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

Conformational Effect in the Zinc Debromination of *sym*-Tetrabromoethane[1]

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A direct estimate of a conformational effect in the zinc debromination of *gauche*- and *trans-sym*-tetrabromoethanes has been determined. The ratio of *cis*- to *trans*-dibromoethenes in the product is 1.27 at 64.5° and 1.49 at 25°. The free energy differences in the respective transition states are 160 and 240 cal. For the *cis–trans*-dibromoethene equilibrium in methanol $\Delta H = 480$ cal./mole in the temperature range 25–118°. At each stage of reaction, reactants → transition states → products, the *gauche* and *trans* related forms show an energy difference. This difference is a minimum for the transition states in terms of ΔF, but an intermediate value in terms of ΔH. The effect of a polar solvent on these energies is indicated.

Conformational isomers, diastereoisomers and geometric isomers exhibit interesting and theoretically important differences in their reaction rates as well as in their stabilities. (In an equilibrium problem only the free energy difference of the isomers is involved; in a rate problem, not only the free energies of activation but also the free energies of the reactants and transition states should be considered.) These differences in rate or equilibrium behavior presumably arising from non-bonded interactions have been variously labelled "*cis*," "eclipsing" or "conformational" effects.[2,3] Though these effects have been recognized in many reactions, their precise evaluation for rate processes has been limited.[4] One semiquantitative estimate is available in the E2 reactions of the diastereoisomeric 1,2-diphenyl-1-propyl bromides, chlorides and ammonium salts.[5]

We wish to report an interesting conformational rate effect in the system

$$trans\text{- and } gauche\text{-}Br_2CHCHBr_2 + Zn \longrightarrow trans\text{- and } cis\text{-}C_2H_2Br_2 + ZnBr_2 \quad (1)$$

When tetrabromoethane is debrominated with zinc in methanol, the product ratio, *cis/trans*, is 1.27 ± 0.04 at 64.5° and 1.49 ± 0.04 at 25°. Since this is assumed to be a *trans* stereospecific process,[6] then

$$trans\text{-}C_2H_2Br_4 \longrightarrow trans\text{-}C_2H_2Br_2 \text{ and } gauche\text{-}C_2H_2Br_4 \longrightarrow cis\text{-}C_2H_2Br_2 \quad (2)$$

The *trans/cis* product ratio becomes their relative rate of formation, V_t/V_g, where

$$(V_t/V_g) = k_t(t)/k_g(g) = (k_t/k_g)(K) \quad (3)$$

and K is the equilibrium constant for the conversion

$$gauche\text{-}Br_2CHCHBr_2 \rightleftarrows trans\text{-}Br_2CHCHBr_2;\ \Delta H = 910 \pm 50 \text{ cal.}^7 \quad (4)$$

If F_t, F_g, $F_t^{\ddagger}$ and $F_g^{\ddagger}$ are the free energies of the tetrabromoethane rotomers and their corresponding activated complexes and $\Delta F_t^{\ddagger}$ and $\Delta F_g^{\ddagger}$ are their free energies of activation in equation 1, then the terms in parentheses of equation 3 can be related simply to those of 5.[3b,8]

$$(F_t - F_g) + (\Delta F_t^{\ddagger} - \Delta F_g^{\ddagger}) = (F_t^{\ddagger} - F_g^{\ddagger}) \quad (5)$$

Therefore, $(F_t^{\ddagger} - F_g^{\ddagger})$ is $-2.303\ RT \log V_t/V_g$ or 160 ± 20 cal. at 64.5° and 240 ± 20 cal. at 25° in methanol solvent. Spectroscopic data for the liquid isomers give $\Delta H = 910 \pm 50$ cal. for equation 4 and we have used this figure for $(F_t - F_g)$.[7] Finally, $(\Delta F_t^{\ddagger} - \Delta F_g^{\ddagger})$ is −750 ± cal. at 64.5° and −670 ± 70 cal. at 25°.

