a 95% ethanol solution of it with a few crystals of the latter crystalline modification.

Treatment of Nitrile VII with Two Equivalents of Potassium Amide and One of Benzyl Chloride.—To a stirred solution of 0.2 mole of potassium amide in 300 ml. of liquid ammonia[12] was added 37.3 g. (0.1 mole) of 2,3,3,4-tetraphenylbutyronitrile (VII). The resulting green solution was stirred for 15 minutes, and 12.6 g. (0.1 mole) of benzyl chloride in a little ether then was added. The first few ml. of the halide solution produced a purple color which persisted until a few seconds after all of the halide had been added. After stirring for 5 minutes, excess (15 g.) ammonium chloride was added and the ammonia was evaporated as an equal volume of ether was added. The resulting ethereal suspension was shaken with water. The aqueous layer was extracted with ether containing some ethyl acetate and the extracts were combined with the ethereal layer. The ethereal ethyl acetate solution was dried and the solvents removed. The residue was taken up in hot benzene and about 800 ml. of petroleum ether (b.p. 30–60°) was added. The solution was cooled in an ice-bath to precipitate slowly 30.7 g. (83%) of recovered nitrile VII, m.p. 136–138°. The remaining liquors were concentrated to a small volume on the steam-bath and hot ethanol was added. Cooling produced 6.9 g. (77%) of stilbene, m.p. 110–112°, slightly contaminated with the nitrile. Recrystallization of the hydrocarbon from ethanol raised the melting point to 119–121°. Admixture with an authentic sample of stilbene, m.p. 122–124°, did not depress the melting point.

Independent Synthesis of β-Benzyl Derivative VII.—2,3,3-Triphenylacrylonitrile was prepared by the condensation of phenylacetonitrile with benzophenone in the presence of sodium amide.[12]

To a stirred ethereal solution of benzylmagnesium chloride prepared from 0.22 mole each of magnesium turnings and benzyl chloride was added 48.25 g. (0.172 mole) of 2,3,3-triphenylacrylonitrile. After stirring for 5 hours the reaction mixture was poured into iced hydrochloric acid. The ethereal layer was separated from the aqueous mixture containing the insoluble hydrochloride as imine IX, and dried for 12 hours over magnesium sulfate. During this time more of the imine hydrochloride precipitated. The ethereal solution was filtered and the solvent removed. Recrystallization of the residue from ethanol produced 2.8 g. (4.4%) of 2,3,3,4-tetraphenylbutyronitrile (VII), m.p. 137–138°. Admixture of this product with the benzylation product (m.p. 138–139°) of the dicarbanion of nitrile III did not depress the melting point, and their infrared spectra were superimposable.

The imine salt was converted to the corresponding ketone by boiling for one hour with 12 *M* hydrochloric acid. The water was decanted and the residue recrystallized from ethanol and acetone to give 22 g. (34%) of 1,3,4,4-tetraphenylbut-3-ene-2-one (XVI), m.p. 139–144°, yellow needles. Recrystallization from ethanol raised the melting point to 149–150°.

Anal. Calcd. for $C_{28}H_{22}O$: C, 89.80; H, 5.92. Found: C, 89.83; H, 6.06.

The infrared spectrum of the imine hydrochloride showed a broad band at 3.55 and a sharp band at 6.05 μ.[7] These bands were absent in ketone XVI which had a well defined carbonyl band at 5.9 μ.[13]

Benzylation of the Monocarbanion IV to form α-Benzyl Derivative XIII.—To a stirred solution of 0.05 mole of potassium amide in 300 ml. of liquid ammonia was added 14.2 g. (0.05 mole) of solid 2,3,3-triphenylpropionitrile (III) by means of a powder funnel. The resulting light green solution of monocarbanion IV was stirred for 15 minutes, and 6.3 g. (0.05 mole) of benzyl chloride in an equal volume of ether then was added. The reaction mixture was allowed to stir until the ammonia had evaporated completely. Water was added and the product collected on a büchner funnel. The filter cake was washed with water, dried and washed with a little petroleum ether (b.p. 30–60°). There was obtained 18.14 g. (97%) of 2-benzyl-2,3,3-triphenylpropionitrile (XIII), m.p. 182–185°. Two recrystallizations from absolute ethanol raised the melting point to 185.5–187°. The infrared spectrum of this compound showed a band at 4.45 μ attributable to the cyanide group, but an absence of absorption about 6 μ, a region in which imines have been observed to absorb.[7] This spectrum differed from that of 2,3,3,4-tetraphenylbutyronitrile (VII) in the fingerprint region.

