

poured into water and the products were isolated by extraction and concentration to remove the solvent. The oxirane was separated from the higher-boiling diphenyl sulfide by careful distillation (at 24 mm., 100° bath temperature).

Using the above procedure the following carbonyl compounds were converted to oxiranes by diphenylsulfonium ethylide: cyclopentanone, 80% analytical yield, 65% isolated yield (p.v.p.c.); benzaldehyde, 90% analytical yield, 85% isolated yield (distillation), as a 1:1 mixture of *cis* and *trans* isomers (analyzed both by v.p.c. and n.m.r.); benzophenone, 85% analytical yield, 74% isolated<sup>11</sup> yield.

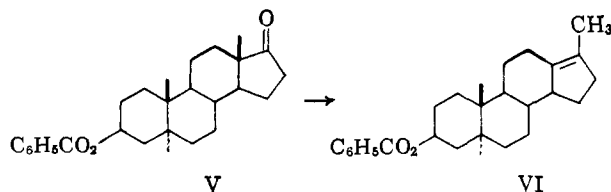
Lithium diethylamide and lithium diisopropylamide are also very useful reagents for the efficient generation of sulfonium ylides. The former when used in the experiment detailed above (allowing 1 hr. for ylide formation) afforded the oxirane IV, R = CH<sub>3</sub>, from diphenylethylsulfonium fluoroborate and cyclohexanone in 71% isolated yield.

The transfer of larger alkyl groups has also been realized experimentally. For example, diphenylsulfonium butylide, prepared from *n*-butyldiphenylsulfonium fluoroborate<sup>7</sup> and lithium diisopropylamide, afforded the oxirane IV, R = *n*-C<sub>3</sub>H<sub>7</sub>, with cyclohexanone in 88% analytical yield, 81% isolated yield (chromatography and distillation); with benzaldehyde a mixture of *trans*- and *cis*-oxiranes (ratio ca. 1.5:1) was isolated in 61% yield (chromatography and distillation).<sup>12</sup>

Solutions of diphenylsulfonium ethylide (0.2 M) in tetrahydrofuran (under nitrogen) decompose at -20° with a half-life of ca. 5 hr. and at +20° with a half-life of ca. 5 min.; at -76° they are stable at least for several hours.

The scope of these alkylidene transfer reactions remains to be determined. However, there does seem to be an important steric limitation. The reaction of diphenylsulfonium ethylide with 17-keto-5 $\alpha$ -androstan-3 $\beta$ -ol benzoate (V), of interest as a route to the pregnan-20-one series, did not afford oxirane but, surprisingly, the pseudo-steroid VI.<sup>13</sup> This observation suggests that hindered ketones (and also highly substituted ylides) are deserving of further study.

Finally, it should be mentioned that the abundantly available triethylsulfonium iodide has been converted to the corresponding ylide (with lithium diethylamide),



(11) In this instance the separation of oxirane from diphenyl sulfide was accomplished by oxidation of the latter to sulfone by permanganate in acetone with a stoichiometric amount of acetic acid followed by extraction of the semisolid reaction product with pentane and distillation. The oxiranes from benzaldehyde and benzophenone are readily isomerized by acids to phenylacetone and *unsym*-diphenylacetone, respectively.

(12) In a recent paper there is reported the generation of diphenylsulfonium butylide using *n*-butyllithium and the subsequent reaction with *p*-nitrobenzaldehyde to form an oxirane in 40% yield (only example given): A. W. Johnson, V. J. Hrubby, and J. L. Williams, *J. Am. Chem. Soc.*, **86**, 918 (1964). These authors maintain that oxirane formation is stereospecific, in contrast to our results.

(13) Identified by mass spectrum (found *m/e* = 378, courtesy of Prof. K. Biemann), n.m.r. and infrared spectra, microanalysis, and conversion to the known 3 $\beta$ -hydroxy derivative; see K. Miescher and H. Kagi, *Helv. Chim. Acta*, **32**, 761 (1949).

which is fairly stable at -76° and which affords the oxirane IV, R = CH<sub>3</sub>, with cyclohexanone; evidently  $\beta$ -elimination can be largely circumvented in this case. Further studies are under way on the chemistry of this class of sulfonium ylides.<sup>14</sup>

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### Isotope Effects for Solvolysis of *t*-Butyl Chloride and *t*-Butyl-*d*<sub>9</sub> Chloride in Solvent Mixtures of Constant Ionizing Power<sup>1</sup>

Sir:

We have determined isotope effects for the solvolysis at 25° of (CH<sub>3</sub>)<sub>3</sub>CCl and (CD<sub>3</sub>)<sub>3</sub>CCl in six solvent mixtures each having the same *Y*-value,<sup>2</sup> *i.e.* (by definition), the same reaction rate for (CH<sub>3</sub>)<sub>3</sub>CCl. Average rate constants and isotope effects are given in Table I. The rate constants were determined by gas chromatographic analysis for unreacted *t*-butyl chloride.<sup>3</sup> The relative amounts of most products can also be determined by gas chromatography, and we are currently studying these, along with other solvent mixtures.

