take place (see preparation of tris-(methylamino)-borane in Experimental section).

Table II compares the percentage conversion of some selected transamination reactions with the basicities of the entering and leaving amine. It is seen that when isopropylamine or diethylamine are the leaving groups, in general the reaction rates increase with increasing basicity of the entering amine which is consistent with a mechanism of simple nucleophilic displacement on boron of one amine by a second amine. However, it also is seen that in general the steric requirements of the entering amine are decreasing with increasing basicity which makes it impossible to separate the relative importance of the amine basicities and steric effects on the reaction rates.

Our findings disagree with those reported by Aubry and Lappert[16] in a paper which appeared since presentation[17] of this work at Cleveland. These workers stated that a primary amine will displace a secondary amine but that the reverse reaction will not occur. However, we observed that both piperidine and N-methylaniline displaced isopropylamine.

In general, secondary amines reacted more slowly than primary amines or piperidine, a secondary amine with the alkyl groups "tied back." The only amine which failed to react was diisopropylamine, which would displace neither isopropylamine nor diethylamine from boron. This might be due to prohibitive steric requirements of a tetrahedral transition state or of the final product. Examination of Fisher–Hirschfelder–Taylor models indicates that the sterically-hindered trigonal coplanar tris-(diisopropylamino)-borane, a compound unsuccessfully sought in this Laboratory, could not be assembled which indicates the impossibility of forming the quadricovalent tetrahedral intermediate or transition state.

Boron–nitrogen compounds which can be transaminated include tris-(alkylamino)-boranes, bis-

(16) D. W. Aubry and M. F. Lappert, *Pro. Chem. Soc.*, 148 (1960).

(17) I. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., revised edition, 1953.

(alkylamino)-arylboranes, B-trialkyl-N-trialkyl-borazoles and B-tris-(alkylamino)-N-trialkylbor-azoles. There have been previous observations[18] that amines and borazoles will react; however, the nature of the reaction and the identity of the products were not elucidated.

It was found in this work that hexaalkylborazoles undergo a reaction

$$3RB(NHR')_2 + 3RNH_2 \quad (3)$$
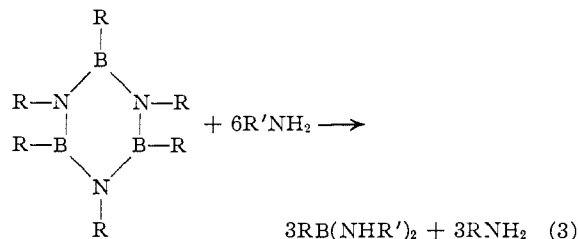
In the aminolysis of B-tris-(isopropylamino)-N-triisopropylborazole with piperidine there was some evidence that the ring B–N bonds were opened before reaction of the exocyclic B–N bonds,[19] since no trace of isopropylamine was evidenced until piperidine in excess of three moles per mole of borazole had been added. It is likely that an intermediate compound such as bis-(isopropyl-amino)-piperidinoborane was formed, although this was not isolated.

$$2\ i\text{-}Pr\cdot NH_2$$
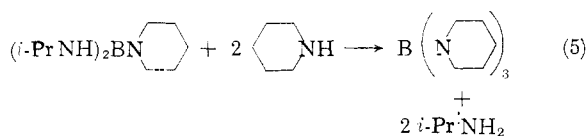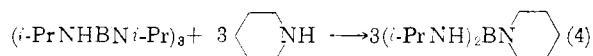
Since the transamination of boron–nitrogen compounds takes place readily with a wide variety of reactants, it appears to be a reaction of significant preparative value.

(18) (a) A. Stock and E. Pohland, *Ber.*, **59**, 2215 (1926); (b) E. Wiberg and A. Bolz, *ibid.*, **73**, 209 (1940).

(19) The hydrolysis of B-aminoborazoles was reported [K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, **81**, 3561 (1959)] to cause initial rupture of the exocyclic B–N bond.