An expression analogous to equation 5 can be written for the enthalpy terms. Where necessary, these can be evaluated by the integration of a modified form of (3)

$$R\frac{d \ln (V_t/V_g)}{d\,(1/T)} = R\frac{d \ln (k_t/k_g)}{d\,(1/T)} + R\frac{d \ln K}{d\ 1/T} \quad (5a)$$

These free energy and enthalpy terms have been collected in Table I.[9] Since process 1 is hetero-

TABLE I

CONFORMATIONAL EFFECT IN THE ZINC DEBROMINATION OF THE *sym*-TETRABROMOETHANES (CAL./MOLE)

Temp., °C.	$(\Delta F_t^{\ddagger} - \Delta F_g^{\ddagger})$	$(F_t - F_g)$	$(F_t^{\ddagger} - F_g^{\ddagger})$	$(F_t' - F_c')^a$
64.5	-750 ± 70^c	910 ± 50^b	160 ± 20	360 ± 25
25	-670 ± 70^c	910 ± 50^b	240 ± 20	370 ± 25
	$(\Delta H_t^{\ddagger} - \Delta H_g^{\ddagger})$	$(H_t - H_g)$	$(H_t^{\ddagger} - H_g^{\ddagger})$	$(H_t' - H_c')^a$
	-100 ± 350^c	910 ± 50^b	810 ± 300	480 ± 25

[a] Figures are for the products, *cis*- and *trans*-$C_2H_2Br_2$. [b] This is actually an enthalpy difference from the liquid $C_2H_2Br_4$ isomers (see footnote 9). [c] This is an upper limit to $(\Delta F_t^{\ddagger} - \Delta F_g^{\ddagger})$ or $(\Delta H_t^{\ddagger} - \Delta H_g^{\ddagger})$.

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(1) Presented in part at the Meeting of the American Chemical Society at Chicago, Ill., September, 1958, Abstracts p. 26-P.

(2) D. Y. Curtin, Abstracts of the Thirteenth National Organic Symposium of the American Chemical Society, Ann Arbor, Mich., June, 1954, p. 40.

(3) (a) D. J. Cram in "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York N. Y., 1956, Chaps. 5 and 6; (b) W. G. Dauben and K. S. Pitzer, *ibid.*, Chap. 1; (c) the terms "*cis*" and "eclipsing" are somewhat misleading in that true *cis* and eclipsed forms often do not participate in the process in question. These terms have also acquired the connotation that *cis* and eclipsed groups are always high energy relative to *trans* or *gauche* forms; in this paper we wish to remove the basis for any such predisposition. The term "conformational" analysis has been used in a general sense with various isomers, including geometric and diastereoisomeric, although these are different from "conformational" or rotational isomers (rotomers).

(4) A number of indirect estimates of eclipsing effects in cyclic systems is available (a). As equilibrium data for the isomeric reactants, *e.g.*, the cyclohexanols, become available, these effects can be evaluated directly (b): (a) see E. L. Eliel and R. G. Haber, THIS JOURNAL, **81**, 1249 (1959), for leading references; (b) R. A. Pickering and C. C. Price, *ibid.*, **80**, 4931 (1958).

(5) D. J. Cram, F. D. Greene and C. H. DePuy, *ibid.*, **78**, 790 (1956).

(6) W. M. Schubert, B. S. Rabinovitch, N. R. Larson and V. A. Sims, *ibid.*, **74**, 4590 (1952).

(7) R. E. Kagarise and D. H. Rank, *Trans. Faraday Soc.*, **48**, 394 (1952); R. E. Kagarise, *J. Chem. Phys.*, **24**, 300 (1956).

(8) S. Winstein and N. J. Holness, THIS JOURNAL, **77**, 5562 (1955).

