solvent factor in such cases is not trivial; it may be comparable or even greater than other factors contributing to an observed effect. In neglecting this factor, the error would be largest, of course, when gas phase equilibrium data were used for isomers reacting in polar solvents.

Acknowledgment.—We wish to thank Dr. W. M. Schubert for some helpful criticism, Dr. S. E. Wood for his thoughts on non-bonded atom interactions and the Research Corporation for financial support.

CHICAGO 16, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

Isomers for Electrophilic Studies. Resolution of 2-Bromomercuributane, Assignment of Configuration and Cleavage of the Enantiomorphs by Bromine[1-13]

BY FREDERICK R. JENSEN, LORIS D. WHIPPLE, DONALD K. WEDEGAERTNER AND JOHN A. LANDGREBE

RECEIVED JULY 21, 1959

An anion exchange method for resolving organometallic salts is suggested, and (−)-2-bromomercuributane, $[\alpha]^{22}\mathrm{D}$ 25.8° (c 5, ethanol), has been resolved using the method. (−)-2-Bromomercuributane is cleaved by bromine to yield either (±)-2-bromobutane or L-(−)-2-bromobutane, depending upon reaction conditions. Since the cleavage under these conditions is known to proceed with retention of configuration, the stereochemical assignment is L-(−)-2-bromomercuributane. From the above rotation for *sec*-butylmercuric bromide and assuming the bromine cleavage in γ-collidine–pyridine (−65°) is completely stereospecific, the rotation of L-2-bromobutane is calculated to be $[\alpha]^{25}\mathrm{D}$ −33.1° (neat).

The absence of suitable stereoisomers has delayed the study of electrophilic aliphatic substitution. In order to obtain suitable isomers for such a study, and to investigate certain aspects of the chemistry of organomercury compounds, the resolution of simple organomercury compounds has been investigated. Since the bromine cleavage of cycloalkylmercuric bromides is known to proceed with retention of configuration,[4] the configurations of the resolved organomercury compounds may be conveniently related to the configurations of the corresponding alkyl bromides.[5,5a] Without knowledge of the stereochemistry of one reaction of organomercurials, only the relative stereochemistry of the various reactions of organomercurials could be determined.

Earlier isolation of stable diastereomeric and geometric organomercurials[6-17] suggested that it should be possible to resolve organomercury compounds containing only one asymmetric center, with the mercury atom attached to the asymmetric carbon atom.

The procedure reported here for the resolution of *sec*-butylmercuric salts involves anion exchange for an optically active anion. 2-Bromomercuributane was selected as the starting organomercury compound since it is conveniently obtained from 2-bromobutane[18] by way of the Grignard reagent and mercuric bromide,[19] and because the configurational relationships of many members of the secondary butyl system have been established.[20] Cohen and Wright reported that an optically active *sec*-butylmercury compound was obtained having a very low rotation from the reaction of *sec*-butylmagnesium chloride with mercuric chloride in optically active 2,3-dimethoxybutane as solvent.[21]

Resolution of *sec*-Butylmercuric Halides.[3,22]—The resolutions were accomplished by converting

---

(1) Electrophilic Aliphatic Substitution V, Organomercurials III.

(2) Acknowledgment is made to the Research Corporation for partial support of this research, and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(3) A preliminary account of these results has been reported; F. R. Jensen, L. D. Whipple, D. K. Wedegaertner and J. A. Landgrebe, THIS JOURNAL, **81**, 1262 (1959).

(4) F. R. Jensen and L. H. Gale, *ibid.*, **81**, 1261 (1959); F. R. Jensen and L. H. Gale, *ibid.*, **82**, 148 (1960).

(5) Nucleophilic substitution reactions which have the same stereochemistry with both isomers in cyclohexyl systems also have the same stereochemistry in open chain systems. This extrapolation requires the assumption that such extrapolations are also valid for electrophilic reactions. The same assignments of configurations for the *sec*-butylmercury compounds have been obtained by acid cleavage reactions. The cleavages by certain deuterioacids of *trans,trans*- and *cis,cis*-di-4-methylcyclohexylmercury occur, depending on reaction conditions, with loss of configuration or stereospecifically with retention of configuration. Similar results are obtained with (−),(−)-di-*sec*-butylmercury. With deuterium chloride in dioxane, (−),(−)-di-*sec*-butylmercury gives L-(+)-butane-2-*d*. Extrapolation of the results from the 4-methylcyclohexyl system indicates that the (−)-*sec*-butylmercury compounds are of the L-series; unpublished results with L. H. Gale and J. A. Landgrebe.