Derivatives of Aromatic Sulfinic Acids. IV. The Absolute Configurations of Asymmetric Sulfur in Epimeric Sulfinic Esters[1]

BY HARRY F. HERBRANDSON AND CARMEN M. CUSANO

Equilibration of (−)-menthyl (+)-p-iodobenzenesulfinate and (−)-menthyl (−)-p-iodobenzenesulfinate in nitrobenzene at 25° gives a mixture which contains 59 ± 3% of the (+)-epimer. To ethoxide-ion catalyzed ethanolysis, the (+)-epimer is more reactive by a factor of about two. These facts have been interpreted in terms of a tentative assignment of absolute configurations to the asymmetric sulfurs and of conformations to the two esters.

Epimeric sulfinic esters which differ only in the configuration of the sulfur previously have not been obtained in a pure form, although Phillips[2] was able to obtain pure (−)-menthyl (−)-p-toluenesulfinate and its impure epimer (−)-

(1) This work was supported in part by the Office of Naval Research.

(2) H. Phillips, *J. Chem. Soc.*, **127**, 2552 (1925).

menthyl (+)-and (±)-p-toluenesulfinate. p-Iodo-benzenesulfinic acid has been found to give (−)-menthyl esters of sufficiently high melting points that the two diastereoisomers can be separated by fractional crystallization. This has permitted a study of the differences in reactivity of the two epimers, and we wish to report on the determina-

tion of their relative stabilities by equilibration measurement and on their relative reactivities to base-catalyzed ethanolysis. Since the differences in stabilities and reactivities of the two epimers is the sole consequence of the difference in configuration of the sulfurs, conformational analysis of these differences permits a tentative assignment of configuration to the asymmetric sulfur.

Results

Equilibration of Epimers.—The epimerizations of optically pure (−)-menthyl (−)-p-iodobenzenesulfinate and (−)-menthyl (+)-p-iodobenzenesulfinate catalyzed by hydrogen chloride and tetraethylammonium chloride in nitrobenzene at 25.00 ± 0.05° were followed polarimetrically. As in previous work,[3] the reactions were pseudo first order in ester, demonstrating good adherence to a first-order plot for more than three half-lives. The pseudo-first-order rate constants, k', were obtained by the method of least squares from data plotted according to Guggenheim.[4] To calculate the concentrations of hydrogen chloride and chloride ion free to catalyze the reactions, the value 500 l. mole^{-1} was used for the association constant of the hydrogen dichloride anion.[3] The third-order rate constants, k, obtained from the expression $k' = k[\text{HCl}][\text{Cl}^-]$, were 66 ± 5 l.^{2} mole^{-2} sec.$^{-1}$ for seven runs with the levorotatory ester and 66 ± 8 l.^{2} mole^{-2} sec.$^{-1}$ for seven runs with the dextrorotatory ester.

The composition of the equilibrated ester mixture was calculated from the rotations of the solutions after equilibration had been achieved, i.e., from the α_∞. The α_∞ for each kinetic run was obtained in two ways: (1) from direct observation after the elapse of about 10 half-lives and (2) from substitution of values of α, α_0, k' and t observed during the course of a kinetic run into the expression ln $((\alpha{-}\alpha_\infty)/(\alpha_0{-}\alpha_\infty)) = k't$. Although results from the two methods agreed within their standard deviations, the values from the second method were chosen as more accurate for the same reason that the method of Guggenheim was used in determining the specific rate constants: contributions from minor side reactions that would lead to drift in the infinite point over a period of 10 half-lives were minimized. The position of equilibrium whether approached from the side of the dextrorotatory or the levorotatory epimer was the same with the dextrorotatory ester being present as 59 ± 3% of the total ester at equilibrium.

Ethanolysis of Epimers.—The rate of the ethoxide-ion catalyzed ethanolysis of (−)-menthyl (+)-p-iodobenzenesulfinate, followed polarimetrically, was about twice that of the (−)-isomer. In both cases the reactions were pseudo first order in ester. The second-order rate constants at 25.00 ± 0.05°, $k'/[\text{OC}_2\text{H}_5{}^-]$, are recorded in Tables I and II, and Table III contains a summary of the second-order rate constants which were determined at 15.00 ± 0.05°, 25.00 ± 0.05° and 35.00 ± 0.05°. The enthalpies and entropies of activa-

(3) Harry F. Herbrandson and Richard T. Dickerson, Jr., *J. Am. Chem. Soc.*, **81**, 4102 (1959).