(9) A statistical factor of 0.5 could have been introduced into V_t, k_t or K. For a specific discussion of the group interactions in the *trans versus gauche* molecules it would perhaps be more appropriate to use $V_t/2$ and $k_t/2$ (because two identical paths for elimination are available in *trans*) and thus raise the corresponding free energy terms by ~400 cal. As for K, we have actually used the $\Delta H = 910$ cal. for $(F_t - F_g)^7$; were entropy data available, these could contain the term due to the symmetry number of *trans*-$C_2H_2Br_4$. For the analogous *sym*-tetrachloroethanes, $T\Delta S \simeq -400$ cal. at 25°.[14a] Both this entropy term and a solvent correction of about 300 cal./mole[10] would tend to make 910 cal./mole a lower limit to $(F_1 - F_g)$.

geneous, conformational differences in diffusion and adsorption as well as in debromination are included in these energy terms.

It was of interest to obtain equilibrium data for the products of reaction 1 in methanol

$$cis\text{-}C_2H_2Br_2 \rightleftarrows trans\text{-}C_2H_2Br_2;\ \Delta H = 480 \pm 25 \text{ cal./mole} \quad (6)$$

This equilibrium was studied in the range 25–118° and the data have been included in Table I. A comparison with other reported data for (6) is given in Table II.

Table II

Equilibrium Data for the *cis–trans*-Dibromoethenes

Temp., °C.	*cis/trans*	$(H_c' - H_t')$, cal./mole	Medium	Ref.
145	0.984	−130 ± 300	Gas phase	a
170	0.975		Gas phase	a
38.94	1.3	−260 ± 200	In CCl_4	b
49.03	1.3		In CCl_4	b
58.82	1.25		In CCl_4	b
20–25	1.7		Liquid isomers	c
150	1.3–1.5		Liquid isomers	c
36	1.80	−480 ± 25	In methanol	d
64.5	1.69		In methanol	d
100	1.58		In methanol	d

[a] R. M. Noyes and R. G. Dickinson, This Journal, **65**, 1427 (1943). [b] H. Steinmetz and R. M. Noyes, *ibid.*, **74**, 4141 (1952). [c] A. R. Olson and W. Maroney, *ibid.*, **56**, 1320 (1934). [d] Calculated results from Fig. 3.

Experimental

Materials.—The solvent was "absolute" methanol (>99.5%). Commercially available *sym*-tetrabromoethane, $n^{18}D$ 1.6386 (lit.[11] $n^{20}D$ 1.6353), was used directly. The dibromoethenes were prepared by the zinc debromination of *sym*-tetrabromoethane followed by fractionation in ethanol[12]: *cis*, $n^{25}D$ 1.5368 (lit.[12] $n^{25}D$ 1.5370); *trans*, $n^{25}D$ 1.5445 (lit.[12] $n^{25}D$ 1.5440). The zinc was reagent grade, 20 mesh.

Debromination and Product Analysis.—The variation of the product ratio with time at 25 ± 3° and 64.5 ± 1° is ven in Fig. 1.

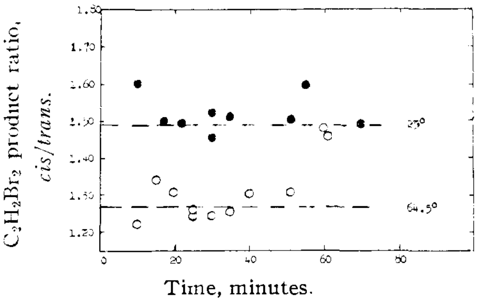

Fig. 1.—Zinc debromination of *sym*-$C_2H_2Br_4$.

Tetrabromoethane (5–15 g.) was dropped into the zinc–methanol mixture in 5–10 minutes at room temperature or at reflux. Since reaction 1 is highly exothermic, dilute solutions (*ca.* 100 ml.) and rapid stirring had to be used in this work. Time was recorded from the beginning of the experiment. In the early experiments, the methanol was poured into water acidified with acetic acid, and the product washed three times with water and dried with calcium chloride. That there was no selective solution by the water or adsorption by the calcium chloride was independently established. In later work the solution was analyzed directly.