(5a) NOTE ADDED IN PROOF.—The rotation for a given configuration may be calculated by a recently reported method (J. Brewster, THIS JOURNAL, **81**, 5475 (1959)). Using this procedure, the same configuration, L-(-)-2-bromomercuributane, is assigned as is reported here.

(6) F. R. Jensen and L. H. Gale, THIS JOURNAL, **82**, 145 (1960).

(7) S. Schrauth, W. Schoeller and R. Struensee, *Ber.*, **43**, 695 (1910).

(8) E. Biilmann, *ibid.*, **43**, 568 (1910).

(9) G. F. Wright, THIS JOURNAL, **57**, 1993 (1935).

(10) W. H. Brown and G. F. Wright, *ibid.*, **62**, 1991 (1940).

(11) A. M. Birks and G. F. Wright, *ibid.*, **62**, 2412 (1940).

(12) M. H. Thomas and F. E. W. Wetmore, *ibid.*, **63**, 136 (1941).

(13) J. Romeyn and G. F. Wright, *ibid.*, **69**, 697 (1947).

(14) A. G. Brook, R. Donovan and G. F. Wright, *Can. J. Chem.*, **31**, 536 (1953).

(15) L. T. Sandborn and C. S. Marvel, THIS JOURNAL, **48**, 1409 (1926); E. Griffith and C. S. Marvel, *ibid.*, **53**, 789 (1931).

(16) A. N. Nesmeyanov, O. A. Reutov and S. S. Poddnbnaya, *Doklady Akad. Nauk, S.S.S.R.*, **88**, 479 (1953).

(17) O. A. Reutov and Tsin-Chzhu Lu, *ibid.*, **110**, 575 (1956).

(18) Experiments were also carried out with the 2-octyl system; however, the work was discontinued because of the low yield of 2-bromomercurioctane obtained by way of the Grignard reagent from commercial 2-bromoöctane; unpublished results with John Bush.

(19) C. S. Marvel and H. O. Calvery, THIS JOURNAL, **45**, 821 (1923).

(20) J. Kenyon, H. Phillips and V. P. Pittmann, *J. Chem. Soc.*, 1080 (1935).

(21) H. L. Cohen and G. F. Wright, *J. Org. Chem.*, **18**, 432 (1953). The compound described is 2-chloromercuributane and not mercuribis-2-butane as reported; private communication from M. Malgiyandi and G. F. Wright.

(22) A preliminary account of the partial resolution of *sec*-butyl-

sec-butylmercuric halides to the diastereomeric *sec*-butylmercuric mandelates utilizing the pure (+)- or (−)- mandelic acids. Two methods were used for carrying out this anion exchange.

In the first method, *sec*-butylmercuric chloride was treated with an equimolar amount of potassium hydroxide in ethanol; the potassium chloride which precipitated was removed by filtration and then active mandelic acid was added to the filtrate.

$$\textit{sec}\text{-}\mathrm{C_4H_9HgCl + KOH \longrightarrow \textit{sec}\text{-}C_4H_9HgOH + KCl} \quad (1)$$

$$\textit{sec}\text{-}\mathrm{C_4H_9HgOH + HO_2CCHOHC_6H_5 \longrightarrow \textit{sec}\text{-}C_4H_9HgO_2CCHOHC_6H_5 + H_2O} \quad (2)$$

In the second method, the *sec*-butylmercuric mandelates were prepared by treating either *sec*-butylmercuric chloride or bromide with (+)- or (−)-silver mandelate in ethanol.

$$\textit{sec}\text{-}\mathrm{C_4H_6HgX + AgO_2CCHOHC_6H_5 \longrightarrow \textit{sec}\text{-}C_4H_9HgO_2CCHOHC_6H_5 + AgX} \quad (3)$$

The (−)-*sec*-butylmercuric (−)-mandelate was recrystallized to constant rotation, $[\alpha]^{22}\mathrm{D}$ −60.5°, using dioxane as solvent.

