

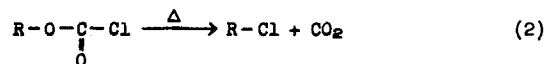
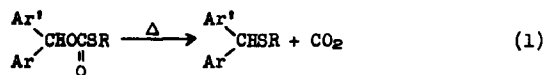
MECHANISMS OF S<sub>N</sub>i REACTIONS. STEREOCHEMICAL EVIDENCE FOR A  
TWO STEP MECHANISM FOR THE DECOMPOSITION OF ARALKYL THIOCARBONATES

John L. Kice and Mary A. Dankleff

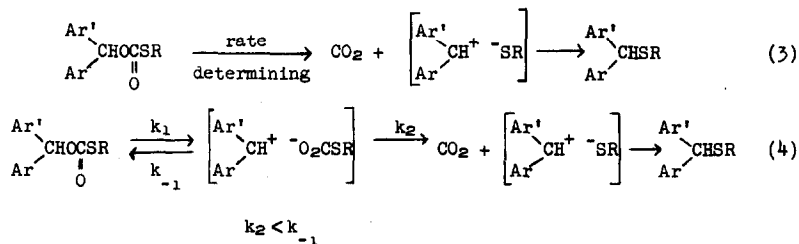
Department of Chemistry, Oregon State University  
Corvallis, Oregon

(Received 15 January 1966)

PREVIOUS work (1) has indicated that there is a substantial similarity between the mechanism of the thermal decomposition of aralkyl thiocarbonates (eq. 1) and the mechanism of the decomposition of chloro-carbonates (eq. 2). The latter reaction is usually cited as a typical



example of an S<sub>N</sub>i reaction. This earlier work also showed that in the thiocarbonate decomposition both the aralkyl-oxygen and carbonyl-sulfur bonds are effectively broken by the time the transition state of the rate-determining step is reached. However, it was not clear whether cleavage of these two bonds takes place in a single step (eq. 3) or, alternatively, involves two successive steps (eq. 4), the first one being reversible.



We now wish to report results obtained during an investigation of the stereochemistry of the decomposition of optically active *p*-chlorobenzhydryl S-methyl thiocarbonate which strongly suggest that the correct mechanism is the one involving two successive bond cleavages (eq. 4).

Optically active *p*-chlorobenzhydryl S-methyl thiocarbonate,  $[\alpha]_D +2.09$  ( $c$  6, acetone), was prepared by reaction of (-)-*p*-chlorobenzhydrol (2),  $[\alpha]_D -8.90$  ( $c$  1.3, acetone), with methyl chlorothioformate (3). Thermal decomposition of the optically active thiocarbonate in benzonitrile at  $166^\circ$  gave *p*-chlorobenzhydryl methyl sulfide in high yield, but the sulfide had an extremely small rotation and was presumably almost completely racemic. This seemed surprising in view of the degree of stereospecificity (15-99% retention) which has been observed (4,5) in chlorocarbonate decompositions.

Further experiments revealed that at least part of the reason the sulfide is so highly racemic is because the optically active thiocarbonate racemizes in benzonitrile considerably faster than it decomposes to sulfide and carbon dioxide. Samples of optically active thiocarbonate were partially decomposed at  $166^\circ$  and the undecomposed thiocarbonate was recovered by procedures shown by control experiments not to alter its optical activity. Thiocarbonate recovered after only 8.6% decomposition (as measured by  $\text{CO}_2$  evolution) had a specific rotation of  $+1.46^\circ$ , corresponding to 31% racemization. That recovered after 50% decomposition

had a rotation of only  $+0.07^\circ$  (97% racemization). The thiocarbonate thus racemizes about four times faster than it decomposes.

Such behavior is easily accounted for by the mechanism shown in eq. 4 ( $k_2 < k_{-1}$ ) since return of  $\text{Ar}'\text{ArCH}^+ \text{ } ^-\text{O}_2\text{CSR}$  ion pairs to covalency will lead to racemization of the thiocarbonate (6). On the other hand, the mechanism shown in eq. 3 cannot explain how the thiocarbonate can racemize prior to decomposition. We therefore feel that the present results provide strong evidence that the correct mechanism for the thiocarbonate decomposition is the one shown in eq. 4.

One further point is worth noting. If it is assumed that the chloro-carbonate decomposition (eq. 2) involves a mechanism equivalent to that in eq. 4, then it must be one in which  $k_2 > k_{-1}$ . Otherwise racemization of the alkyl chlorocarbonate prior to its decomposition would presumably lead to the product alkyl chloride being much more racemic than is normally observed. That  $k_2 > k_{-1}$  for the ion pair  $\text{R}^+ \text{ } ^-\text{O}_2\text{CCl}$  while  $k_2 < k_{-1}$  for  $\text{R}^+ \text{ } ^-\text{O}_2\text{CSCH}_3$  is, however, perfectly plausible, given the presumed difference in the stability of  $\text{Cl}^-$  and  $\text{CH}_3\text{S}^-$  suggested by their considerable difference in basicity.

Acknowledgement. This research supported by the National Science Foundation under Grant GP-1975.

#### REFERENCES AND FOOTNOTES

1. J. L. Kice, R. A. Bartsch, M. A. Dankleff and S. L. Schwartz, J. Am. Chem. Soc., 87, 1754 (1965).
2. Partially resolved by fractional crystallization of the brucine salt of p-chlorobenzhydryl hydrogen phthalate.
3. To ensure that no significant racemization occurred during this synthesis a sample of the thiocarbonate was subjected to alkaline hydrolysis, the p-chlorobenzhydryl formed was isolated, and its rotation was determined. No decrease in rotation was observed.
4. K. B. Wiberg and T. M. Shryne, J. Am. Chem. Soc., 77, 2774 (1955).

5. K. L. Olivier and W. G. Young, ibid., 81, 5811 (1959).
6. Goering et al. (7), in an elegant series of experiments in which they determined the relative rates of racemization and  $O^{18}$ -equilibration of ester oxygens accompanying the solvolysis of p-chlorobenzhydryl p-nitrobenzoate in aqueous acetone, showed that in that system, in the absence of added scavengers for external ion pairs such as azide ion, ion pair return occurs with about 40% racemization.
7. H. L. Goering, R. G. Briody and J. F. Levy, J. Am. Chem. Soc., 85, 3059 (1963).