Anal. Calcd. for $C_{28}H_{23}N$: C, 90.04; H, 6.21; N, 3.75. Found: C, 90.14; H, 6.33; N, 3.88.

Treatment of Dicarbanion V with Methylene Chloride.—To a stirred solution of 0.2 mole of potassium amide in 500 ml. of liquid ammonia was added 28.3 g. (0.1 mole) of 2,3,3-triphenylpropionitrile (III). The resulting red solution of dicarbanion V was stirred for 10 minutes, and 10.2 g. (0.12 mole) of methylene chloride in 50 ml. of ether then was added. After stirring for 1.5 hours (red color still present), the ammonia was replaced with ether. Water was added and the ethereal layer washed with 6 *M* hydrochloric acid, followed by water. The ethereal solution was dried and the solvent removed. The residue was taken up in hot methanol, and then treated with Norite to give on cooling 18.7 g. (64%) of apparently 1,2,2-triphenylcyclopropyl cyanide (XVII), m.p. 118–121°. Five recrystallizations from methanol raised the melting point to 131.5–132.5°.

Anal. Calcd. for $C_{22}H_{17}N$: C, 89.46; H, 5.80; N, 4.74; mol. wt., 295. Found: C, 89.69; H, 5.80; N, 4.73; mol. wt., 299, 286, 278, 291.

The infrared spectrum of the nitrile gave the following bands: 3.27, 4.45, 6.25, 6.30, 6.68, 6.88, 8.62, 9.26, 9.70, 9.85, 10.17, 12.68, 13.29, 14.15, 14.37 μ. The nuclear magnetic resonance spectrum of a saturated carbon disulfide solution of XVII indicated the presence of both aromatic and aliphatic hydrogens in the molecule.[14] The aromatic absorption was much stronger and could be resolved into four distinct bands.

DURHAM, N. C.

---

(12) *Org. Syntheses*, **31**, 52 (1951).

(13) See ref. 7, p. 114.

(14) We are indebted to G. S. Paulett for the interpretation of the nuclear magnetic resonance spectrum which was determined in this Laboratory on a Varian N.M.R. Spectrometer, model V4300B.

[CONTRIBUTION FROM THE WALKER LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

Derivatives of Aromatic Sulfinic Acids. III. Evidence for the Hydrogen Dichloride Ion from Epimerization Reactions[1]

BY HARRY F. HERBRANDSON AND RICHARD T. DICKERSON, JR.

RECEIVED AUGUST 11, 1958

Asymmetric sulfinic esters, ArS(O)OR, epimerize at the sulfur atom when treated in nitrobenzene with hydrogen chloride and chloride ions as co-catalysts. The mechanism of the reaction is discussed, and the kinetics is interpreted as giving a value of 500–1000 l. mole^{-1} for the association constant of the hydrogen dichloride ion in nitrobenzene at 25°: $Cl^- + H\cdot Cl \leftrightarrows ClHCl^-$.

The reactions of alkyl sulfites and alkyl arenesulfinates with thionyl chloride are very similar,[2] but kinetic studies are complicated by the ease of hydrolysis of the thionyl chloride. Since these es-

---

(1) This work was supported in part by the Office of Naval Research and in part by a grant from the R. P. I. Research Fund.

(2) H. F. Herbrandson, R. T. Dickerson, Jr., and J. Weinstein, THIS JOURNAL, **78**, 2576 (1956).

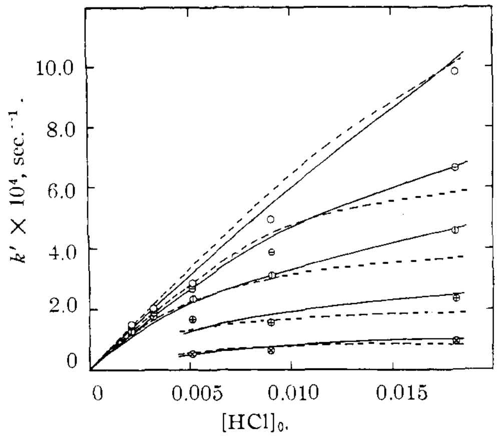


Fig. 1.—Epimerization of *l*-menthyl *l*-*p*-methoxybenzenesulfinate with tetraethylammonium chloride as co-catalyst (in mole/l.): ○, 0.01784; ⊖, 0.00892; ⦶, 0.00540; ⊕, 0.00270; ⊗, 0.00108; dashed curves from eq. 1; solid curves from eq. 8.