The *sec*-butylmercuric mandelates are converted to the bromides in almost quantitative yield by reaction with bromide ion (4). By this method, (−)-*sec*-butylmercuric bromide, $[\alpha]^{22}\mathrm{D}$ −25.8°, was

$$\textit{sec}\text{-}\mathrm{C_4H_9HgO_2CCHOHC_6H_5 + Br^- \longrightarrow \textit{sec}\text{-}C_4H_9HgBr + C_6H_5CHOHCO_2^-} \quad (4)$$

obtained from the diastereomer which had been recrystallized to constant rotation. The (+)-*sec*-butylmercuric bromide was obtained, depending upon solvent, in varying degrees of purity from the mother liquors.

Recrystallization of partially resolved *sec*-butylmercuric bromide results in enrichment of the inactive form. It is convenient that the rotation does not greatly change after recrystallization from ethanol.

The anion exchange method described here is a very simple procedure and should be generally applicable for the resolution of organomercurials and other stable organometallic compounds. Since the mercuri group can be easily substituted in and removed from many types of compounds, this method should be adaptable for resolving other types of compounds. Such compounds include those containing aromatic, olefinic and active methylene groups. The scope of the method is under investigation.

Stability of Optical Isomers at Elevated Temperature.—In several experiments the rotations of the *sec*-butylmercuric mandelate and partially resolved *sec*-butylmercuric bromide changed in an expected manner during the recrystallizations. This behavior was only observed with samples which contained impurities. The stabilities of the pure compounds toward heat were tested, but no racemization was observed at temperatures up to 75°. Racemization of these compounds by various reagents will be reported in a future communication.

Cleavage of Active *sec*-Butylmercuric Bromide by Bromine.—The cleavage of organomercurials by bromine[4] and iodine[23] has been shown to occur both by polar and free radical mechanisms. Utilizing the simple isomeric *cis*- and *trans*-4-methylcyclohexylmercuric bromides, it has been shown that the cleavage by bromine occurs completely stereospecifically with retention of configuration for the polar mechanism. In contrast, the reaction by the free radical mechanism occurs with complete interconversion of isomers. Depending on the reaction conditions, each reaction path can be made to predominate or to be competitive.[4]

Under the reaction conditions which favor the free radical mechanism, carbon disulfide as solvent, active *sec*-butylmercuric bromide is also cleaved by bromine with complete loss of configuration (Table I). In non-polar solvents containing a small amount of alcohol, the product is obtained with partial retention of configuration. The same effect was noted previously, but with more stereospecificity, in the cleavages of *cis*- and *trans*-4-methylcyclohexylmercuric bromides by bromine. Under the reaction conditions in which the 4-methylcyclohexylmercuric bromides are cleaved exclusively by the polar mechanism (pyridine, 0°), (+)-*sec*-butylmercuric bromide is cleaved only partially stereospecifically.[24] At lower temperatures (−40 to −65°) the reaction occurs more stereospecifically. The product distributions obtained at 0 and −40° are different, and therefore the competing processes must have different activation energies. Since the product distributions obtained at −40 and −65° are almost identical, the reactions are no longer competitive and one reaction must occur almost exclusively. Therefore, it is highly probable that the cleavage by bromine occurs completely stereospecifically at −65°. Because the polar reaction occurs with retention of configuration, and the mercury compound and resulting alkyl bromide have the same sign of rotation, the stereochemical assignment is L-(−)-2-bromomercuributane.[5,5a] From the data in Table I, and the highest rotation obtained for *sec*-butylmercuric bromide, $[\alpha]^{22}\mathrm{D}$ 25.8°, the calculated rotation of L-2-bromobutane is $[\alpha]^{25}\mathrm{D}$ 33.1° (neat).[24a]

In the preliminary account of these results,[3] it was assumed that the cleavage in pyridine at 0° occurs completely stereospecifically and that the *sec*-butylmercuric bromide was completely resolved because the rotation obtained for the 2-bromobutane, $[\alpha]\mathrm{D}$ 28.5°, was in excellent agreement with the empirically calculated rotation, $[\alpha]\mathrm{D}$ 28.6°, and the maximum observed rotation,[25] $[\alpha]\mathrm{D}$ 28.45°. Since a higher rotation has been obtained for 2-

---

mercury salts has been reported by H. B. Charman, E. D. Hughes and C. K. Ingold, *Chemistry & Industry*, 1517 (1958). The results reported here were mostly completed prior to the submission of the above communication.