Though the zinc debromination was probably complete (98%) in 20 min. at 64.5°, 30 min. at 25°, even traces of unreacted tetrabromoethane could affect the refractive index of the products. This method of analysis was attempted then abandoned. All of our reported data are based on analyses by gas phase chromatography. Here the *cis/trans* ratio could be determined even in the presence of solvent, starting material or other contaminants. The accuracy of the chromatographic analyses was within 1–2% on synthetic *cis-trans* mixtures whose composition was known from refractive index or infrared measurements.

In Fig. 1, points beyond 60 min. turned upward to higher *cis–trans* ratios. This established that the following reaction occurred at 64.5°

$$BrCH{=}CHBr + Zn \longrightarrow ZnBr_2 + C_2H_2 \quad (7)$$

Thus, 100 ml. of methanolic tetrabromoethane (0.052 *M*) and zinc at 64.5° gave 0.052 *M* zinc bromide in the time 20–100 min. and additional bromide only slowly thereafter; see Fig. 2. Process 7 would presumably enrich the product in *cis*-dibromoethene.[6] Therefore, points beyond 60 min. are not included in Fig. 1.

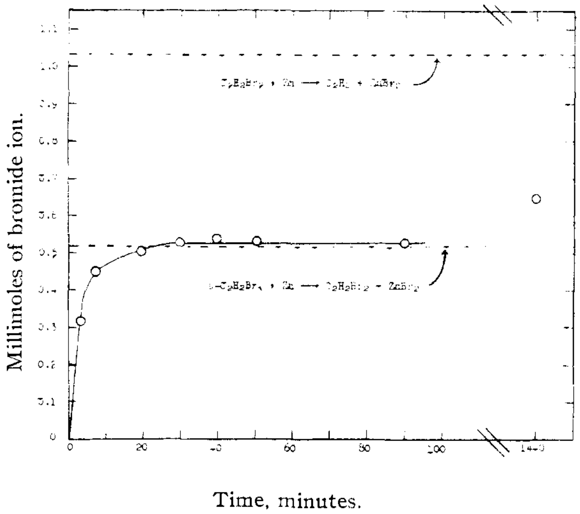

Fig. 2.—Zinc debromination of 0.052 *M* *sym*-tetrabromoethane at 64.5° in methanol aliquots contain 0.52 mmole.

Equilibrium of the Dibromoethenes.—*cis-* or *trans*-rich dibromoethene in methanol was used for the equilibrium studies. Of the various procedures, the following proved most convenient: 1–2 ml. of a 0.669 *M* solution of dibromoethene in methanol was sealed in a small ampule made of quartz or Vycor tubing. A trace of iodine was usually included in the ampule. These ampules were placed in Vycor flasks in which various liquids were gently refluxed at 36–118° under ultraviolet or infrared lamps. A few ampules containing traces of iodine or bromine or both were left in dark thermostats. The contents of the ampules were analyzed by gas phase chromatography.

The approach to equilibrium was relatively slow. (The rate of isomerization of the *trans* appeared to be greater than that of the *cis*). After 30 days at 100°, a once *trans*-rich sample containing iodine had reached equilibrium. At 37, 64 and 100°, the composition of such ampules exposed to infrared light leveled off after *ca.* 30, 20 and 10 days. Exposed to ultraviolet light at 64.5°, such ampules, initially rich in *cis* or *trans*, appeared to be equilibrated after 4 days.

In general, samples exposed to ultraviolet light gave less reliable results. For example, samples rich in *cis* at first gave an increasing *trans/cis* ratio then a decreasing ratio. Both volatile and high-boiling by-products were indicated in the chromatographic analyses. In contrast, samples exposed to infrared lamps gave "cleaner" chromatograms; this method of equilibration is to be preferred.

In Fig. 3 are recorded some of the equilibrium data for the dibromoethenes. Because of the number of determinations involved, the points at 36 and 100° were weighted

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(10) A. Wada, *J. Chem. Phys.*, **22**, 198 (1954).

