178 ($m^+$), calcd 178. Anal. Calcd for $C_8H_{10}Cl_2$: C, 54.26; H, 5.69. Found: C, 54.55; H, 5.72.

**Reaction of 7,7-Dichloro-1-methylbicyclo[4.1.0]hept-2-ene (37) with Potassium *tert*-Butoxide in Tetrahydrofuran.** A solution of **37** (581 mg, 3.3 mmol) in tetrahydrofuran (95 mL) was added dropwise under nitrogen to a solution of potassium *tert*-butoxide (5.51 g, 49.2 mmol) in dry tetrahydrofuran (30 mL) which was maintained at 0 °C by means of an ice bath. After being stirred at room temperature for 72 h, the reaction mixture was diluted with water (100 mL) and extracted with ether (100 mL). The ether extract was washed with brine (100 mL) and dried over $MgSO_4$. Solvent evaporation in vacuo afforded 567.6 mg of dark brown oil which was shown by GLC (column A, 170 °C) to contain starting material (11.3% yield) and *o*-xylyl *tert*-butyl ether (**40**, 40.5% yield). Compound **40** was isolated by preparative GLC and shown to be identical (IR and NMR) with an authentic sample: NMR $\delta$ 1.26 (s, 9 H), 2.30 (s, 3 H), 4.37 (s, 2 H), 7.03–7.20 (m, 3 H), 7.20–7.37 (m, 1 H); mass spectrum, 178 ($M^+$, calcd 178).

**Synthesis of *o*-, *m*-, and *p*-Xylyl *tert*-Butyl Ethers (40–42).** An authentic sample of each ether was prepared in >95% yield by reaction of the corresponding bromoxylene with potassium *tert*-butoxide in tetrahydrofuran for 12–20 h.

**Acknowledgment.** We gratefully acknowledge The Robert A. Welch Foundation for support of this work.

**Registry No.** **6**, 37608-29-0; **7** (isomer 1), 52688-71-8; **7** (isomer 2), 52688-68-3; **12**, 52688-72-9; **12** disulfone, 75948-99-1; **14**, 75949-00-7; **16**, 75949-01-8; **18**, 55831-21-5; **19**, 60096-40-4; **20**, 66-77-3; **21** (isomer 1), 75949-02-9; **21** (isomer 2), 76010-85-0; **22**, 75949-03-0; **23**, 65130-35-0; **24**, 65130-36-1; **25**, 65130-37-2; **35**, 75949-04-1; **37**, 75949-05-2; **40**, 56636-82-9; **41**, 40677-59-6; **42**, 75949-06-3; phenanthrene, 85-01-8; tetrahydrofuran, 109-99-9; methyl mercaptan, 74-93-1; 9-methylphenanthrene, 883-20-5; 7,7-dichloro-3,4-benzobicyclo[4.1.0]heptane, 60096-38-0; 1-methyl-3,4-dihydronaphthalene, 4373-13-1; $\alpha$-tetralone, 529-34-0; methyl iodide, 74-88-4; 1-bromo-2-(bromomethyl)naphthalene, 37763-43-2; 1-bromo-2-methylnaphthalene, 2586-62-1; 2-methylcyclohexenone tosylhydrazone, 75949-07-4; 2-methylcyclohexenone, 1121-18-2; 2-methyl-1,3-cyclohexadiene, 1489-57-2; *o*-bromoxylene, 89-92-9; *m*-bromoxylene, 620-13-3; *p*-bromoxylene, 104-81-4.

# S → N and N → S Reverse Rearrangement of *S*- and *N*-(2,4-Dinitrophenyl)cysteines[1]

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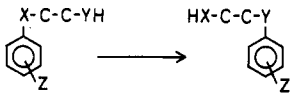
*Received July 30, 1980*

The reversible Smiles rearrangement between *S*-(2,4-dinitrophenyl)cysteine (**1a**) and *N*-(2,4-dinitrophenyl)cysteine (**2a**) has been kinetically studied in methanol, DMF, and $Me_2SO$ containing an organic base such as imidazole or DBU. The overall reaction is composed of the spontaneous and base-catalyzed reactions. In methanol the rearrangement from **1a** to **2a** goes virtually to completion in most cases. In DMF containing DBU, the reverse rearrangement from **2a** to **1a** becomes observable to afford eventually an equilibrium mixture of **1a** and **2a**. During this transformation an intermediate was spectroscopically detected, which showed an absorption band around 500 nm. The amide derivative of **1a** (**1b**) failed to undergo a facile rearrangement except under much severer conditions. In this case the normal Smiles rearrangement was accompanied by some side reactions.

