mixture of 9.559 g. (0.0283 mole) of (+)-sec-butylmercuric bromide, $[\alpha]^{22}$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, $[\alpha]^{22}$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, $[\alpha]^{22}$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 $[\alpha]^{25}$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.

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

BY FREDERICK R. JENSEN

In a typical reaction sequence, sec-butylmagnesium bromide with (−)-sec-butylmercuric bromide, $[\alpha]^{22}$D −6.49°, gave (−)-(±)-di-sec-butylmercury, $[\alpha]^{22}$D −5.52°; and the dialkylmercury compound with mercuric bromide gave (−)-sec-butylmercuric bromide, $[\alpha]^{22}$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

$$R{-}Hg{-}R + HgX_2 \longrightarrow 2\ R{-}HgX \qquad (1)$$
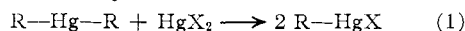
reaction is of theoretical interest since it probably occurs by electrophilic substitution on carbon.

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).

reacts non-stereospecifically with mercuric bromide,[10] a later reinvestigation has shown that this cleavage is also stereospecific.[11] In each of the above investigations, because of the possible intervention of neighboring group effects, various interpretations of the results are possible. Winstein, Traylor and Garner[9] noted that the strong preference for retention rather than inversion of configuration obtained suggests that retention may be a generally favored result of concerted electrophilic substitution, but that their result with one electrophilic reagent on a cyclohexyl system, and even then with a β-alkoxyl group, should not be generalized without data on other reagents and systems.

The starting compound for the present investigation, (−)-sec-butyl-(±)-sec-butylmercury, was obtained by treating (±)-sec-butylmagnesium bromide with (−)-sec-butylmercuric bromide.

$$(\pm)\text{-}sec\text{-BuMgBr} + (-)\text{-}sec\text{-BuHgBr} \longrightarrow$$
$$(-)\text{-}sec\text{-Bu-}(\pm)\text{-}sec\text{-BuHg} \quad (2)$$
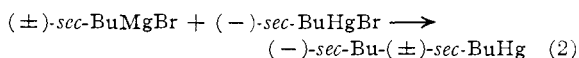
The yields of dialkylmercury compound were 75–90% depending on the scale of the reaction. Since the volumes of the products were less than 6 ml. and the products were fractionated through a column with a hold-up of about 0.5 ml., the actual yields were likely in excess of 90% in most instances.

Reaction 2 probably occurs by nucleophilic substitution on mercury and should not affect the optical center. Because of the large size of mercury, and because the reaction with the Grignard reagent is fast, the probability of asymmetric induction in the incoming sec-butyl group appeared to be small. To test for possible asymmetric induction under comparable conditions, reactions were carried out adding the Grignard reagent at different rates and using a deficiency or excess of Grignard reagent. The over-all results were similar when the Grignard reagent was added slowly or in one portion, and whether a 5% deficiency or 12% excess or reagent was used.

The cleavages of the dialkylmercury compounds by mercuric bromide were carried out in ethanol, and the yields of alkylmercuric bromide were about 90%. The yields in solution were undoubtedly higher, since in control experiments the recovery of

$$(-)\text{-}sec\text{-Bu-}(\pm)\text{-}sec\text{-BuHg} + \text{HgBr}_2 \longrightarrow$$
$$2(-)\text{-}sec\text{-BuHgBr} \quad (3)$$
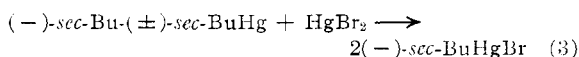
sec-butylmercuric bromide was about 90%. sec-Butylmercuric bromide undergoes no change in ethanol, but can be conveniently recovered from ethanol in yields of 90% only by flooding the solution with water. The reactants and product were stable under the reaction conditions.

The over-all sequence of reactions (reactions 2 and 3) converts one mole of sec-butylmercuric bromide to two moles of the same compound. The cleavage reactions (3) should occur statistically on the two carbon–mercury bonds. Therefore, reaction 3 should give one mole of (+)-sec-butylmercuric bromide, 0.5 mole of sec-butylmercuric bromide with the same rotation as that used in reaction

(10) A. N. Nesmeyanov, O. A. Reutov and S. S. Poddubraya, Doklady Akad. Nauk S.S.S.R., 88, 479 (1953).

(11) O. A. Reutov, Angew. Chem., 69, 688 (1957).