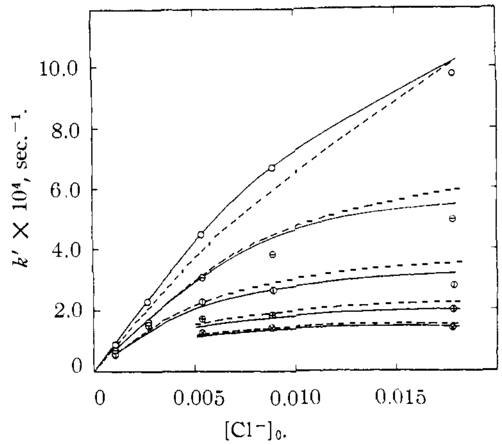
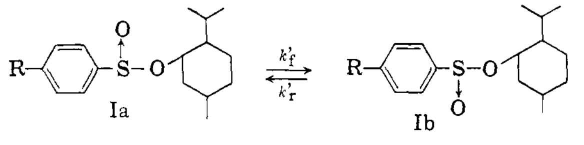


Fig. 2.—Epimerization of *l*-menthyl *l*-*p*-methoxybenzenesulfinate with hydrogen chloride as co-catalyst (in mole/l.): ○, 0.01816; ⊖, 0.00905; ⦶, 0.00514; ⊕, 0.00322; ⊗, 0.00218; dashed curves from eq. 1; solid curves from eq. 8.

ters serve as mild alkoxylating agents, an alkoxide acceptor other than thionyl chloride was sought which would simplify kinetic studies. Anhydrous hydrogen chloride, in nitrobenzene, has been found to serve this purpose very well.

Optically active *l*-menthyl esters of arenesulfinic acids (Ia, b) epimerize at the sulfur in the presence of low concentrations (0.001–0.02 molar) of hydrogen chloride and tetraethylammonium chloride.



Ia

Ib

The conclusion that the reaction is an epimerization[3] is a consequence of a number of observations. Concentration of the combined nitrobenzene solutions from a number of completed kinetic experiments gave, after recrystallization, 67% of the initially used *l*-menthyl *l*-*p*-toluenesulfinate. Thus, even though the reaction had ceased, as observed polarimetrically, unreacted levorotatory ester remained. This clearly resulted from the establishment of an equilibrium involving the ester, as the kinetics of the reaction (pseudo-first-order in ester) demonstrated no consumption of the catalysts.

Further evidence for an equilibrium between epimers resulted from the use of the catalysts on a preparative scale. The usual preparation of *l*-menthyl arenesulfinates from the arenesulfinyl chloride and *l*-menthol, in the presence of a base such as pyridine or potassium carbonate, leads to a mixture of the two epimers from which the less soluble, crystalline one can be isolated in about 30% yield.[4] Addition of gaseous hydrogen chloride or hydrogen chloride and tetraethylammonium chloride to the remaining liquid ester causes rapid conversion of the liquid ester to its crystalline epimer and permits its recovery in 70–90% yields.

Kinetic Results

The epimerization of *l*-menthyl *l*-arenesulfinates, catalyzed by tetraethylammonium chloride and hydrogen chloride in nitrobenzene at 25°, was followed polarimetrically. Three esters which behaved similarly were used, namely, *l*-menthyl *l*-benzenesulfinate, *l*-menthyl *l*-*p*-toluenesulfinate and *l*-menthyl *l*-*p*-methoxybenzenesulfinate. The rates-of-change in rotation were strictly first order for more than 2–3 half-lives, with the pseudo-first-order rate constant increasing only 2% for a 13-fold increase in initial ester concentration. Tetraethylammonium chloride alone had no effect on the esters, nor did hydrogen chloride, which in nitrobenzene is essentially un-ionized,[5] have any effect at concentrations below about 0.01 molar. At higher concentrations, hydrogen chloride led to a change in rotation that was dependent on the hydrogen chloride concentration approximately to the 2.5 power. Since this effect was observed only at relatively high concentrations of hydrogen chloride, it was not troublesome in most of the kinetic runs, and because the magnitude of the effect was known it could be corrected for in runs to which it did contribute.[6]

At a constant concentration of one of the catalysts, an increase in the concentration of the co-catalyst led to an increase in the pseudo-first-order rate constant that indicated a diminishing effectiveness of the catalysts at higher concentrations (Figs. 1 and 2). Typical data are recorded in Table I; the pseudo-first-order rate constant, k', was obtained from the expression $\ln(\alpha_2 - \alpha_1) = k't + C$ for the rate of epimerization of *l*-menthyl *l*-*p*-methoxybenzenesulfinate.