The mean of the isotope effects, 2.39, is almost within experimental error of all of our observed results. However, the isotope effects for ethanol-water and acetic-formic acids differ by experimentally significant, although small, amounts from that for pyridine-water. It may be that a small amount of bimolecular elimination occurs in the presence of large amounts of pyridine, increasing the observed isotope effect; however, bimolecular elimination is thought to be generally unimportant in solvolysis of *t*-butyl chloride.<sup>2</sup>

The reaction of *t*-butyl chloride was chosen for study because it was known to exhibit a large isotope effect, 2.3271 in 60:40 ethanol-water at 25°<sup>4</sup> and ca. 2.39 in water at 25°.<sup>5</sup> Specific effects of different solvents on the nature of the transition state should change the isotope effect by especially large amounts because of the cumulative effect on nine deuterium atoms.

It can be seen that the isotope effects are hardly solvent-dependent at all. We conclude that the structural features of the transition states for solvolysis of *t*-butyl chloride in the various solvents studied are very similar. Three hypotheses which explain these observations occur to us.

First, it may be that the ionization of the substrate is truly unimolecular, with practically no participation by solvent. This mechanism is almost like a gas-phase ionization except that the ions are formed in a medium

(1) Supported in part by the Air Force Office of Scientific Research.

(2) S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951); E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

(3) Ten-microliter aliquots of solutions initially ca. 0.02 M in *t*-butyl chloride were analyzed in a 12-ft. column at 60° using a nonreacting standard, carbon tetrachloride, in about the same concentration as the substrate. The temperature was 25.00  $\pm$  0.01°, standardized with an N.B.S. calibrated platinum resistance thermometer. After analysis of each aliquot, the solvent was removed from the column by back-flushing.

(4) V. J. Shiner, Jr., B. L. Murr, and G. Heinemann, *J. Am. Chem. Soc.*, **85**, 2413 (1963).

(5) Corrected from the value of 2.568 at 2° [K. T. Lefk, J. A. Llewellyn, and R. E. Robertson, *Can. J. Chem.*, **38**, 2171 (1960)] by assuming the isotopic effect occurs entirely in the enthalpy of activation.

TABLE I  
RATES AND ISOTOPE EFFECTS FOR SOLVOLYSIS AT 25° OF *t*-BUTYL CHLORIDE IN SOLVENTS OF CONSTANT  $Y$

Solvent <sup>a</sup>	$k_H^b$ [(CH <sub>3</sub> ) <sub>3</sub> CCl] × 10 <sup>4</sup> , sec. <sup>-1</sup>	$k_D^{b,c}$ [(CD <sub>3</sub> ) <sub>3</sub> CCl] × 10 <sup>4</sup> , sec. <sup>-1</sup>	$k_H/k_D$
Ethanol-water (54:46)	22.4 ± 0.3	9.52 ± 0.06	2.35 ± 0.03
Acetone-water (49:51)	22.5 ± 0.3	9.40 ± 0.26	2.40 ± 0.08
Acetic acid-water (63:37)	22.7 ± 0.5	9.32 ± 0.25	2.41 ± 0.07
Pyridine-water (51:49)	22.3 ± 0.2	9.08 ± 0.06	2.46 ± 0.03
Isopropyl alcohol-water (48:52)	22.4 ± 0.6	9.28 ± 0.12	2.42 ± 0.07
Acetic acid-formic acid (29:71) <sup>d</sup>	23.3 ± 0.3	10.15 ± 0.16	2.30 ± 0.05

<sup>a</sup> Numbers in parentheses are per cent by volume before mixing. <sup>b</sup> Average rate constant (in most cases for three or four runs), followed by standard deviation from mean. <sup>c</sup> >99% deuterated. <sup>d</sup> The acetic acid used contained 0.02 *M* acetic anhydride to ensure absence of water in the reaction mixture; also, 0.2 *M* anhydrous lithium formate was added to ensure complete reaction.

of fairly high dielectric constant; however, it is probably not energetically feasible.

Second, it may be that the isotope effects *fortuitously* remain similar in spite of widely different transition state structures. The fact that the isotope effect in the nonaqueous solvent is similar to the others appears to eliminate the possibility of "solvent-sorting"<sup>6</sup> as a major factor in making the isotope effects so similar.