(4) E. A. Guggenheim, *Phil. Mag.*, [VII] **2**, 538 (1926).

TABLE I

ETHOXIDE-ION CATALYZED ETHANOLYSIS OF (−)-MENTHYL (−)-p-IODOBENZENESULFINATE AT 25.00 ± 0.05°

Init. ester, mole/l.	Ethoxide ion, mole/l.	$k' \times 10^3$, sec.$^{-1}$	$k'/[\text{OC}_2\text{H}_5{}^-]$, l. mole^{-1} sec.$^{-1}$
0.0050	0.00158	0.468	0.296
.0050	.00315	0.923	.293
.0050	.00315	1.12	.356
.0050	.00630	2.11	.335
.0050	.00944	3.32	.352
.0050	.00158	0.442	.280
.0028	.00158	0.445	.282
.0050	.00463	1.56	.336
.0050	.00309	0.908	.294

TABLE II

ETHOXIDE-ION CATALYZED ETHANOLYSIS OF (−)-MENTHYL (+)-p-IODOBENZENESULFINATE AT 25.00 ± 0.05°

Init. ester, mole/l.	Ethoxide ion, mole/l.	$k' \times 10^3$, sec.$^{-1}$	$k'/[\text{OC}_2\text{H}_5{}^-]$, l. mole^{-1} sec.$^{-1}$
0.0099	0.00155	0.805	0.519
.0099	.00309	1.81	.586
.0099	.00463	2.80	.604
.0099	.00618	3.38	.547
.0099	.00309	1.55	.502
.0100	.00463	2.40	.518

TABLE III

SECOND-ORDER RATE CONSTANTS FOR THE ETHOXIDE-ION CATALYZED ETHANOLYSIS OF EPIMERIC (−)-MENTHYL p-IODOBENZENESULFINATES (IN L. MOLE^{-1} SEC.$^{-1}$)

Temp., °C.	(+)-Epimer	(−)-Epimer
15.00 ± 0.05	0.28 ± 0.02	0.15 ± 0.02
25.00 ± .05	0.55 ± .04	.31 ± .03
35.00 ± .05	1.21 ± .05	.64 ± .04

TABLE IV

ENTHALPIES AND ENTROPIES OF ACTIVATION FOR THE ETHOXIDE-ION CATALYZED ETHANOLYSIS OF EPIMERIC (−)-MENTHYL p-IODOBENZENESULFINATES

	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.
(+)-Epimer	12.4 ± 0.7	−18.1 ± 2.4
(−)-Epimer	12.1 ± 1.3	−20.3 ± 4.2

tion, determined by the least squares method, and their precision[5] are recorded in Table IV.

The relatively large errors in the activation parameters result from a lack of precision in the kinetic measurements that is a consequence of the low solubilities of the esters in ethanol. The maximum solubility of the less soluble (−)-epimer is approximately 0.01 mole l.$^{-1}$ and the total changes in rotation observed were in the order of 0.2 − 0.3°.

Discussion

Equilibration of Epimers.—The identity of the rates of the hydrogen chloride–chloride ion catalyzed reactions of the epimeric esters, 66 ± 5 and 66 ± 8 l.^{2} moles^{-2} sec.$^{-1}$, is confirmatory evidence that the reaction being followed is the equilibration of the epimers, since the rate of the reaction, observed polarimetrically, is the sum of the rates for the forward and reverse reactions.[3]

The difference of 215 ± 45 cal. in stability of the (+)- and (−)-epimers must result from the

(5) W. A. Pavelich and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **79**, 4935 (1957).