Intramolecular rearrangements shown in eq 1 are known




(1)

as Smiles rearrangements.[2] They may take place with various combinations of hetero atoms for X and Y (e.g., O, S, and N), when the migrating phenyl ring is activated by substituent Z. In addition to the synthetic utility the Smiles rearrangement provides a good opportunity to study the mechanism of aromatic nucleophilic substitution reactions, because the anionic $\sigma$ complex intermediate (**4**)


4

observed in some of the Smiles rearrangements[3,4] appears to be common to the aromatic nucleophilic substitution reactions as well.[5] The stability of the $\sigma$ complex, however, varies due to the substrate. Therefore when a stable complex is not detected by conventional means, the mechanism of the rearrangement remains unclear with regard to the involvement of such a complex. If the complex is extremely labile so as not to be detected readily, it is kinetically equivalent to having such a complex present only at the transition state. This situation occurred in the rearrangement of DL-2-aminododecanoic acid *N*-methyl-*p*-nitroanilide (**5**), where the reaction took place




5

without any stable intermediate under mild conditions.[6] Introducing another nitro group into the benzene ring would stabilize the complex and allow it to be detected readily, because the existence of similar anionic $\sigma$ complexes has been previously confirmed.[3,4] Our current choice

(1) Abbreviations used in this article for bases are the following: Dabco, 1,4-diazabicyclo[2.2.0]octane; DBU, 1,5-diazabicyclo[5.4.0]undec-5-ene.

(2) W. E. Truce, E. M. Kreider, and W. W. Brand, *Org. React.*, 18, 99 (1970).

(3) C. F. Bernasconi, R. H. DeRossi, and C. L. Gehriger, *J. Org. Chem.*, 38, 2838 (1973).

(4) S. Sekiguchi and K. Okada, *J. Org. Chem.*, 40, 2782 (1975).

(5) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, 49, 275 (1951).

(6) J. Sunamoto, H. Kondo, F. Yanase, and H. Okamoto, *Bull. Chem. Soc. Jpn.*, 53, 1361 (1980).

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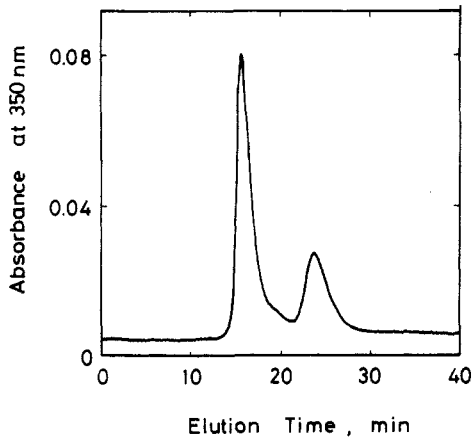
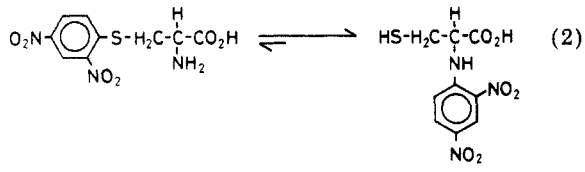



**Figure 1.** High-performance LC analysis of *S*-(2,4-dinitrophenyl)cysteine (**1a**) and its N isomer (**2a**) under the conditions given in the text. The peak coming off first is **2a**.

of substrate is *S*-(2,4-dinitrophenyl)cysteine (**1a**), which is known to undergo a facile rearrangement under mild conditions (eq 2).[7,8] Although no $\sigma$-complex intermediate




(2)

derived from **1a** was detected in aqueous media,[7,8] it is suspected that the complex, if present, may be stabilized in an appropriate organic solvent. As expected a $\sigma$-complex intermediate was spectroscopically observed under limited conditions as shown below. In addition, a possibility of intramolecular participation of the carboxyl group during the rearrangement was also suggested.

