90°; recrystallization from cyclohexane gave colorless plates, m.p. 90–91°.

DL-**N-Bromo-α-chlorohydrocinnamamide.**—DL-α-Chlorohydrocinnamamide, 6.96 g., was dissolved with vigorous stirring in a solution of 2.03 g. of bromine in 23.3 g. of 20% sodium hydroxide at 0°. The solution was cooled to −20° and 6.4 ml. of glacial acetic acid was added. The precipitated oil was extracted with cold chloroform, dried over sodium sulfate, filtered, and concentrated. Petroleum ether was added to turbidity, the solution cooled to −30° and the resulting colorless crystals collected. The product weighed 4.29 g. (43%), m.p. 93–95°, increased by recrystallization to 95–96°. The active halogen content was 98.7% by thiosulfate titration. In a variation of this procedure, the separated oil, after addition of acetic acid, was held at −20° until it solidified. The resulting crystalline solid was filtered, washed with water, dissolved in chloroform, and concentrated to a small volume. Crystallization was induced by the addition of petroleum ether, yielding prisms, m.p. 103°.

Anal. Calcd. for $C_9H_9BrClNO$: C, 41.17; H, 3.45; Br, 30.44. Found: C, 41.56; H, 3.83; Br, 30.10.

DL-**1-Bromo-1-chloro-2-phenylethane. A.**—Freshly prepared DL-N-bromoamide, 2.0 g., was dissolved in 8 ml. of 1 *N* sodium hydroxide and this solution was added over a 3-min. period to a distilling solution of 15 ml. of 4 *N* sodium hydroxide. The crude *gem*-dihalide was isolated by extraction with chloroform and weighed about 0.2 g. (12%).

B.—Owing to difficulty in isolating the N-bromoamide in pure form, the preferred procedure used the α-chloroamide as starting material with the N-bromoamide prepared *in situ*. In a typical experiment bromine, 1.7 ml., 10% excess, was dissolved at 0° in a solution of 9.6 g. of sodium hydroxide in 60 ml. of water. Then 5.6 g. of DL-α-chlorohydrocinnamamide was dissolved and steam was passed vigorously through the solution for 3 min. The *gem*-dihalide was collected in a cooled receiver, extracted with ether, dried over sodium sulfate, and the ether evaporated to yield 2.0 g. (30%) of crude oil. Four grams of crude oil were then distilled through an unpacked 30 cm. by 5 mm. column and 3.0 g. of product boiling at 86–87° (3.5 mm.) was collected. This fraction was redistilled and a center fraction taken at the same boiling point. The *gem*-dihalide was shown to be 97% pure by vapor chromatographic analysis (see below) and this material was that employed as reference standard for the optical rotation studies.

An analytical sample was obtained by washing a pentane solution of the *gem*-dihalide with concentrated sulfuric acid in the cold and evaporative distillation at 3 mm. pressure, $n^{25}D$ 1.5610, d^{25}_4 1.472.

Anal. Calcd. for C_8H_8ClBr: C, 42.40; H, 3.67. Found: C, 42.55; H, 3.60.

C.—The deuterium exchange experiment was performed in essentially the same manner except the amide was dissolved at −20°. To a solution of sodium hypobromite, prepared from 8 g. of sodium hydroxide (0.2 mole) in 40 ml. of deuterium oxide and 1.5 ml. of bromine (0.0275 mole) at 0°, 4.6 g. of DL-α-chlorohydrocinnamamide (0.025 mole) was added at −20°. When the amide was dissolved, the reaction mixture was steam distilled with deuterium oxide. The *gem*-dihalide was collected under ice-cooled deuterium oxide, extracted with ether, the ether solution dried over sodium sulfate, and the ether removed. Two fractional distillations, as described above, gave 450 mg. of product boiling at 82° (2 mm.), $n^{25}D$ 1.5638. Vapor chromatography indicated a purity comparable to the other optical isomers, *i.e.*, *ca.* 97.1%. Infrared spectra were superimposable and no C–D bond absorption was apparent. Deuterium analysis showed 5.0 excess atom per cent deuterium, indicating 40% exchange at one atom.

L-α-**Chlorohydrocinnamamide** was prepared from L-phenylalanine. Experimental techniques differed only in that the α-chloroacid intermediate was not distilled and the conversion of the latter in crude form to the acid chloride was performed in excess thionyl chloride without other solvent and without heating. The conversion of the acid chloride to the amide was the same as for the DL-compound. The crude yield, based on L-phenylalanine, was 24%. After one recrystallization from cyclohexane, the yield was 21%, m.p. 103.5–104.5°, $[\alpha]^{25}D$ −10.7° (*c* 1.79 in ethanol); this material was used for conversion of *gem*-dihalide for the optical rotation studies. Two additional recrystallizations gave an analytical sample, m.p. 105°, $[\alpha]^{25}D$ −12.6° (*c* 1.86 in ethanol).