(23) S. Winstein and T. G. Traylor, THIS JOURNAL, **78**, 2597 (1956).

(24) It is easy to establish that the cleavage of cyclohexyl compounds occurs completely stereospecifically since *cis-trans*-isomers are formed. Addition of 1% of the other isomer to either cleavage product causes the appearance of a number of new bands, which are characteristic of the added isomer, in the infrared spectrum of the cleavage product.

(24a) NOTE ADDED IN PROOF.—A new maximum rotation for active *sec*-butyl bromide has been reported recently (P. S. Skell, R. G. Allen and G. Helmkamp, THIS JOURNAL, **82**, 410 (1960)). Using this value, $[\alpha]\mathrm{D}$ 39.4°, and the results of the bromine cleavage, the calculated maximum rotation for 2-bromomercuributane is $[\alpha]\mathrm{D}$ 30.7°.

(25) G. K. Helmkamp, C. D. Joel and H. Sharman, *J. Org. Chem.*, **21**, 844 (1956).

TABLE I

STEREOCHEMICAL RESULTS OF THE BROMINE CLEAVAGE OF ACTIVE 2-BROMOMERCURIBUTANE IN VARIOUS SOLVENTS

Solvent (temp., °C.)	$[\alpha]^{22}_{\mathrm{D}}$ 2-Bromomercuributane	$[\alpha]^{22}_{\mathrm{D}}$ 2-Bromobutane	Retention,[b] %
Carbon disulfide (25)	+3.62°	0°	0
Carbon disulfide, 10% methanol (25)	+3.42	+0.24	5
Methylene chloride, 10% methanol (25)	+3.11,	+0.43,	11
	−3.28	−0.51	12
Pyridine (0)	+3.76	+4.15	86
Pyridine (−45)	−4.94	−6.31[a]	99.7
γ-Collidine, 30% pyridine (−65)	−4.94	−6.33[a]	100

[a] Rotation at 25°. [b] Calculated assuming that the cleavage at −65° occurs completely stereospecifically.

bromobutane, the stereospecificity of the bromine cleavage of *sec*-butylmercuric bromide and the completeness of the resolution are open to question. For reasons indicated above, the cleavage is believed to be stereospecific at −65°. The extent of the resolution is being investigated by other methods.

In summary, for the bromine cleavage, *sec*-butylmercuric bromide and *cis*- and *trans*-4-methylcyclohexylmercuric bromide respond in a similar manner to changes in the reaction conditions. However, the relative tendency toward the polar reaction is somewhat less with the *sec*-butyl compounds than noted previously with the 4-methylcyclohexylmercuric bromides. Under comparable conditions, the percentage of the reaction proceeding stereospecifically is greater for the cyclohexyl compounds. Possible mechanisms for the polar reaction have been noted previously.[5,23] A detailed discussion of the mechanisms of the polar and free radical reactions will be discussed in future publications.

Experimental Part[26]

Preparation of *sec*-Butylmercuric (−)-Mandelate. Method I.—To 98.4 g. (0.335 mole) of (+)-*sec*-butylmercuric chloride dissolved in 100 ml. of warm absolute ethanol was added an equivalent amount of alcoholic potassium hydroxide solution (718 ml., 0.467 *N*). The potassium chloride was removed by filtration, washed with acetone and weighed. The yield of potassium chloride was almost quantitative. To the filtered solution, 35.7 g. (0.235 mole) of (−)-mandelic acid, $[\alpha]^{22}_{\mathrm{D}}$ −155°, was added. The (−), (−)-diastereomer can be obtained in impure form by cooling the ethanol solution; however, since another solvent was used for the recrystallization, the ethanol was removed at this stage under reduced pressure utilizing a rotary film evaporator. The residue was dissolved in 40 ml. of 1:1 glyme–dioxane mixture at 70°, allowed to cool to room temperature and then cooled at 5° overnight, yielding 62.2 g. (0.152 mole) of the impure (−), (−)-diastereomer.

Method II.—To 10 g. (0.066 mole) of (−)-mandelic acid, $[\alpha]^{22}_{\mathrm{D}}$ −152.5°, dissolved in 150 ml. of water warmed to 50°, was added a drop of phenolphthalein solution. A 20% sodium hydroxide solution was added slowly with stirring until the mixture was slightly pink. A solution of 11.1 g. (0.066 mole) of silver nitrate in 50 ml. of water was added with stirring, and the silver mandelate which precipitated was removed by filtration. After drying, 12 g. (71%) of the silver salt was obtained.