---

[3] The more soluble, lower-melting epimers of the esters used in this study have never been purified completely. However, Phillips[4] has demonstrated that *l*-menthyl *d*- + *dl*-*p*-toluenesulfinate isomerizes on long standing to *l*-menthyl *l*- + *dl*-*p*-toluenesulfinate. Recently we have obtained pure both epimers of a sulfinic ester. These will be the subject of a later communication.

[4] H. Phillips, *J. Chem. Soc.*, **127**, 2552 (1925).

[5] M. Hlasko and E. Michalski, *Rocz. Chem.*, **6**, 534 (1926); *C. A.*, **21**, 3523^9 (1927); D. M. Murray-Rust, H. J. Hadow and H. Hartley, *J. Chem. Soc.*, 215 (1931).

[6] The correction was made by subtracting from the k' obtained with the combined catalysts the value of k' obtained with hydrogen chloride as the sole catalyst. The values of k' were chosen at equal concentrations of available hydrogen chloride, [HCl] (see below).

TABLE I

EPIMERIZATION OF *l*-MENTHYL 1-*p*-METHOXYBENZENESULFINATE IN NITROBENZENE AT 25.00 ± 0.05°

Initial ester, mole/l.	Total HCl, mole/l.	Tetraethylammonium chloride, mole/l.	$k' \times 10^4$, sec.$^{-1}$
0.0349	0.01816	0.00108	0.947
.0349	.01816	.00270	2.33
.0349	.01816	.00540	4.58
.0349	.01816	.00892	6.67
.0349	.01816	.01784	9.85
.0358	.00905	.00108	0.643
.0358	.00905	.00270	1.550
.0358	.00905	.00540	3.12
.0358	.00905	.00892	3.90
.0358	.00905	.01784	4.97
.0372	.00514	.00108	0.502
.0372	.00514	.00270	1.605
.0372	.00514	.00540	2.33
.0372	.00514	.00892	2.65
.0372	.00514	.01784	2.85
.0385	.00218	.00540	1.275
.0385	.00218	.00892	1.483
.0385	.00218	.01784	1.422
.0385	.00322	.00540	1.770
.0385	.00322	.00892	1.878
.0385	.00322	.01784	2.000
.0349	.01816	0	0.432
.0358	.00905	0	.096
.0372	.00514	0	.067
.0349	0	0.0357	0

Discussion

The epimerization reaction may be treated kinetically as approaching the equilibrium concentration of epimers by a simple first-order reaction, with the observed rate contant, k', being the sum of the rate constants for the forward and reverse reactions, $k'_f + k'_r$.[7] This pseudo-first-order rate constant contains the specific rate constant for the reaction, k, and the concentrations of hydrogen chloride and chloride ion, which within any single run are invariant.

$$\ln(\alpha_2 - \alpha_1) = (k_f' + k_r')t + C = k't + C = k[\mathrm{HCl}][\mathrm{Cl}^-]t + C \quad (1)$$

However, the ineffectiveness of added catalyst at higher concentrations suggests that the hydrogen chloride and chloride ion may be reacting to give an inert species, the hydrogen dichloride anion, HCl_2^- comparable to HF_2^- (the bifluoride or hydrogen difluoride ion) but presumably less stable.