interaction of the asymmetrically placed substituents on the sulfur with the asymmetric menthyl group. Nine conformations about the sulfinic ester group may exist for each epimer if relatively

$$\overset{O}{\underset{\|}{}}$$

free rotation is permissible about both the –S–O– and the –O–C– bonds. With the analogous carboxylic

$$\overset{O}{\underset{\|}{}}$$

esters, restriction of rotation about the –C–O– bond[6] is quite well understood and may be expressed in terms of resonance interaction, which tends to hold the carbonyl and alkoxy groups coplanar, and of either dipole repulsion between the carbonyl and alkoxy bond dipole[7] or repulsion between lone-pair electrons on the alkoxy oxygen and the lone-pair electrons and/or the π-electrons of the carbonyl group.[8] The consequence is the observed, relatively planar, *trans* conformation:

$$R-\overset{O}{\overset{\|}{C}}\diagdown\diagup R'.$$
$$\overset{}{O}$$
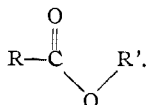
There is no comparable knowledge concerning

$$\overset{O}{\underset{\|}{}}$$

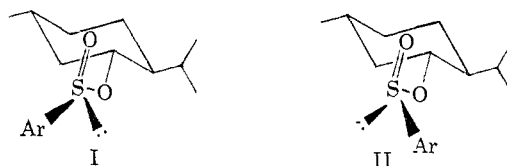possible restriction of rotation about the –S–O– bond. Although experimental evidence for conjugation in the ground state of sulfinyl compounds has been reported,[9] resonance interaction between the alkoxy oxygen and the sulfur through p-d-orbital overlap is presumably small and in any case need not constrain the alkoxy and sulfinoxy groups to be coplanar.[10] However, the sulfinoxy group is even more polar than the carbonyl group,[11] so dipole repulsions tending to hold the groups at 180° to each other should be even greater with sulfinic esters than with carboxylic esters. Until evidence is forthcoming concerning the exact structure of sulfinic esters, we propose that this dipole repulsion may be sufficient to hold the sulfinic ester group in a conformation which would be equivalent to the *trans* form of the carboxylic ester.

$$\underset{Ar}{\overset{O}{\overset{\|}{\diagup}}S}\diagdown\underset{O}{}\diagup R$$
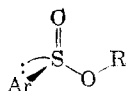
Of the three conformations about the –O–$C_{10}H_{19}$ bond, the one with the sulfoxide oxygen located between the small (H) and the medium (CH_2) groups should be of lowest energy.[14] Since the

(6) D. Tabuchi, *J. Chem. Phys.*, **28**, 1014 (1958).

(7) R. F. Curl, Jr., *ibid.*, **30**, 1529 (1959); C. P. Smyth, "Dielectric Behavior and Structure," McGraw–Hill Book Co., Inc., New York, N. Y., 1955, p. 303; R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 1383 (1936).

(8) D. Cook, *J. Am. Chem. Soc.*, **80**, 49 (1958).

(9) F. G. Bordwell and P. J. Boutan, *ibid.*, **79**, 717 (1957); S. Detoni and D. Hadzi, *J. Chem. Soc.*, 3163 (1955); G. Cilento, *Chem. Revs.*, **60**, 147 (1960).

(10) H. H. Jaffé, *J. Phys. Chem.*, **58**, 185 (1954).

(11) Compare, for example, the dipole moments of diethyl sulfoxide, 3.85 D.,[12] and diethyl ketone, 2.72 D.[13]

(12) E. N. Gur'yanova, *Zhur. Fiz. Khim.*, **24**, 479 (1950); *C. A.*, **44**, 8181 (1950).

(13) J. Granier, *Compt. rend.*, **223**, 893 (1946).

(14) (a) D. J. Cram and F. A. A. Elhafez. *J. Am. Chem. Soc.*, **74**, 5828 (1952); (b) V. Prelog, *Helv. Chim. Acta*, **36**, 308 (1953).

absolute configuration of (–)-menthol is known,[14b,15] the two epimers may then tentatively be written as I and II. Structure II results in extensive inter-

ference between the aromatic ring and the isopropyl group on the C_4 of the menthol and should represent the thermodynamically less stable (–)-menthyl (–)-p-iodobenzenesulfinate or, now including the configuration of the asymmetric sulfur,[16] (–)-menthyl S(–)-p-iodobenzenesulfinate; structure I should represent the more stable (–)-menthyl R(+)-p-iodobenzenesulfinate.