The silver mandelate (0.046 mole) was dissolved in 200 ml. of warm methanol, the temperature was adjusted to 50°, and a solution of 15.7 g. (0.046 mole) of *sec*-butylmercuric bromide in 100 ml. of methanol was added. The mixture was stirred at 50° for 2.5 hr., and the mixture was filtered while warm. The silver bromide was obtained in a yield of 8.19 g. (93.5%). The diastereomers were treated as described in method I.

The diastereomeric *sec*-butylmercuric mandelates are crystalline solids which separate from many organic solvents, including ethanol, ethylene glycol dimethyl ether, tetrahydrofuran, acetone, methyl ethyl ketone and dioxane. In order to obtain a quantity of partially resolved material for stereochemical studies any of the solvents indicated above may be used.

The purest sample of (−)-*sec*-butylmercuric (−)-mandelate was obtained by recrystallization from dioxane. From 155 g. of the impure diastereomer, 1.2 g. of material was obtained which had shown essentially the same rotation, $[\alpha]^{22}_{\mathrm{D}}$ −60.5° (*c* 3, ethanol), during the last three recrystallizations.

In order to test the stability of this compound toward heat, pure samples were dissolved in ethanol, aliquots were sealed in tubes (air atmosphere) and the tubes were placed in a bath for various lengths of time. The most drastic treatment given samples of (−)-*sec*-butylmercuric (−)-mandelate was to heat for 45 min. at 70°. The initial and final rotations of the solution were identical with $[\alpha]^{23}_{\mathrm{D}}$ −48.9° (*c* 3, ethanol).

Preparation of Active *sec*-Butylmercuric Bromide. (−)-Isomer.—The 62.2 g. (0.152 mole) of solid (−),(−)-diastereomer obtained in method I above was shaken vigorously with a twofold excess of aqueous sodium bromide solution. After the solid had dissolved, the methylene chloride solution was treated with a similar sodium bromide solution, and then the aqueous solutions were washed with more methylene chloride. After combining the extracts and drying with magnesium sulfate, the methylene chloride was removed under reduced pressure using a rotary film evaporator. The crude (−)-*sec*-butylmercuric bromide, 46.0 g., was dissolved in 320 ml. of absolute ethanol, which had been pre-heated to 50°, and the solution was filtered. While stirring, 7 ml. of water was added and the solution was allowed to cool. When the temperature reached 40°, the mixture was seeded. The (−)-isomer was recovered in a yield of 40.3 g. and had −5.51° (*c* 5, ethanol).

The (−)-*sec*-butylmercuric (−)-mandelate with $[\alpha]^{22}_{\mathrm{D}}$ −60.5° was cleaved in a similar manner to give (−)-*sec*-butylmercuric bromide with $[\alpha]^{22}_{\mathrm{D}}$ −25.8° (*c* 5, ethanol), $[\alpha]^{22}_{\mathrm{D}}$ −25.9° (*c* 3, acetone) (lit.,[22] $[\alpha]^{30}_{\mathrm{D}}$ −24.0° (*c* ~ 5, acetone)).

(+)-Isomer.—The (+)-isomer was obtained from the mother liquors from the diastereomer formation reactions. The solvent from the mother liquor of method I was removed at reduced pressure. By treating the residue as described above for the (−)-isomer, 47.4 g. of (+)-*sec*-butylmercuric bromide, $[\alpha]^{22}_{\mathrm{D}}$ + 14.4° (*c* 5, ethanol), was obtained.

The rotation of active *sec*-butylmercuric bromide changes only slightly on recrystallization from ethanol. Typical initial and final specific rotations, respectively, are: −4.94° and −4.63° (80% recovery), −4.63° and −4.47° (91% recovery), −5.51° and −5.30° (82% recovery). The melting points of various samples of (−)-*sec*-butylmercuric bromide vary somewhat irregularly from 42 to 45°. Partially resolved material behaves similarly and shows little or no depression. The pure (−)-*sec*-butylmercuric bromide, $[\alpha]_{\mathrm{D}}$ −25.8°, has m.p. 44.0–44.8°.