Other evidence besides that already cited[8] for the interaction of hydrogen chloride and chloride ions has been summarized recently by Sharp.[9] In addition should be mentioned the early work by Hunter[10] and the observation by Pinner,[11] who first synthesized imino ethers, that the salts of these as first formed contained two moles of hydrogen chloride and that upon standing one mole was slowly lost. Similarly, it appears that dicyclopentadienylrhenium hydride gives a salt that contains the hydrogen dichloride anion.[12] Tetraphenylarsonium hydrogen dichloride also has been reported.[13] Recently, evidence on the conductivity of the hydrogen dichloride ion has been published[14] as has evidence for the symmetry of the hydrogen bond in this anion.[15]

The postulation of the intervention of the hydrogen dichloride anion in the epimerization reaction would be supported if it were to permit the calculation of the actual concentrations of the free hydrogen chloride and chloride ion which serve to catalyze the epimerization reaction. Assuming an equilibrium constant

$$K = \frac{[\mathrm{HCl_2}^-]}{[\mathrm{HCl}][\mathrm{Cl}^-]} \quad (2)$$

can be written for the association, knowledge of the correct value of K would permit determination of the product $[\mathrm{HCl}][\mathrm{Cl}^-]$. This plotted *vs.* k' should give a straight line of slope k.

The constant K has been determined by a series of successive approximations from the data on the epimerization of the three esters. The hydrogen chloride, $[\mathrm{HCl}]$, and chloride ion, $[\mathrm{Cl}^-]$, available for catalysis of the reaction can be expressed in terms of the stoichiometric concentrations of hydrogen chloride and tetraethylammonium chloride, $[\mathrm{HCl}]_0$ and $[\mathrm{Cl}^-]_0$, respectively,[16] with $a = [\mathrm{HCl}]_0 - [\mathrm{Cl}^-]_0$ and $b = [\mathrm{HCl}]_0 + [\mathrm{Cl}^-]_0$, and the equilibrium constant K from equation 2, neglecting extraneous roots.

$$[\mathrm{HCl}] = \frac{Ka - 1 + \sqrt{K^2a^2 + 2Kb + 1}}{2K} \quad (3)$$

$$[\mathrm{Cl}^-] = \frac{-Ka - 1 + \sqrt{K^2a^2 + 2Kb + 1}}{2K} \quad (4)$$

The product of these concentrations for use in equation 1 is

$$[\mathrm{HCl}][\mathrm{Cl}^-] = \frac{Kb + 1 - \sqrt{K^2a^2 + 2Kb + 1}}{2K^2} \quad (5)$$

These equations are most easily applied when $[\mathrm{HCl}]_0 = [\mathrm{Cl}^-]_0$, *i.e.*, $a = 0$, in which case they reduce to equations 6 and 7.

$$[\mathrm{HCl}] = [\mathrm{Cl}^-] = \frac{-1 + \sqrt{2Kb + 1}}{2K} \quad (6)$$

$$[\mathrm{HCl}][\mathrm{Cl}^-] = \frac{Kb + 1 - \sqrt{2Kb + 1}}{2K^2} \quad (7)$$

From equation 6 by use of various assumed values of K and interpolated values of $[\mathrm{HCl}]_0 =$

---

[7] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 102.

[8] H. F. Herbrandson, R. T. Dickerson, Jr., and J. Weinstein, THIS JOURNAL, **76**, 4046 (1954).

[9] D. W. A. Sharp, *J. Chem. Soc.*, 2558 (1958).

[10] W. H. Hunter and G. D. Byrkit, THIS JOURNAL, **54**, 1948 (1932).

[11] A. Pinner, *Ber.*, **16**, 353, 1654 (1883).

[12] M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 3916 (1958).

[13] F. Blicke and E. Monroe, THIS JOURNAL, **57**, 720 (1935).

[14] E. D. Hughes, C. K. Ingold, S. Patai and Y. Pocker, *J. Chem. Soc.*, 1206 (1957).

[15] J. C. Waddington, *ibid.*, 1708 (1958).

[16] The assumption has been made that all of the chloride ion not bound as hydrogen dichloride is available to catalyze the reaction. Actually, some is present as free chloride ions and some as undissociated tetraethylammonium chloride.[17] To a first approximation at the low concentrations used, most of the quaternary salt is dissociated. Furthermore, it has been suggested that ions in ion pairs may be almost as reactive as free ions.[18] Work is being done with a related system to determine the effect of the undissociated quaternary chloride.

[17] C. R. Witschonke and C. A. Kraus, THIS JOURNAL, **69**, 2472 (1947).

[18] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, New York, N. Y., 1940, p. 52.