The $\Delta F°$ of –215 ± 45 cal. for conversion of the (–)-epimer to the (+)-epimer compares with values of from 0–800 cal. for the differences between other acyclic diastereoisomeric pairs as cited by Cram.[17]

Ethanolysis of the Epimers.—Very precise measurements of the rates of ethanolysis were precluded by the insolubility of the esters, a fact that necessitated the use of very dilute solutions, and the very high rates of reaction, more than 10^4 times as great as for the base-catalyzed methanolysis of the analogous (–)-menthyl benzoates.[18] In every case, the optical activity of the solution at the completion of the ethanolysis corresponded to that value to be expected from a concentration of (–) menthol equivalent to the amount of ester originally present. This, together with the fact that the pseudo-first-order reaction was truly second order, first order in ester and first order in ethoxide, is good evidence for attack by ethoxide on sulfur in the rate-determining step comparable to Ingold's $B_{Ac}2$ mechanism for carboxylic esters.[19] In contrast to the acyl fission reactions of carboxylic esters, which take place through nucleophilic attack perpendicular to the plane of the carboxyl group,[13b] the uncatalyzed alcoholysis of sulfinic esters results in inversion at the sulfur, presumably as a consequence of attack on the side opposite to that of the leaving group.[2] That the reactions exhibited good pseudo-first-order kinetics over periods of 2–3 half-lives provides evidence that if the reaction proceeds through a back-side attack on sulfur by the alkoxide ion, the ethyl p-iodobenzenesulfinate formed by inversion must not maintain its optical identity for any finite period of time. The optically active ethyl p-iodobenzenesulfinate that is formed must undergo rapid racemization by alkoxide interchange. No evidence

(15) A. J. Birch, *Ann Repts. Progr. Chem. (Chem. Soc. London)*, **47**, 191 (1950).

(16) R. S. Cahn and C. K. Ingold, *J. Chem. Soc.*, 612 (1951); R. S. Cahn, C. K. Ingold and V. Prelog, *Experientia*, **12**, 81 (1956).

(17) D. J. Cram in "Steric Effects in Organic Chemistry," M. S. Newman, editor, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 272.

(18) R. W. Taft, Jr., M. S. Newman and F. H. Verhoek, *J. Am. Chem. Soc.*, **72**, 4511 (1950).

(19) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry." Cornell University Press, Ithaca, New York 1953, p. 754; (b) M. L. Bender, *Chem. Revs.*, **60**, 53 (1960).
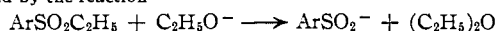
for prior complex formation between the ethoxide and ester was evident, as extrapolation back to zero time of log $(\alpha - \alpha_\infty)$ gave values for α in good agreement with those to be expected from the amounts of ester used initially.

The following sequence of reactions with $k_2 \gg k_1$ can account for the observations.[20]
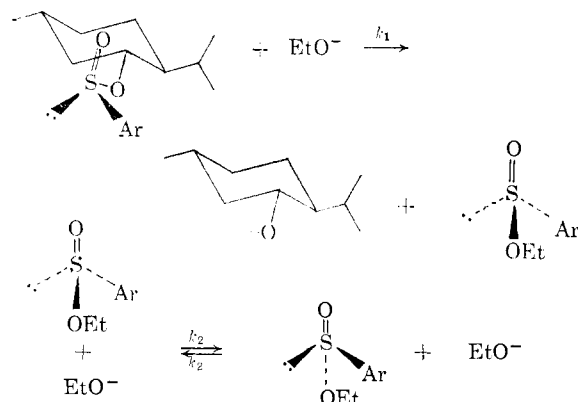
The data of Table III show that $(-)$-menthyl $(+)$-p-iodobenzenesulfinate (I), the thermodynamically more stable epimer in nitrobenzene, undergoes ethoxide ion-catalyzed ethanolysis in ethanol more rapidly than its less stable epimer. If the reaction proceeds as shown above, backside attack on the sulfur of either epimer by the ethoxide ion should proceed with equal ease, since the ethoxide ion in attacking is confronted by the same groups in either case, only arranged in opposite order around the sulfur. That the more stable isomer is more reactive by a factor of about two must be the consequence of stereochemical interaction between the asymmetrically placed groups on the sulfur and the asymmetric menthyl ring. If the absolute configurations of the sulfurs are as they were assigned on the basis of the thermodynamic stabilities of the esters, the lower reactivity of II, the less stable epimer, may be interpreted in terms of increased steric

interaction between the aromatic ring and the isopropyl group in the transition state as the sulfur goes through a planar configuration in the course of inverting. This steric interaction in the transition state should be more marked with the less stable $(-)$-menthyl $S(-)$-p-iodobenzenesulfinate (II) than with the $(-)$-menthyl $R(+)$-p-iodobenzenesulfinate (I).