## Experimental Section

**Materials.** *S*-(2,4-Dinitrophenyl)-L-cysteine (**1a**) was prepared in 45% yield according to the literature.[9] Anal. Calcd for $C_9H_{10}N_3O_6S$: C, 37.63; H, 3.16; N, 14.62; S, 11.16. Found: C, 37.13; H, 3.01; N, 14.42; S, 10.96. *S*-(2,4-Dinitrophenyl)-L-cysteinamide (**1b**) was synthesized similarly in 60% yield by reacting L-cysteinamide with 2,4-dinitrofluorobenzene: mp 169–171 °C; NMR ($CF_3CO_2H$) $\delta$ 3.96 (d, $J$ = 6 Hz, 2 H, $CH_2$), 4.87 (m, 1 H, CH), 7.50 (br s, 2 H, $NH_2$), 7.70 (br s, 3 H, $NH_3$), 7.86 (d, $J$ = 9 Hz, 1 H, 6-H), 8.52 (dd, $J$ = 9, 2 Hz, 1 H, 5-H), 9.10 (d, $J$ = 2 Hz, 1 H, 3-H). Anal. Calcd for $C_9H_9N_4O_5S$: C, 37.76; H, 3.52; N, 19.57. Found: C, 37.66; H, 3.37; N, 18.91. *N,N'*-Bis(2,4-dinitrophenyl)-L-cystine (**3a**) was synthesized in 75% yield according to the established method.[10] Anal. Calcd for $C_{18}H_{16}O_{12}N_6S_2$: C, 37.77; H, 2.82; N, 14.68. Found: C, 37.32; H, 2.71; N, 14.56. *N,N'*-Bis(2,4-dinitrophenyl)-L-cystinamide (**3b**) was prepared from L-cystinamide and 2,4-dinitrofluorobenzene in a similar manner in 26% yield; mp 195–196 °C; NMR ($Me_2SO$-$d_6$) $\delta$ 3.35 (d, $J$ = 6 Hz, 2 H, $CH_2$), 4.65 (q, $J$ = 6 Hz, 1 H, CH), 7.06 (d, $J$ = 9 Hz, 1 H, 6-H), 7.50 and 7.80 (each br s, 2 H, $NH_2$), 8.22 (dd, $J$ = 9, 2 Hz, 1 H, 5-H), 8.88 (d, $J$ = 2 Hz, 1 H, NH), 8.79 (d, $J$ = 8 Hz, 1 H, 3-H). Anal. Calcd for $C_{18}H_{18}O_{10}N_8S_2$: C, 37.90; H, 3.18; N, 19.64. Found: C, 37.76; H, 2.82; N, 19.20.

**Apparatus.** Electronic spectra were determined on a Hitachi 200-10 spectrophotometer with a thermostatted cell holder. NMR spectra were taken with a JEOL JNM-MH-100 spectrometer. High-performance liquid chromatography (LC) was run on a Kyowa Seimitsu liquid chromatograph K 880 with Kyowa gel ODS 4102 as a stationary phase. The sample was eluted with methanol at about 0.26 mL/min and the effluents were monitored by UV light at 350 nm. An example of high-performance LC analysis of dinitrophenylcysteine isomers is given in Figure 1.

**Kinetics.** Kinetic experiments were carried out in methanol at 25.0 °C unless otherwise stated. A single run was initiated by addition of a base solution to the substrate (**1a**) in a cuvette (3 mL). Base was present in excess (10–20-fold) over substrate. Reaction rate was determined by following the appearance of **2a** at 350 nm. The relevant spectral data are summarized in Table I. The reaction followed good first-order kinetics with some exceptions. With DBU, as base, the first-order plot gave a convex curve owing to the contamination with the reverse reaction. In this case the apparent first-order rate constants were estimated only from the early stage of reaction.

**Table I. Electronic Absorption Spectral Data of *S*- and *N*-(2,4-Dinitrophenyl)-L-cysteine and Cysteinamide in Methanol**

| compd | $\lambda_{max}$, nm | $\epsilon_{max}$, $M^{-1}$ $cm^{-1}$ |
|---|---|---|
| **1a** | 330 | $1.10 \times 10^4$ |
| **1b** | 332 | $1.12 \times 10^4$ |
| **2a**[a] | 350 | $1.52 \times 10^4$ |
| **2b**[a] | 350 | $1.55 \times 10^4$ |

[a] These compounds were prepared by the reduction of *N,N'*-bis(2,4-dinitrophenyl)-L-cystine (**3a**) or cystinamide (**3b**) with 2-mercaptoethanol