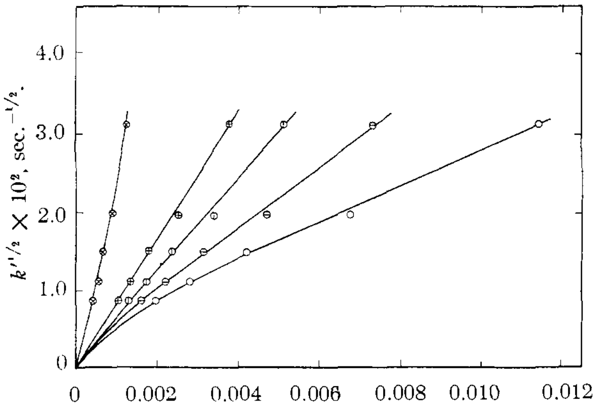


Fig. 3.—Equations 1 and 6 with various values for K: ○, 50; ⊖, 200; ⦶, 500; ⊕, 1000; ⊗, 10,000.

$[Cl^-]_0$ from Figs. 1 and 2, approach to a linear relationship for $\sqrt{k'}$ *vs.* [HCl] with $K = 500$ to 1000 gave a first approximation (Fig. 3). These values, as well as others were then used in equation 5, with all of the experimental data for each ester, as in Fig. 4, in an attempt to improve the approximation of K. The value $K = 1000$ seemed to fit as well as $K = 500$. Finally, using the third-order rate constant obtained from Fig. 4 and the calculated concentrations of available hydrogen chloride and chloride ions from equations 3 and 4, curves were constructed (Figs. 1 and 2) which should have corresponded to the experimentally observed results. The best fit was obtained using $K = 500$. The two calculated curves are of identical form because of the symmetry of the expression which is used, but the experimental data deviate non-symmetrically from these curves. It must be concluded that increments in $[HCl]_0$ and $[Cl^-]_0$ are not equivalent in their effects on the rate.

If the hydrogen dichloride ion could serve in place of the chloride ion as a co-catalyst with hydrogen chloride, then the curvature of the k' *vs.* [HCl] plot should be less than that of the k' *vs.* [Cl⁻] plot, since as chloride ion is consumed by added hydrogen chloride, its role can be filled by the hydrogen dichloride ion. The pseudo-first-order rate constant then would not be $k' = k[HCl][Cl^-]$ but rather $k' = k[HCl][Cl^-] + k^*[HCl][HCl_2^-]$ with k^* the sum of the rate constants for forward and reverse reactions for the hydrogen dichloride-catalyzed reactions. Treatment of this in a manner similar to that accorded equation 1 yields equation 8

$$k' = k\,\frac{Kb + 1 - \sqrt{K^2a^2 + 2Kb + 1}}{2K^2} + k^*\,\frac{(Kb + 1 - \sqrt{K^2a^2 + 2Kb + 1})^2}{2K^2(-Ka - 1 + \sqrt{K^2a^2 + 2Kb + 1})} \tag{8}$$

By successive approximations a value of $k/k^* = 18.7$ was found to be fairly satisfactory for all three esters. The values of the rate constants determined from this equation with $K = 500$ are listed in Table II and theoretical curves based on these values for *l*-menthyl *l-p*-methoxybenzenesulfinate are included in Figs. 1 and 2. The better agreement with the observed experimental points suggests that participation by the hydrogen dichloride anion may in fact occur.

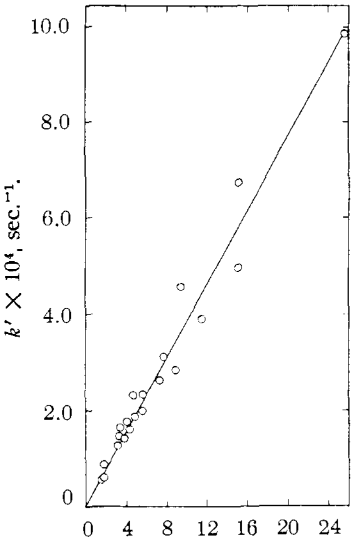


Fig. 4.—Equations 1 and 5 with $K = 500$.

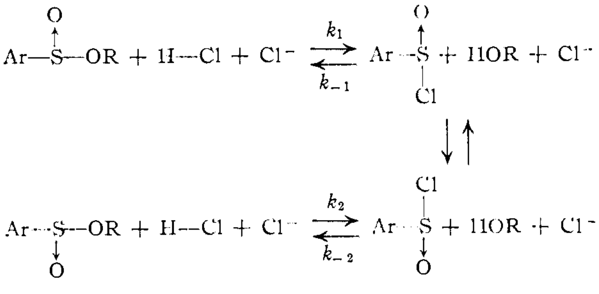
Kinetically the catalysis which we have interpreted as being by hydrogen chloride and chloride ion could as well be by the hydrogen dichloride ion alone. On other grounds this alternative appears to be rather unlikely and is rendered improbable kinetically by the difficulty of fitting into any simple scheme based upon this the term which we attribute to hydrogen chloride and hydrogen dichloride catalysis.