The enthalpies and entropies of activation, Table IV, although not precise, tend to support the above conclusions. The major contribution to the difference in free energies of activation is provided by the entropies of activation which favor the reaction of the more stable $(+)$-epimer.

Another example of faster reaction of the more stable of two epimers as a consequence of less steric compression in the transition state is provided by the more rapid saponification of trans-4-t-butylcyclohexyl acid phthalate compared to its cis-isomer.[24]

Experimental[25]

p-**Iodobenzenesulfinic acid** was prepared in 90% yield from p-iodobenzenesulfonyl chloride in a manner analogous to the preparation of the p-chloro acid.[26] It had a m.p. that depended upon the rate of heating; values from 129–130° dec. to 157° dec. were obtained (lit. m.p. 100°,[27] 137°,[28] 160°[29]); neut. equiv. calcd. 268, found 272.

p-**Iodobenzenesulfinyl Chloride.**—Freshly purified thionyl chloride (170 g., 1.43 moles) was added slowly with stirring to 76.6 g. (0.285 mole) of p-iodobenzenesulfinic acid, and the mixture was refluxed for 30 minutes. Rapid filtration removed a small amount of suspended material, after which concentration in vacuo with subsequent addition and distillation of dry benzene gave 80 g. (0.28 mole, 98%) of crude product free of thionyl chloride; m.p. 92–95°.

Reaction of p-**Iodobenzenesulfinyl Chloride with** $(-)$-**Menthol.**—A solution of 44 g. (0.28 mole) of $(-)$-menthol in 22.5 g. (0.285 mole) of dry pyridine was added slowly, with stirring, to 80 g. (0.280 mole) of p-iodobenzenesulfinyl chloride suspended in 400 ml. of dry ether. After completion of the reaction, the pyridine hydrochloride was extracted with water, and the insoluble ester, 55 g., m.p. 100–140°, was removed by filtration. The ether layer, after being washed with dilute hydrochloric acid, sodium carbonate solution and water, was dried and the ether was removed to yield 55 g. of more soluble ester, m.p. 84–100°.

$(-)$-**Menthyl** $(-)$-p-**Iodobenzenesulfinate.**—One crystallization from acetone of the less soluble ester fraction, m.p. 100–140°, gave a product of m.p. 135–145°, $[\alpha]^{22}D - 117°$ (in acetone). Further simple recrystallizations failed to accomplish any more separation, but large, well-formed crystals, m.p. 146–148°, $[\alpha]^{26}D - 145°$ (in acetone), could be grown from a 10% solution in acetone at 32°. Two further recrystallizations by this method gave a product (20 g.) of m.p. 145.5°, $[\alpha]^{22}D - 145.80$ (c 0.6 in acetone), $[\alpha]^{25}D - 150.7°$ (c 0.6 in nitrobenzene).

Anal. Calcd. for $C_{16}H_{23}O_2SI$: C, 47.26; H, 5.68; S, 7.89; I, 31.35. Found: C, 47.15; H, 5.44; S, 8.14; I, 31.30.