Third, it may be that the structure of the transition state for the solvolysis of *t*-butyl chloride is determined largely by the structure of the substrate, the function of the solvent being to allow the molecule to reach this transition state structure by whatever means are available. Assistance by the solvent could be quite specific, but different for each solvent. The structure of the transition state, *e.g.*, the extent of bond breaking, would depend only on the *amount* of solvent assistance and not on the detailed *nature* of the assistance.

The fact that such large isotope effects as those reported here, *ca.* 2.4, should be very sensitive to changes in structure or environment of the transition state has provided a very sensitive tool for elucidating the nature of solvolysis reactions. The constancy of the isotope effects seems to indicate that the activation process is remarkably insensitive to the presence of solvent species of widely variable electrophilic and nucleophilic properties.

(6) See J. B. Hyne, R. Wills, and R. E. Wonkka, *J. Am. Chem. Soc.*, **84**, 2914 (1962); also E. M. Arnett, P. M. Duggleby, and J. J. Burke, *ibid.*, **85**, 1350 (1963).

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### Liquid Ion-Exchange Membranes of Extreme Selectivity and High Permeability for Anions

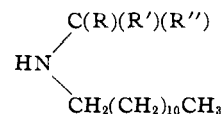
Sir:

Liquid membranes of extreme degrees either of anionic or cationic selectivity which facilitate the exchange of inorganic ions in readily analyzable quantities across their thickness between two adjacent electrolyte solutions seemingly have not been described. Such membranes can now be made of so-called "liquid ion exchangers."<sup>1</sup> These liquid ion exchangers are solutions, in water-insoluble organic solvents, of substances consisting of an ionogenic group which is attached to an organic molecule of proper size (mol. wt. 250–500) and configuration to make these compounds sparingly soluble in aqueous electrolyte solutions. The best

(1) R. Kunin and A. G. Winger, *Angew. Chem. Intern. Ed. Engl.*, **1**, 149 (1962).

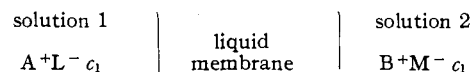
liquid exchangers have only a minimal solubility in aqueous solutions. Generally, these liquid ion exchangers in contact with aqueous electrolyte solutions behave similarly to weak base and weak acid ion-exchange resins. However, many do not absorb measurable quantities of water, nor is there any invasion by "nonexchanger electrolyte."

Since liquid anion exchangers are available with a greater variety of structures than cation exchangers, we started with anion exchangers, mainly a secondary amine, lauryl(trialkylmethyl)amine (mol. wt. *ca.* 360), "Amberlite LA-2," Rohm and Haas Co.



R, R', and R'' being short aliphatic chains having altogether 11 to 14 carbons. Before use this material was brought into a salt form by treatment with acid

The *rates of exchange of anions* and of *leakage of cations*, and thereby the *ionic selectivity of a membrane*, are determined in cells



the liquid membrane floating on the two solutions which are separated by a glass wall. The membranes were 5–80% solutions of anion-exchange compound in benzene, xylene, or nitrobenzene, which had been equilibrated beforehand with an equimolar mixture of the (strong) electrolytes A<sup>+</sup>L<sup>-</sup> and B<sup>+</sup>M<sup>-</sup>. Until a quasi-stationary state is reached under the dynamic conditions of the experiment, the quantities of L<sup>-</sup> appearing in solution 2 and of M<sup>-</sup> appearing in solution 1 are not necessarily strictly equivalent, and hydrolysis of the functional material in the membrane phase which depends on the concentrations of the adjacent solutions enters as another complication. These secondary factors, however, do not blur the main effect: a fairly fast exchange of L<sup>-</sup> and M<sup>-</sup> occurs between the two solutions while barely measurable quantities of A<sup>+</sup> and B<sup>+</sup> appear in solutions 2 and 1. The rates of exchange are approximately proportional to the concentration of the ion-exchange compound in the membrane phase.

For instance, with 20% LA-2 in xylene, 1.0 *N* KCl in solution 1, and 1.0 *N* NaSCN in solution 2 (and all three liquids stirred), the rates of exchange of Cl<sup>-</sup> and SCN<sup>-</sup> were about 95  $\mu\text{equiv./cm}^2 \text{ hr.}$ ; the rates for K<sup>+</sup> and Na<sup>+</sup> were less than  $1.1 \times 10^{-3}$  and  $4.9 \times 10^{-4}$   $\mu\text{equiv./cm}^2 \text{ hr.}$  The ionic selectivity of the membrane, that is the ratio of its permeabilities for anions and cations, was thus 80,000:1 for Cl<sup>-</sup> *vs.* K<sup>+</sup>, and 200,000:1