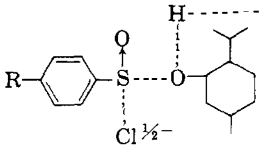
TABLE II

RATE CONSTANTS FOR THE EPIMERIZATION OF *l*-MENTHYL *l*-ARENESULFINATES BY HYDROGEN CHLORIDE, CHLORIDE IONS AND HYDROGEN DICHLORIDE IONS IN NITROBENZENE AT 25.00 ± 0.05°, ASSUMING K = 500 l./MOLE

l-Menthyl ester	Rate constants, l.² mole⁻² sec.⁻¹	
	Cl^- catalysis	HCl_2^- catalysis
l-Benzenesulfinate	28.2	1.51
l-p-Toluenesulfinate	28.0	1.50
l-p-Methoxybenzenesulfinate	35.0	1.87

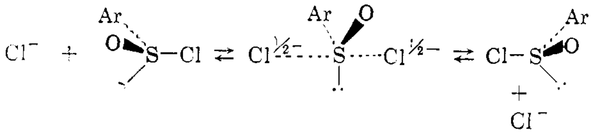
A reversible reaction of the ester with the two catalysts to give the sulfinyl chloride and *l*-menthol *via* a transition state approximating II may account for the observations.





II

If the asymmetric sulfur undergoes a displacement reaction by inversion and a re-esterification in the same manner, no epimerization should occur. However, if reaction through II is rate determining, a subsequent rapid interchange of chloride ions by the sulfinyl chloride with racemization at the sulfur could account for the epimerization.



If this picture of the reaction is correct, equation 1 must be replaced by equation 9.

$$\ln(\alpha_1 - \alpha_2) = \left[k_1'\left(1 - \frac{k'_{-1}}{k'_{-1} + k'_{-2}}\right) + k_2'\left(1 - \frac{k'_{-2}}{k'_{-1} + k'_{-2}}\right)\right]t + C \quad (9)$$

Here the specific rate constants for the forward and reverse reactions of the simple epimerization equation are diminished by that fraction of the racemized sulfinyl chloride that reverts to the epimeric ester from which it was formed.

Although the accelerating effect of the *p*-methoxyl on the rate is relatively small, it suggests an increase in positive charge on the sulfur in the transition state.

Experimental[19]

l-**Menthyl** *l*-**Benzenesulfinate.**—Benzenesulfinyl chloride[20] from 34.7 g. (0.244 mole) of benzenesulfinic acid in an equal volume of dry ether was caused to react with 38.0 g. (0.243 mole) of *l*-menthol in 20 ml. of dry pyridine. Removal of the ether *in vacuo* after washing with water, dilute hydrochloric acid, twice again with water, and drying over sodium sulfate gave an almost colorless oil. The higher-melting epimer was separated from the mixture by careful cooling, with solid carbon dioxide, of a solution in three volumes of methanol. The colorless crystals, 20 g. (0.071 mole, 29%), of *l*-menthyl *l*-benzenesulfinate were collected, washed with cold, aqueous methanol, and recrystallized from methanol. Another recrystallization from methanol and three from pentane gave a product of m.p. 49–51°, $[\alpha]^{25}D$ −205.5° (*c* 2.0 in acetone), $[\alpha]^{25}D$ −210.4° (*c* 1.1 in nitrobenzene).

Anal. Calcd. for $C_{16}H_{24}O_2S$: C, 68.51; H, 8.62; S, 11.43. Found: C, 68.63; H, 8.80; S, 11.25.