$(-)$-**Menthyl** $(+)$-p-**Iodobenzenesulfinate.**—Several fractional crystallizations from acetone of the more soluble ester fraction, m.p. 84–100°, gave 22 g. of product, m.p. 96–98°, $[\alpha]^{26}D + 21.6°$ (in acetone), that could be purified no further by simple fractional crystallizations. Further removal of the less soluble, higher melting epimer was accomplished by crystallization from aqueous acetone with isolation of the desired, more soluble epimer from the mother

(20) A referee has suggested that a change from the menthyl to ethyl ester should not increase the rate of the displacement reaction enough that $k_2 \gg k_1$ and suggests instead that racemization may be caused by the reaction

$$\text{ArSO}_2\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{O}^- \longrightarrow \text{ArSO}_2^- + (\text{C}_2\text{H}_5)_2\text{O}$$

This reaction would appear *a priori* to be unimportant since if it were ot have a rate constant significantly greater than k_1, *i.e.*, of the order of magnitude of 10 l. mole^{-1} sec.$^{-1}$, th reaction would be at least 3 × 10³ times faster than the simple nucleophilic displacement reaction of ethyl p-bromobenzenesulfonate with ethoxide ion in ethanol.[21] There is no evidence in the literature supporting the view that aromatic sulfinates are better by a factor of 10³ as leaving groups than are aromatic sulfonates, but there is ample evidence that nucleophilic attack by strong bases on the sulfur of sulfinates (see above) and of the analogous sulfite esters[22] is extremely rapid. This view is supported by our isolation of racemic ethyl p-nitrobenzenesulfinate, m.p. 50.2–51.2° (lit.[23] m.p. 49–51°), in a 30% yield from the reaction of $(-)$-menthyl $(-)$-p-nitrobenzenesulfinate with sodium ethoxide in anhydrous ethanol. The low recovery of ethyl ester may be attributed largely to the difficulty of separating it from $(-)$-menthol (unpublished results).

(21) M. S. Morgan and L. H. Cretcher, *J. Am. Chem. Soc.*, **70**, 375 (1948).

(22) C. A. Bunton, P. B. D. de la Mare, A. Lennard, D. R. Llewelyn, R. B. Pearson, J. G. Pritchard and J. G. Tillett, *J. Chem. Soc.*, 4761 (1958).

(23) T. Dewing, W. H. Gray, B. C. Platt and D. Stephenson, *ibid.*, 239 (1942).

(24) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955).

(25) Melting points are corrected. Microanalyses by Dr. G. Weiler and Dr. F. B. Strauss, Oxford, Eng.

(26) M. Kulka, *J. Am. Chem. Soc.*, **72**, 1215 (19 50).

(27) M. E. Hanke, *ibid.*, **45**, 1321 (1923).

(28) E. Knoevenagel and L. Polack, *Ber.*, **41**, 3323 (1908); J. Troeger and F. Hurdelbrink, *J. prakt. Chem.*, [2] **65**, 82 (1902).

(29) J. Troeger and F. Volkmer, *ibid.*, [2] **71**, 236 (1905).

liquor. This ultimately gave 8 g. of ester, m.p. 97–98°, $[\alpha]^{25}$D + 22.70° (c 1.5 in acetone), $[\alpha]^{25}$D + 22.00° (c 1.5 in nitrobenzene).

Anal. Calcd. for $C_{15}H_{23}O_2SI$: C, 47.26; H, 5.68; S, 7.89; I, 31.35. Found: C, 47.26; H, 5.08; S, 8.11; I, 31.50.

Although the esters appeared to be quite stable, they were kept in a desiccator in the dark.

Kinetic Measurements.—The kinetics of the epimerization reactions were determined at 25.00 ± 0.05° as reported previously.[3]

For the ethanolysis reactions, stock solutions of sodium ethoxide were prepared by dissolving sodium, cleaned and weighed under dry ether, in dry ethanol[30] and transfer of the supernatant solution from traces of undissolved material

to a polyethylene bottle that was stored in a desiccator in the dark. The solution was standardized just before use by addition of an aliquot to an excess of standard acid and back titration with standard sodium hydroxide solution. The ethoxide solutions were discarded after two weeks of use.

To carry out a kinetic run, ester was weighed into a volumetric flask and dissolved in anhydrous ethanol. This solution, as well as the other reagents, was then thermostated at the appropriate temperature for 30 minutes. The sodium ethoxide solution, standardized at the temperature of use, was added to the flask to start the reaction and the flask was immediately filled to the mark with anhydrous ethanol. After mixing, the solution was transferred to a thermostated polarimeter tube. Determination of the water temperature at the inlet and outlet of the thermostating jacket of the tubes showed that the maximum temperature variation was ±0.05°.