(11) A. I. Vogel, *J. Chem. Soc.*, 1850 (1948).

(12) R. M. Noyes, W. A. Noyes and H. Steinmetz, This Journal, **72**, 33 (1950).

twice and the point at 64.5° was weighted five times; all of the other points were obtained from duplicate or triplicate determinations and were given single weighting in the least squares calculation. Many points which served merely to indicate the progress toward equilibrium have been omitted. The scatter in Fig. 3 may be due to the interference of by-products in the chromatographic analyses; more probably, it may be ascribed to the difficulty in knowing precisely when the samples were at equilibrium.

Discussion

This appears to be the first direct estimate of conformational rate effect for a set of rotomers. The "more" eclipsed (in terms of bulk, not of bond angles) reactant, *gauche*-tetrabromoethane and the eclipsed product, *cis*-dibromoethene are the stable isomers. Each one of the terms of equations 3 or 5 contributing to the rate difference is significant. None of the usual qualitative criteria for predicting isomer stabilities or rate preferences is useful for predicting results in this system.[13]

These results are both odd and instructive but probably not unique. There are many compounds, often containing halogen, in which the *trans* form is less stable.[14] There is also a reaction analogous to 1 in which the product ratio *cis*/*trans* $\simeq$ 2

$$C_2H_5CCl_2CHCl_2 + Zn \longrightarrow C_2H_5CCl{=}CHCl$$

In the same paper, a similar reaction

$$CH_3CCl_2CCl_2CH_3 + Zn \longrightarrow CH_3CCl{=}ClCH_3$$

gave, conventionally, *trans*/*cis* > 9.[15]

The origins of conformational energy differences have yet to be described adequately.[16,14g] Consequently a simple additive group interaction probably does not exist. It may be expedient, of course, to assume that additivity applies and that group interactions are derivable from model compounds. This approach has in fact been exceedingly fruitful in the conformational analysis of cyclic systems.[3b] It is useful, however, to examine a typical failure.

Consider the interactions of atoms on adjacent carbon atoms in *sym*-dibromoethane and *sym*-tetrabromoethane. Assuming constancy in the group interactions, one would assign the *gauche* → *trans* energy difference in both compounds to the same expression[17]

$$(bb)_{60} + (hh)_{60} - 2(bh)_{60}$$

Experimentally, $\Delta H = -750$ cal./mole[10] in one case and $\Delta H = 910$ cal./mole in the other for the pure liquids.[7] A similar difficulty was encountered in the comparisons made by Eliel and Haber of alkyl with cyclohexyl bromides.[4a]

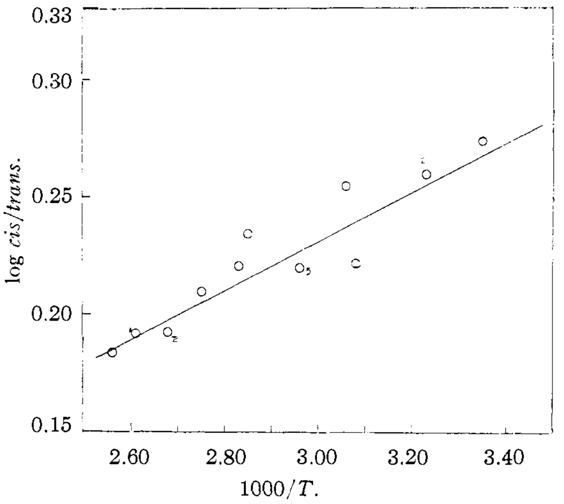

Fig. 3.—The *cis*–*trans*-CHBrCHBr equilibrium (the numbers indicate weighting factors other than 1).