The oil which remained from the original crystallization had not solidified in a refrigerator after three months, but one week after adding hydrogen chloride gas more solid ester was recovered: 17.4 g. after one recrystallization.

l-**Menthyl** *l*-*p*-**toluenesulfinate** was prepared as reported previously,[2] except that after separation of the initially-formed solid ester, a few crystals of tetraethylammonium chloride and some hydrogen chloride gas were added. A second crop was removed after one day, and retreatment with quaternary chloride and hydrogen chloride gave yet another crop. The total yield of *l*-ester was 90.7%.

l-**Menthyl** *l*-*p*-**Methoxybenzenesulfinate.**—*p*-Methoxybenzenesulfinic acid[21] (27 g., 0.157 mole) was added gradually to 21.5 g. (0.18 mole) of thionyl chloride, the excess thionyl chloride was removed *in vacuo*, and the residue cooled and diluted with 50 ml. of dry ether. With cooling, 20 g. (0.128 mole) of *l*-menthol in 11 g. (0.14 mole) of pyridine and 10 ml. of dry ether was added. More ether was added and the solution washed with dilute hydrochloric acid. The ester, which was not very soluble in ether, was recovered by filtration, hydrogen chloride was passed into the solution and it was refrigerated for three days. Ester, which had crystallized after this time, was separated and the ether was evaporated from the filtrate to give additional product; yield 27.7 g. (0.089 mole, 69%). After six recrystallizations from aqueous acetone, the ester had a m.p. 116–117.5° and a constant rotation of $[\alpha]^{25}D$ −190.3° (*c* 1.2, acetone), $[\alpha]^{25}D$ −193.5° (*c* 1.0, nitrobenzene).

Anal. Calcd. for $C_{17}H_{26}O_3S$: C, 65.77; N, 8.44; S, 10.33. Found: C, 65.93; H, 8.32; S, 10.11.

Tetraethylammonium chloride stock solutions in nitrobenzene were prepared as previously.[2] Care was necessary to assure that in the preparation of the chloride from the hydroxide no excess of hydrochloric acid was used, as it was impossible to remove hydrogen chloride from the salt by recrystallization.

Hydrogen chloride stock solutions, in nitrobenzene, were prepared by passing dry hydrogen chloride into dry nitrobenzene. Exact concentrations were determined immediately preceding use, since hydrogen chloride is lost quite rapidly even from dilute solutions in nitrobenzene.

The kinetic determinations were made at 25.00 ± 0.05°, as reported previously. The spent solutions from a series of kinetic runs with *l*-menthyl *l*-*p*-toluenesulfinate, in one instance, were combined and the nitrobenzene was removed at 10^{-3} mm., at 50°. Initially 1.0 g. of ester, 0.008 g. of tetraethylammonium chloride and 0.018 g. of hydrogen chloride were present. A residue, 0.9 g., largely crystalline, remained, which after recrystallization weighed 0.67 g. and had a m.p. 102–103°. A mixed m.p. with pure *l*-menthyl *l*-*p*-toluenesulfinate was undepressed.

After distillation of the nitrobenzene, a few mg. of white crystals deposited in the side-arm of the distilling flask. The odor, m.p. 69°, and mixed m.p. showed these to be *p*-toluenesulfonyl chloride.

l-Menthol, dissolved in nitrobenzene with added hydrogen chloride and tetraethylammonium chloride, was unchanged in rotation after 16 hours at 25°.

TROY, N. Y.

---

[19] Analyses were performed by Clark Microanalytical Laboratory, Urbana, Ill.

[20] J. v. Braun and W. Kaiser, *Ber.*, **56B**, 549 (1923).

[21] L. Gattermann, *ibid.*, **32**, 1136 (1899).

COMMUNICATIONS TO THE EDITOR

CONVENIENT NEW PROCEDURES FOR THE HYDROBORATION OF OLEFINS

Sir:

The hydroboration reaction provides a convenient new route from olefinic derivatives to organoboranes,[1] and to the many derivatives to which organoboranes can be converted.[1,2]

We have described procedures which utilized sodium borohydride, diglyme (diethylene glycol dimethyl ether) as solvent, and boron trifluoride etherate to liberate diborane from the salt. We have learned that the unavailability of one or more

---

[1] H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **78**, 5694 (1956); *J. Org. Chem.*, **22**, 1135 (1957).

[2] H. C. Brown and G. Zweifel, THIS JOURNAL, **81**, 247, 1512 (1959); H. C. Brown and K. Murray, *ibid.*, **81**, 4108 (1959); J. B. Honeycutt, Jr., and J. M. Riddle, *ibid.*, **81**, 2593 (1959); M. F. Hawthorne and J. A. Dupont, *ibid.*, **80**, 5830 (1958).