In order to test the stability of active *sec*-butylmercuric bromide, samples were dissolved in ethanol and heated for various lengths of time (protected from light). The samples had initially $[\alpha]^{22}_{\mathrm{D}}$ −13.5°; after 8 hr. at 74°, $[\alpha]^{22}_{\mathrm{D}}$ −13.4° and after 8 hr. at 100°, $[\alpha]^{22}_{\mathrm{D}}$ −13.1°.

The (−)-mandelic acid was recovered from the aqueous sodium bromide solution by use of a continuous extractor. After extracting the solution for two hours with ether, the extract was discarded, a fresh portion of ether (alcohol-free) was added and the aqueous solution was acidified with phosphoric acid to *p*H 2. The extraction was continued for 24 hr., and then the ether was removed under reduced pressure. The crude acid was recrystallized from a 5:95 mixture of acetone–benzene using 19 ml. of solvent for each gram of acid.

Cleavage of (+)-*sec*-Butylmercuric Bromide with Bromine. Pyridine, 0°.—A solution of bromine in pyridine was prepared by adding 4.8 g. (0.03 mole) of bromine dropwise to 15 ml. of pyridine which was cooled in an ice–salt-bath. This solution was added over a period of 2 min. to a

---

[26] Optical rotations were measured using a Universal High Precision Polarimeter, No. 80, O. C. Rudolph and Sons, Caldwell, N. J.

mixture of 9.559 g. (0.0283 mole) of (+)-*sec*-butylmercuric bromide, $[\alpha]^{22}\text{D}$ +3.76°, in 40 ml. of pyridine. The reaction was very fast as indicated by the observation that the color disappeared almost immediately after the addition of each drop of bromine solution. A slight bromine color persisted at the end of the addition.

After stirring the solution 1 min., 15 ml. of 1,2,4-trichlorobenzene, b.p. 211–213°, was added and the resulting mixture was poured into 200 ml. of water. The mercuric bromide was separated by filtration and then washed several times with trichlorobenzene. The organic layer was separated and washed alternately with 200 ml. of water, 100 ml. of 1 *N* hydrochloric acid, 100 ml. of 2% sodium carbonate solution and 100 ml. of water. Each of the above solutions was extracted in turn with three 5-ml. portions of trichlorobenzene. The solutions were dried with anhydrous magnesium sulfate, filtered and combined. About 0.5 g. of phosphorus pentoxide was added and the material distilled at 20 mm. until the temperature in the distillation flask reached 110°. The receiver flask was cooled in a Dry Ice–trichloroethylene-bath. The distillate was redistilled at atmospheric pressure through a 15-in. tantalum wire spiral column to give 2.18 g. (56%) of (+)-2-bromobutane, b.p. 88–90°. The material was redistilled and a center fraction taken of (+)-2-bromobutane, $[\alpha]^{22}\text{D}$ + 4.15° (neat).

Pyridine, −40°.—The reaction was carried out in a similar fashion but the work-up was varied. The *sec*-butyl bromide and the solvent were removed from the mercuric bromide at low pressure (2 mm.) utilizing a rotary film evaporator. The distillate was collected in a trap placed in a Dry Ice–trichloroethylene-bath. Since in this procedure it is not necessary to wash the product from the mercuric bromide cake, a volatile extraction solvent may be used. Identical results were obtained using methylene chloride and trichlorobenzene as extraction solvents. In the experiments where methylene chloride was used as the extracting agent, the majority of the methylene chloride was distilled from the *sec*-butyl bromide using a column rated at 35 plates. The product was obtained in yields of 65–75%.

γ-Collidine–Pyridine (7:3) −65°.—Since the pyridine used as solvent had m.p. −42°, the reaction at −65° was carried out using a mixture of collidine (m.p. −43°) and pyridine.

A solution of 7.5 g. (0.047 mole) of bromine in 25 ml. of pyridine was added dropwise over 10 min. to a stirred mixture of 15.0 g. (0.044 mole) of (−)-*sec*-butylmercuric bromide, $[\alpha]^{22}\text{D}$ −4.94° (*c* 5, ethanol), 20 ml. of pyridine and 70 ml. of γ-collidine, which was cooled to −65°. The bath was removed and the mixture was allowed to warm while stirring until the solution became clear. Immediately after the solution became clear, the mixture was worked up using the procedure described for the −40° reaction. The product was obtained in a yield of 4.77 g. (78.4%) and had $[\alpha]^{25}\text{D}$ −6.33° (neat) and $d^{25}{}_4$ 1.252. The rotation was identical upon refractionating the sample.

