put from the computer permits the magnification of the tracing to the desired level (Figure 1, F; Figure 2, C and D), which increases the sensitivity of the technique and is necessary for careful evaluation of the position and the magnitude of the ellipticity bands.

The CD spectrum of L-tryptophan in the wavelength region 250–300 mμ consists of at least three positive dichroic bands, centered at 291, 281, and 272 mμ. The positions of these bands are approximately the same as those of the absorption peaks of the indole chromophore, thus suggesting their origin. Below 250 mμ, of the four ellipticity bands, only two seem to reflect their counterparts in the absorption spectrum. The shoulder at about 218 mμ corresponds to the exceedingly strong indole absorption peak at 218 mμ (Figure 2, C), and the negative dichroic band centered at about 200 mμ possibly reflects the carboxyl transition (absorption maximum at 194 mμ). Since there seems to be no directly perceivable absorption band corresponding to the relatively large positive ellipticity peak at about 224 mμ, any comments without further investigations would be presumptive. We are currently investigating the ORD and CD spectra of various amino acids and their derivatives and of peptides containing aromatic amino acids. These and other results will be reported in due course.

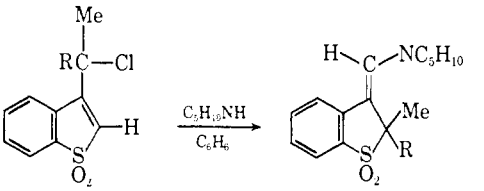
The use of the modified technique, as described, results in an improvement of about 3–4-fold in the signal-to-noise ratio and a 4–6-fold decrease in the uncertainty of the absolute value. This, with the scale expansion (Figures 1 and 2), shows that a more than 10–12-fold increase in the sensitivity is readily obtainable by this technique. There is no reason, however, to believe that this represents the limit of the improvement of the data. Further refinement of the measurements can be attained by employing a larger number of scans. Because of the time factor required for repeated scanning, this may, in certain cases, be a practical limitation. The fundamental limitation of this modified instrument still lies in the capability of the basic instrument, the minimum dichroic absorption detectable by the dichrograph. The other limitation may be the limited number of memory locations available in the computer. This could be overcome by covering small sections of wavelength region at a time and utilizing all the 1024 locations. This technique should, therefore, be useful in obtaining CD spectra of greater precision, especially in unfavorable situations. Since the basic instrument used for modification is a combination of dichrograph, polarimeter, and absorption spectrophotometer, this technique may also be applied to ORD and absorption spectrophotometric measurements.

Yash P. Myer, Lawrence H. MacDonald
Department of Chemistry
State University of New York at Albany
Albany, New York 12203
Received August 30, 1967

Concerning an Unusual SNi′ Rearrangement and the Application of the SN2′ Mechanistic Label

Sir:

When 3-(α-chloroalkyl)benzo[*b*]thiophene 1,1-dioxides **1a** and **1b** are treated with piperidine in benzene they react rapidly to form enamines **5a** and **5b** in good yields.



1a, R = H
b, R = Me

5a, R = H
b, R = Me

The rate of release of chloride ion is in each instance first order in piperidine. For **1b** the rate (titrimetric) is equal to the rate of product formation (spectrophotometric rate). For **1a** the spectrophotometric rate was considerably slower than the titrimetric rate and was independent of piperidine concentration. When the latter reaction was interrupted after four titrimetric half-lives an intermediate was present which was identified as **3a** from its nmr spectrum; further reaction of **3a** with piperidine gave **5a**. These data indicate that **1** undergoes an SN2′ reaction with piperidine to give **2**, which rapidly loses a proton to form **3**; the latter rearranges to **5** in a final step (a special type of SNi′ reaction). Dipolar ion **4** is visualized as being formed from **3**. Rotation of the cationic part of **4** around the Ar–C bond interchanges the positions of the C-1 and C-3 carbon atoms in the allyl grouping leading to **4′**. Restoration of the C–S bond gives **5**. For **1a** the rate-controlling step in formation of the product is the SNi′ reaction whereas for **1b** it is the SN2′ reaction. The rate data are summarized in Table I.