2 and 0.5 mole of sec-butyl-mercuric bromide whose rotation will depend upon the stereochemistry of reaction 3. The resulting mixture will have a rotation of zero if reaction 3 occurs with inversion of configuration, a rotation one-fourth of the starting sec-butylmercuric bromide (reaction 2) if reaction 3 occurs with inversion of configuration, and one-half the rotation of the same material if reaction 3 occurs with the retention of configuration.

TABLE I

OPTICAL ROTATIONS OF STARTING sec-BUTYLMERCURIC BROMIDE, THE DI-sec-BUTYLMERCURY OBTAINED BY REACTION WITH THE GRIGNARD REAGENT AND THE sec-BUTYLMERCURIC BROMIDE OBTAINED BY REACTION OF THE DIALKYL WITH MERCURIC BROMIDE

Expt.	$[\alpha]^{25}D$ starting L-(−)-sec-butylmercuric bromide^a	$[\alpha]^{25}D$ (±),(−)-Di-sec-butylmercury^a	$[\alpha]^{25}D$ Final L-(−)-sec-butyl mercuric bromide^a
1	−16.14^{ob}	−11.50°	−7.49^{od}
2^i	− 6.49^b	− 5.52	−3.36^e
3	− 4.94^b	− 3.95	−2.33^f
4	−19.28^c	−15.54	−9.37^g
			−9.46^h

^{a} ($c \sim 5$, EtOH). ^{b} Grignard solution slowly added to alkylmercuric salt. ^{c} Grignard solution added in one portion to alkylmercuric salt. ^{d} Dialkyl cleaved with mercuric bromide (1 mole) in polarimeter cell and product not isolated. ^{e} Yield, 90.7%. ^{f} Dialkyl cleaved with mercuric bromide (1.05 moles) in polarimeter cell and product not isolated. ^{g} Dialkyl cleaved with mercuric bromide (1.10 moles) in polarimeter cell. ^{h} Yield 88.7%. ^{i} Rotations at 22°.

The results are summarized in Table I and indicate that the sec-butylmercuric bromide obtained in reaction 3 has about one-half the rotation of sec-butylmercuric bromide used in reaction 2. Therefore, the most reasonable interpretation of the results is that reaction 3 occurs with retention of configuration.

Although the experimental results presented here are very simple, they provide convincing evidence that the cleavage occurs with retention of configuration, even in the absence of structural features which might alter the course of the reaction. These results and a study of the cleavage of organomercurials by bromine,[12] which also occurs with retention of configuration, represent the only reported stereochemical studies of concerted electrophilic aliphatic substitution using simple stereoisomers.

Possible mechanisms for the cleavage reaction 3 have been discussed by previous workers.[7,9,11] Although mechanisms have been discussed only in terms of reaction by the un-ionized mercuric salt, possible reactions by XHg$^+$ and attack of mercury on mercury followed by rearrangement should also be considered. Since the results presented here give only the stereochemistry of the reaction and not the molecularity of the reaction, a discussion of possible mechanisms is deferred.

Experimental

(−)-sec-Butyl-(±)-sec-butylmercury.—A typical experiment was carried out as follows: A solution of sec-butylmagnesium bromide in ether was prepared in the usual manner. The concentration (1.71 M) of the Grignard reagent was determined by adding an aliquot to excess standard acid and then back titrating with standard base.

(12) F. R. Jensen and L. H. Gale, THIS JOURNAL, 81, 1261 (1959).

To a stirred suspension of 11.582 g. (0.0343 mole) of (−)-sec-butylmercuric bromide, $[\alpha]^{22}D$ −6.49°, was added 25 ml. of the Grignard solution dropwise, over a period of two hours. The addition was conducted under a nitrogen atmosphere and the reaction vessel was placed in a water-bath at 23°. The reaction was exothermic and appeared to occur very rapidly.

A cold water-bath was placed around the flask and 200 ml. of water was added while stirring. The ether layer was separated and washed with 50 ml. of water. The water solutions were extracted with two 5-ml. portions of methylene chloride and the organic solutions were combined. After distilling the solvents at atmospheric pressure, the residue was distilled at reduced pressure to give 9.318 g. (86.1%) of (−)-sec-butylmercury, b.p. 63° (3 mm.), $[\alpha]^{22}D$ −5.52° (c 5.3, ethanol). Upon redistillation, the sample had the identical rotation.

Cleavage of (−)-sec-Butyl-(±)-sec-butylmercury by Mercuric Bromide.—A mixture of 0.5330 g. of (−)-sec-butyl-(±)-sec-butylmercury, $[\alpha]^{22}D$ −5.52°, and 0.621 g. of mercuric bromide was dissolved in 15 ml. of ethanol. The solution was allowed to stand at room temperature for 40 hours and then heated to 50° for 30 minutes. After cooling to room temperature, water was slowly added until a precipitate formed. The solution was cooled to give white crystals, 1.033 g. (90.7%), of (−)-sec-butylmercuric bromide, m.p. 40.2–42.8° and $[\alpha]^{22}D$ −3.36° (c 5, ethanol).