This lack of additivity is inherent in the complex nature of non-bonded interactions. As applied to conformational rate effects, we recognize explicitly van der Waals and electrostatic factors[16] contributing to the energy difference of a pair of isomers.[18] These two factors enter in the reactants, transition states and products. Because they are different functions of the structure of the molecule, they need not enter this series in parallel fashion. Since the conformational effect can be associated with three energy terms (see equations 5 and 5a), there are six possible ways in which the magnitudes of these terms can be ordered. Our point is that *it is unsafe either to identify or to bracket* $(F_t^{\ddagger} - F_g^{\ddagger})$ *with the corresponding difference in reactants or products.*

Finally, the important role of the solvent in determining conformational effects must be mentioned. Taken together, all of the work on the dibromoethene equilibrium indicates that the *cis* form is increasingly favored as the medium becomes more polar (see Table II). This was predictable. Wada found that the percentage *gauche*-1,2-dichloroethane or 1,2-dibromoethane at equilibrium increased with solvent polarity.[10] Indeed, the stability of the *sym*-dichloroethanes is reversed in going from the gas phase to methanol solution. There is a change in ΔH of 1530 cal./mole which amounts to a factor of *ca.* 13 at 300°. Clearly, the

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(13) M. S. Newman, *J. Chem. Educ.*, 32, 344 (1955).

(14) The *trans* form appears to be the less stable isomer in *sym*-tetrachloroethane (a), 1,2-dibromo-2,2-difluoroethane (b), propyl bromide (c), dichloroethene (d), 1,2-dicyanoethane (e), and hexafluorobutadiene-1,3 (f), 1,1,2-trifluoro-1,2,2-trichloroethane (g). Also, contrary to previous ideas, the axial form of α-chlorocyclohexanone appears to be the less stable isomer (h). (a) A. Langseth and H. J. Bernstein, *J. Chem. Phys.*, **8**, 410 (1940); (b) R. E. Kagarise, *ibid.*, **24**, 1264 (1956); (c) T. Yoshino and H. J. Bernstein, *Can. J. Research*, **35**, 339 (1957); (d) K. S. Pitzer and S. L. Hollenbery, THIS JOURNAL, **76**, 1493 (1954); (e) W. E. Fitzgerald and C. J. Janz, *Mol. Spectroscopy*, **1**, 49 (1957); (f) J. C. Albright, J. R. Nielsen and J. Nielsen, *J. Chem. Phys.*, **26**, 370 (1957); (g) M. Iwasaki, *Bull. Chem. Soc. Japan*, **32**, 194, 205 (1959); (h) K. Kozima and Y. Yamanouchi, THIS JOURNAL, **81**, 4159 (1959).

(15) A. T. Morse and L. C. Leitch, *Can. J. Research*, **33**, 6 (1955).

(16) Recently Kreevoy and Mason used a simplified model to evaluate van der Waals and electrostatic interactions between non-bonded groups (a). They estimated both energy differences between isomers and potential barriers to rotation. While their approach is promising, in its present form it is not capable of explaining the greater stability of *gauche*- over *trans*-tetrabromoethane, the greater stability of *cis*- over *trans*-dibromoethene and the maximum in the energy barrier to internal rotation in the graded series: ethane (2.9 kcal.), chloroethane (3.7 kcal.), 1,1-dichloroethane (3.8 kcal.) and 1,1,1-trichloroethane (3.0 kcal.) (b): (a) M. M. Kreevoy and E. A. Mason, THIS JOURNAL, **79**, 4851 (1957); (b) J. C. M. Li and K. S. Pitzer, *ibid.*, **78**, 1077 (1956).

(17) $(bb)_{60}$ is the interaction of two bromine atoms making an angle of 60 degrees when projected on a plane perpendicular to the carbon bond. $(hh)_{60}$ and $(bh)_{60}$ are hydrogen–hydrogen and bromine–hydrogen interactions. More remote interactions of the type $(bh)_{120}$ and $(hh)_{180}$ are neglected.

(18) Depending on the theoretical approach, the contributions of orbital rehybridization, multipole interactions, resonance, solvent stabilization or other factors may be implicit.[2,16]

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.

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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

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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

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(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-