(30) E. L. Smith, *J. Chem. Soc.*, 1288 (1927).

The Kinetics of Bromination of Polymethylbenzenes in Chloroform. Catalysis by Iodine Bromide

By Roy Josephson, R. M. Keefer and L. J. Andrews

In chloroform, as contrasted to carbon tetrachloride, polymethylbenzenes are subject to uncatalyzed nuclear bromination. The reactions are second order in halogen. In the presence of iodine bromide as a catalyst these reactions are first order in bromine and first order in the catalyst. The corresponding reactions in carbon tetrachloride are second order with respect to the catalyst. At moderately high concentrations of aromatic hydrocarbon the observed third-order rate constants diminish with increasing hydrocarbon concentration. Some of this decrease is attributable to the formation of molecular complexes and some of it results because of the change in the polar character of the medium. The activation energies for the reactions in chloroform are very small or slightly negative. These results are discussed in terms of the probable mechanism for polar aromatic halogenations.

In acetic acid mesitylene undergoes nuclear bromination by a third-order process (first order in mesitylene and second order in bromine).[1,2] At very low bromine concentrations a term which is first order in halogen also makes a significant contribution to the over-all rate law. The two reactants show an appreciable tendency to interact to form a molecular complex (eq. 1) in acetic acid. Even at moderate mesitylene concentrations

$$\text{ArH} + \text{Br}_2 \rightleftharpoons \text{ArH·Br}_2 \qquad K_1 = \frac{[\text{ArH·Br}_2]}{[\text{ArH}][\text{Br}_2]} \quad (1)$$
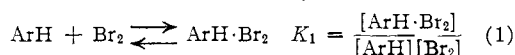
the extent of the interaction is sufficient so that the difference between the total $[\text{Br}_2]_T$ and free bromine concentration of the medium is appreciable (eq. 2). It should follow, therefore, that if

$$[\text{Br}_2]_T = [\text{Br}_2] + [\text{ArH·Br}_2] \qquad (2)$$

the rate-determining step of the third-order reaction involves one mesitylene and two free bromine molecules (or a bromine molecule and the 1:1 complex), the experimental k_1 values for that third-order reaction which are based on eq. 3 should diminish according to eq. 4 with increasing mesitylene concentration of the medium. Actually the

$$-d[\text{Br}_2]_T/dt = k_1[\text{ArH}][\text{Br}_2]_T{}^2 \qquad (3)$$

$$k_1 = k_a/(1 + K_1[\text{ArH}])^2 \qquad (4)$$

depression in k_1 with increases in mesitylene concentration is much larger than predicted on the basis of the experimental value for K_1. Presumably, then, the dilution of the polar solvent with even

relatively small amounts of the non-polar aromatic hydrocarbon has a significantly unfavorable "medium effect" on the polar bromination process.

In moist carbon tetrachloride mesitylene undergoes hydrogen bromide-catalyzed bromination by a process which is first order with respect to each reactant and half order with respect to the catalyst.[3] As should be the case if a mesitylene molecule and a *free* bromine molecule (or a 1:1 mesitylene–bromine complex) are involved in the rate-determining step, the experimental rate constants, k_{obs}, diminish with increasing mesitylene concentration as predicted by eq. 5. That is, in

$$\frac{-d[\text{Br}_2]_T}{dt} = k_{obs}[\text{Br}_2]_T[\text{ArH}][\text{HBr}]^{1/2} =$$
$$\frac{k'[\text{Br}_2]_T[\text{ArH}][\text{HBr}]^{1/2}}{1 + K_1[\text{ArH}]} \quad (5)$$

contrast to what is observed for reaction in acetic acid, no significant rate effects attributable to changes in character of the medium with changes in the aromatic hydrocarbon content are found for the reaction in carbon tetrachloride.

The bromination of mesitylene in carbon tetrachloride is also catalyzed by iodine bromide.[4,5] The reaction is first order in total bromine and second order with respect to the catalyst. Iodine bromide, as well as bromine, interacts with mesitylene in carbon tetrachloride, and the equilibrium

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(5) J. H. Blake and R. M. Keefer, *J. Am. Chem. Soc.*, **77**, 3707 (1955).