Other Solvents.—The cleavages were carried out and worked up essentially as described for the pyridine reactions. The presence of hydrogen bromide was very noticeable in these experiments, especially when carbon disulfide was used as solvent. The yields varied from 27 to 38% depending upon solvent.

BERKELEY 4, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

The Stereochemistry of the Cleavage of Di-*sec*-butylmercury by Mercuric Bromide[1-4]

BY FREDERICK R. JENSEN

RECEIVED JULY 21, 1959

In a typical reaction sequence, *sec*-butylmagnesium bromide with (−)-*sec*-butylmercuric bromide, $[\alpha]^{22}\text{D}$ −6.49°, gave (−)-(±)-di-*sec*-butylmercury, $[\alpha]^{22}\text{D}$ −5.52°; and the dialkylmercury compound with mercuric bromide gave (−)-*sec*-butylmercuric bromide, $[\alpha]^{22}\text{D}$ −3.36°. Since the rotation of the starting (−)-*sec*-butylmercuric bromide was twice that of the final product, the electrophilic cleavage by mercuric bromide must have occurred with retention of configuration. This is the second example using simple stereoisomers which indicates that the stereochemical course of concerted electrophilic aliphatic substitution is retention of configuration.

Dialkylmercury compounds are readily cleaved by inorganic mercuric salts to give alkylmercuric salts in excellent yield.[5] The mechanism of this

$$\text{R—Hg—R} + \text{HgX}_2 \longrightarrow 2\ \text{R—HgX} \qquad (1)$$

reaction is of theoretical interest since it probably occurs by electrophilic substitution on carbon.

The stereochemistry of the cleavage has been investigated previously. In each case, the observed stereochemical course of the reaction was retention of configuration. However, the stereoisomers used in the studies contained structural features which could have contributed to the stereochemistry of the reactions. Also, in most studies, only one member of a pair of geometric isomers was used, and the observed product could be that obtained from either isomer. The availability of optically active *sec*-butylmercuric bromide[6] has made possible a study of the stereochemistry of the cleavage using simple stereoisomers.

The first stereochemical study was by Wright[7] who found that *cis*-*cis*-bis-2-methoxycyclohexylmercury[8] is cleaved by mercuric chloride to yield only *cis*-2-methoxycyclohexylmercuric chloride. In a related investigation, Winstein, Traylor and Garner[9] cleaved *cis*-2-methoxycyclohexylneophylmercury[8] by radio-mercuric chloride and found that the *cis*-2-methoxycyclohexylmercuric chloride obtained a substantial amount of radio-mercury. None of the *trans* isomer was obtained. Although it was originally reported that each pure diastereomer of *l*-menthoxy α-mercuri-bis-phenylacetate

---

(1) Electrophilic Aliphatic Substitution VI, Organomercurials IV.

(2) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, and to the Research Corporation for partial support of this research.

(3) These results have been reported in preliminary form; F. R. Jensen, L. D. Whipple, D. K. Wedegaertner and J. A. Landgrebe, THIS JOURNAL, **81**, 1262 (1959); F. R. Jensen, L. D. Gale, L. D. Whipple and D. K. Wedegaertner, Abstracts of Papers, 135th Meeting of the American Chemical Society, Boston, Mass., 1959, p. 80-O.

(4) A similar investigation has been reported; H. B. Charman, Abstracts of Papers, 135th Meeting of the American Chemical Society, Boston, Mass., 1959, p. 81-O.

(5) F. C. Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co. (Reinhold Publishing Corp.), New York, N. Y., 1921, p. 40.

(6) F. R. Jensen, L. D. Whipple, D. K. Wedegaertner and J. A. Landgrebe, THIS JOURNAL, **82**, 2466 (1960).

(7) G. F. Wright, *Can. J. Chem.*, **30**, 268 (1952).

(8) The structures of the corresponding *cis-trans* isomers have not been assigned unequivocally. The designation here of *cis-* and *trans-* corresponds to the β and α, respectively, designation by Wright.[7]

(9) S. Winstein, T. F. Traylor and C. S. Garner, THIS JOURNAL, **77**, 3741 (1955).