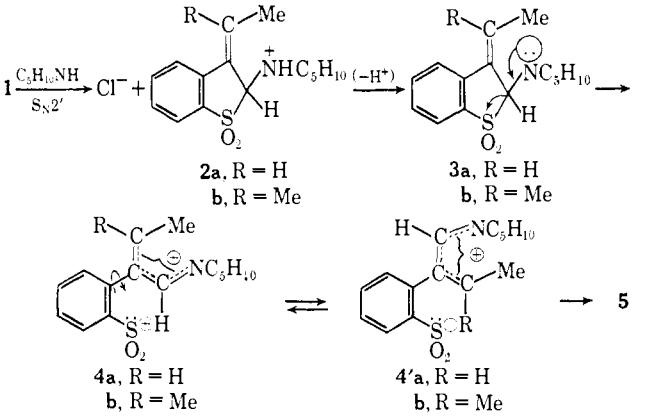


Table I. Kinetic Data for the Reactions of **1a** and **1b** with Piperidine in Benzene at 50°

Halide	k, M^{-1} sec^{-1}	E_a, kcal mole^{-1}	$\Delta S^{\ddagger}$, eu
1a	2.1×10^{-3}	10	−42
1a	$(4 \times 10^{-5})^{a,b}$	20	−18
1a	$(3.4 \times 10^{-2})^{c}$	8	−43
1b	1.6×10^{-4}	11	−43
1b	$(1.4 \times 10^{-4})^{a}$		
1b	$(1.8 \times 10^{-5})^{d}$	17	−32

[a] Spectrophotometric rate. [b] First-order constant, sec^{-1}. [c] Rate for the corresponding bromide. [d] Rate in methanol at 50°.

The titrimetric rates for **1a** and **1b** are about 500-fold greater and 50-fold greater, respectively, than the rate of the (SN2′) reaction of diethylamine with α-methylallyl chloride in benzene.[1] The unusual facility of the SN2′

(1) (a) W. G. Young, I. D. Webb, and H. L. Goering, *J. Am. Chem. Soc.*, 73, 1076 (1951); (b) D. C. Dittmer and A. F. Marcantonio, *ibid.*, 86, 5621 (1964).

reactions with **1a** and **1b** can be attributed to lowered electron density in the C=C bond (making easier the approach of the nucleophile) and to delocalization by the sulfonyl group of the negative charge developed at the β position in the SN2′ transition state (or intermediate).

For most abnormal displacement reactions in allylic systems it is extremely difficult to chose between the SN2′ and SNi′–SN2 mechanistic labels. SNi′ rearrangements can be very rapid,[2] and the rate of formation of the ion pair (or intermediate) is no doubt even faster.[3] The demonstration of the absence of rearranged chloride in an incomplete reaction does not conclusively rule out the SNi′–SN2 pathway since the rearranged chloride usually undergoes SN2 displacement much faster than does the unrearranged halide and may, therefore, be removed selectively. Furthermore, attack of the nucleophile may occur on the SNi′ ion pair (or intermediate); if this occurs, rearrangement to the isomeric halide is by-passed. The SNi′–SN2 route for chlorides **1a** and **1b** is excluded by their extreme reluctance to undergo ionization.[4] These halides are, therefore, good models for assessing the ability of nucleophiles to effect SN2′ reactions.

Halides **1a** and **1b** proved to be inert to the action of thiourea in alcohol or N-methylpiperidine in benzene. Sodium bromide in acetone gave the SN2 product with **1a**. No reaction could be detected with **1b** and lithium bromide in acetone in 31 days at room temperature; no reaction occurred with N-methylpiperidine in 23 days at 50° plus 35 days at room temperature. The rate for the reaction of N-methylpiperidine with **1b** must be *at least* 10^3 times slower than that with piperidine, whereas with allyl bromide the rates differ by only one order of magnitude. It would appear that the hydrogen atom on nitrogen in piperidine is playing an important role in the reaction, probably through hydrogen bonding, as originally suggested.[5] This conclusion is strengthened by the observation that the rate for **1b** is ninefold *faster* in benzene than in methanol (Table I); the solvent effect in SN2 reactions is equally large but in the reverse direction.[6]

Our conclusion is that SN2′ reactions can be realized only with a select group of allylic systems and nucleophiles. The assignment of the SN2′ mechanistic label in many earlier studies wherein thiourea, bromide ion, a tertiary amine, or an alkoxide ion was used as the nucleophile needs to be reexamined, and the label needs to be used with increased caution in the future.