Anal. Calcd. for $C_9H_{10}ClNO$: C, 58.84; H, 5.49. Found: C, 58.59; H, 5.62.

A mixture melting point study with the DL-α-chloroamide, m.p. 90–91°, gave for 100%, 66%, 50%, and 33% L-compound, melting points of 104.0°–105.0°, 91.0–98.5°, 91.5–93.5°, and 90.5–91.5°, respectively.

L-**N-Bromo-α-chlorohydrocinnamamide.**—Although the yield was poor, a small amount of the L-N-bromoamide sufficient to obtain optical rotations was isolated. In this case, the solid, precipitated from an alkaline hypobromite solution of 1.84 g. of L-α-chlorohydrocinnamide, was washed with water and carbon tetrachloride. The product, 1.5 g., was recrystallized with difficulty from chloroform–petroleum ether to yield 90 mg. as prisms, m.p. 80–81°, $[\alpha]^{25}D$ +56° (*c* 1.76 in 10% sodium hydroxide), the latter solution becoming turbid after 1 hr.

Anal. Calcd. for $C_9H_9BrClNO$: C, 41.17; H, 3.45; Br, 30.44. Found: C, 41.41; H, 3.57; Br, 30.05.

D-α-**Chlorohydrocinnamamide** was prepared from D-phenylalanine in the same manner as for the L-isomer in an over-all yield of 23% crude and 14% after one recrystallization from cyclohexane. The m.p. was 103.4–104.5°, $[\alpha]^{25}D$ +11.0° (*c* 1.86 in ethanol); this material was used for conversion to the *gem*-dihalide employed for the optical rotation studies.

Anal. Calcd. for $C_9H_{10}ClNO$: C, 58.84; H, 5.49. Found: C, 58.82; H, 5.56.

D- **and** L-**1-Bromo-1-chloro-2-phenylethane.**—Both *gem*-dihalides were prepared by the same procedure (B) as that described for the DL- compound. The D- and L-α-chloroamides indicated above were dissolved in alkaline hypobromite to form the N-bromoamide *in situ* and immediately vigorously steam distilled for a 3-min. period. After work-up, crude *gem*-dihalide in *ca.* 30% yield was obtained and twice fractionated to yield products of 97% purity by vapor chromatography (see below) for the optical rotation studies.

Optical Rotations of the 1-Bromo-1-chloro-2-phenylethanes.—All readings were performed neat at *ca.* 25° in 1- and 2-dm. tubes using the DL-*gem*-dihalide as a reference blank. Ten independent readings were made in the 1-dm. tube by each of two observers, J. K. and H. D., except that 20 readings each were made for the L-isomer. The L-isomer was also studied in the 2-dm. tube, ten readings being made by each of two independent observers. Measurements of observed rotations in the 1-dm. tube by J. K. gave 0.321 ± 0.002° for the D-isomer *vs.* 0.382 ± 0.008° for the blank and H. D. obtained 0.312 ± 0.006° for the D-isomer *vs.* 0.380 ± 0.009° for the blank. Similarly, measurements by J. K. gave 0.459 ± 0.010° for the L-isomer *vs.* 0.382 ± 0.008° for the blank and H. D. found 0.443 ± 0.005° *vs.* 0.380 ± 0.009° for the blank. In the 2-dm. tube, J. K. found 0.509 ± 0.007° for the L-isomer *vs.* 0.383 ± 0.008° for the blank and H. D. obtained 0.506 ± 0.008° for the L-isomer and 0.383 ± 0.006° for the blank. Using the 2-dm. readings as an example, J. K. obtained a net reading of 0.126 ± 0.015° for L-isomer and H. D. obtained 0.123 ± 0.014° for the L-isomer; correcting these values for tube length, J. K. obtained $\alpha^{25}D$ 0.063 ± 0.015° and H. D. obtained 0.062 ± 0.014° for the L-isomer.

Vapor Chromatography Studies.—Studies were performed using a column prepared with Dow 702 silicone, 20% on 42–60 mesh firebrick and operated at 160° at 10–11 lb. helium pressure. The three twice-distilled *gem*-dihalides, DL-, L-, and D- were found to contain two minor impurities in substantially the same amounts, *i.e.*, *ca.* 2.4% β-bromostyrene and *ca.* 0.3% β-chlorostyrene. Identification was made by comparison with authentic samples, substantiated by isolation of fractions enriched in these compounds obtained from the successive fractional distillation of crude DL-*gem*-dihalide. (Attempts to isolate the impurities by vapor chromatography were only partially successful.) β-Phenylacetaldehyde was present in the crude *gem*-dihalide, but was removed by the fractional distillation process.