In several experiments the cleavage reaction was carried out in a polarimeter tube, and it was found that a constant rotation was obtained very rapidly. A yield of 88.7% was obtained when the reaction mixture was allowed to stand for 20 minutes at room temperature (expt. 4).

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Alumina: Catalyst and Support. I. Alumina, its Intrinsic Acidity and Catalytic Activity[1]

BY HERMAN PINES AND WERNER O. HAAG[2]

Evidence has been gathered showing that pure alumina has intrinsic acidity. This acidity could be demonstrated in various ways: (a) The reactions catalyzed by alumina are typically acid catalyzed, such as dehydration of alcohols and skeletal isomerization of 3,3-dimethylbutene and cyclohexene. The relative ease with which different compounds react, and the nature of the products, are in accord with a carbonium ion mechanism. (b) Trimethylamine is strongly chemisorbed on alumina. (c) Indicators, which give colored complexes with typical Lewis acids, produce the same colors when adsorbed on alumina. The various test methods gave the same picture of the acidity for certain aluminas, but not for all. The lack of correlation results from the fact that the various methods respond in a different way to the two aspects of acidity—the quantitative and the qualitative aspect. Amine chemisorption and alcohol dehydration are primarily a function of the number of acid sites; both can be caused by relatively weak acids. The color change of Lewis indicators and the isomerization of cyclohexene both occur only on acid sites of considerable strength. Therefore, no correlation between the acidity, as determined by amine chemisorption, and the activity for cyclohexene isomerization is found. The total conversion of 3,3-dimethyl-1-butene is a somewhat less satisfactory measure of the number of acid sites than amine chemisorption, but the product distribution is a sensitive indication of the strength of the acids. Pure alumina from aluminum isopropoxide or from nitrate and ammonia, and calcined at 700°, showed optimum activity on a weight and on a unit surface area basis. Heating at higher temperatures decreased the number of acid sites as well as their acid strength. Impregnation of pure alumina with either sodium hydroxide or sodium chloride was shown to lead to a partial poisoning of the active sites without appreciably changing the acid strength of the remaining sites. With increasing amount of alkali, there is a parallel decrease in the activity for cyclohexene conversion, for butanol dehydration, and for amine chemisorption. Aluminas from sodium or potassium aluminate contain alkali in an amount which depends on the way of precipitation and the number of washings. Samples with 0.08–0.65% sodium have a large amount of weakly acid sites, as was indicated by the value for amine chemisorption, and were therefore excellent dehydration catalysts. At the same time they did not isomerize cyclohexene, showing the absence of strong acid sites. From the poisoning studies, the upper limit of the total number of acid sites (capable of dehydrating butanol) and of the number of strong sites (capable of isomerization of cyclohexene) was found to be 10×10^{13} and 0.8×10^{13} sites per cm.^{2}, respectively. Chemisorption of trimethylamine at 300° led to a value of 2.5×10^{13} sites/cm.^{2}.

Introduction

The importance of alumina as a catalyst or support has been widely recognized. As a support or co-catalyst it is used in many catalytic processes of industrial importance such as isomerization, alkylation, catalytic cracking, hydroforming, etc.

In spite of the extensive use of alumina, the literature reveals surprising discrepancies with respect to its catalytic activity. For example, the dehydration of primary alcohols such as 1-butanol[3a−f] and others was reported by many

authors to give pure 1-olefins, whereas others found mixtures of double bond isomers. It was further reported that olefins such as n-hexenes[4a,b] undergo only double bond shift without skeletal rearrangement over alumina in agreement with the widespread belief that alumina is not a catalyst for the skeletal isomerization of hydrocarbons.[5a−c]

On the other hand, rearrangement of the carbon skeleton has been observed in a few cases as in the isomerization of 1-hexene[6] or in the interconversion of cyclohexene and methylcyclopentenes.[7]

(1) Presented in part before the Division of Colloid Chemistry at the Symposium on "Recent Approaches in the Study of Contact Catalysis," American Chemical Society Meeting, San Francisco, Calif., April 13–18, 1958; and before the Gordon Research Conferences in Catalysis, June 23–27, 1958, New London, N. H.

(2) Predoctoral Fellow Toni Co., 1957–1958; Universal Oil Products Co., 1956–1957.

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