Acknowledgment. This investigation was supported by Public Health Service Research Grant No. CA-07351 from the National Cancer Institute.

(2) W. G. Young, S. Winstein, and H. L. Goering, *J. Am. Chem. Soc.*, 73, 1958 (1951).

(3) S. Winstein, J. S. Gall, M. Hojo, and S. Smith, *ibid.*, 82, 1010 (1960).

(4) No chloride ion could be detected from tertiary allylic chloride **1b** even after heating a methanolic solution at 50° for 21 days; a further period of 35 days at room temperature still gave no chloride ion.

(5) R. E. Kepner, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, 71, 115 (1949). See also W. G. Young, R. A. Clement, and C. H. Shih, *ibid.*, 77, 3061 (1955), and ref 1b.

(6) N. Menschutkin, *Z. Physik. Chem.*, 6, 43 (1890).

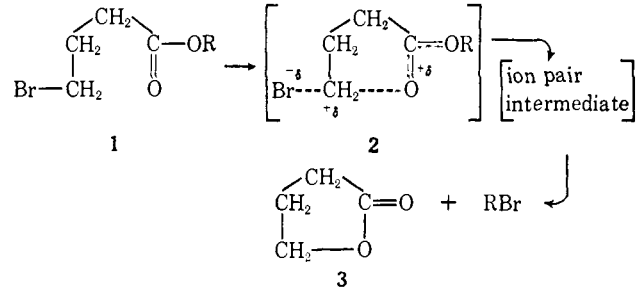
F. G. Bordwell, Robert W. Hemwall, Donald A. Schexnayder
Department of Chemistry, Northwestern University
Evanston, Illinois 60201
Received October 16, 1967

Regarding the Mechanism of Gas-Phase Dehydrohalogenation

Sir:

Gas-phase dehydrohalogenation, a reaction which has been extensively studied and discussed in numerous reviews,[1] has been characterized by a mechanism involving the intermediate formation of a tight carbonium halide ion pair. We are concerned here with the question of just how closely joined the counterions may be in gas-phase heterolysis, as compared to the corresponding reaction in solution to which it is frequently referred as a model for interpretation.[2]

A case in point may now be submitted which appears to afford increased understanding of the differences in heterolytic nature that distinguish the gas- and solution-phase reactions. We have been able to demonstrate that a reaction which involves neighboring group participation and ionic intermediates in solutions of widely varying dielectric properties does not take place in the gas phase at all accessible temperatures. The reaction of interest is the lactonization of γ-bromo esters.[3]



The rate data we have gathered and presented in Table I confirm the ionic nature of this process.

Table I. Rates of Lactonization of Ethyl-γ-bromobutyrate at 200° in Various Media

Solvent	Dielectric constant	$K \times 10^6$ sec^{-1}	Relative rate
Acetonitrile	37.5	850[a]	320
Dimethyl phthalate	20	320	139
Chlorobenzene	5.7	35	16
Pure hydrocarbon[b]	1.9	2.7	1
Gas phase	1+		0

[a] Extrapolated from data at 150, 160, 170, and 186°. [b] 1,3-Dimethyl-5-ethyladamantane was kindly provided by Dr. A. Schneider, Sun Oil Co.

The solvent dielectric clearly is an important factor controlling rate such that a less than 20-fold change in ϵ is correlated with a rate factor of >300. Among the solvents chosen ionizing power also appears to parallel dielectric strength.[4] Furthermore, the presence of small amounts of added neutral salts in the medium accelerates reaction. It is also to be noted that, even in solvents of extremely low dielectric strength such as the pure hydrocarbon solvent, the rate of formation of

(1) The most recent review has been presented in A. Maccoll, *Advan. Phys. Org. Chem.*, 3, 91 (1965).

(2) A. Maccoll and E. S. Swinbourne, *Proc. Chem. Soc.*, 409 (1960); *J. Chem. Soc.*, 149 (1964).

(3) For a discussion of the course and mechanism of this reaction see D. B. Denney and J. Giacin, *Tetrahedron*, 20, 1377 (1964), and J. Weinstock, *J. Am. Chem. Soc.*, 78, 4967 (1956).

(4) C. Reichardt, *Angew. Chem. Intern. Ed. Engl.*, 4, 29 (1965).