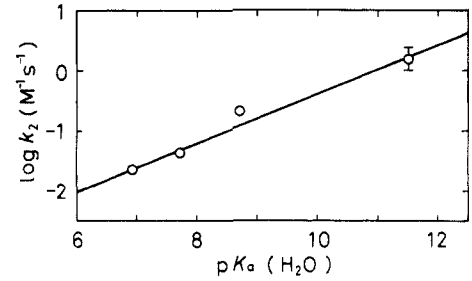



**Figure 2.** Brønsted plot for the rearrangement of **1a** in methanol at 25.0 °C. Bases employed are imidazole, *N*-ethylmorpholine, Dabco, and DBU in increasing order of basicity.

## Results

When **1a** was incubated with a suitable organic base such as imidazole or Dabco in methanol, its absorption spectrum changed with time and the final spectrum was identical with that of authentic **2a**. Thus, it is obvious that the dinitrophenyl moiety migrated intramolecularly from sulfur to nitrogen (eq 2). The rate of rearrangement is dependent on the concentration of a base. Thus the relationship shown in eq 3 was valid for all the bases employed; $k_1 = 1.05 \times 10^{-4}$ $s^{-1}$ at 25.0 °C. Figure 2 shows the Brønsted plot of the second-order rate constants obtained for imidazole, *N*-ethylmorpholine, Dabco, and DBU vs. acid strength of the conjugate acid of bases in water. It is evident that a stronger base facilitates the rearrangement more, though the plot itself is rather qualitative because the p$K_a$ values evaluated in water were adopted.

$$k_{obsd} = k_1 + k_2[B] \quad (3)$$

With DBU a first-order rate plot deviated downward at the late stage of reaction irrespective of the base concentration. This was seen also at high concentrations of Dabco. It turned out that this is due to the presence of equilibrium between **1a** and **2a** under these conditions. This was confirmed by an experiment where **2a** was employed as the starting substrate. Incubation of **2a** under the identical conditions gave rise to a reverse spectral change. The spectrum determined after attainment of equilibrium was almost identical with that obtained for

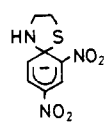
(7) H. P. Burchfield, *Nature*, **181**, 49 (1958).
(8) K. Wallenfels and C. Streffer, *Biochem. Z.*, **346**, 119 (1966).
(9) A. Patchornich and M. Sokolvsky, *J. Am. Chem. Soc.*, **86**, 1212 (1964).
(10) F. Sanger, *Biochem. J.*, **39**, 507 (1945).

the system starting with **1a**. The molar ratio of **2a** to **1a** in the equilibrium mixture first decreased with an increase in the DBU concentration but tended to level off at ~2 × $10^{-3}$ M. The ratio of **2a** to **1a** was about 9 to 1. This corresponds to a free energy difference of 1.3 kcal/mol in favor of **2a**. When the strong base DBU or a large excess of Dabco is employed, the sulfhydryl group of **2a** partially ionizes. The resulting $S^-$ group is much more nucleophilic than the unionized SH group and tends to reverse the reaction toward **1a**.

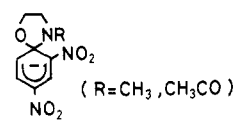
The energies of activation for both spontaneous and base-catalyzed reactions in the presence of different amounts of Dabco were evaluated from the conventional Arrhenius plot. Experiments were carried out at 15, 20, 25, and 30 °C and the values were 14.9 and 16.6 kcal $mol^{-1}$ for the spontaneous and base-catalyzed reactions, respectively. These values are somewhat smaller than that for **5** (17.7 kcal $mol^{-1}$), which should be due to the fact that the C–S bond has become more scissile owing to (i) the presence of two nitro groups on the phenyl ring and (ii) the phenyl moiety being bound to sulfur which is a better leaving group than nitrogen.

It is of special interest that the S → N rearrangement is retarded very much when **1b** is substituted for **1a**. Thus no reaction occurred when **1b** was warmed in methanol with imidazole, *N*-ethylmorpholine, or Dabco below 40 °C. With DBU **1b** underwent transformations, but the reaction was not clean. The elimination reaction to afford 2,4-dinitrothiophenolate and α-aminoacrylamide appears to be involved as a side reaction, because a new absorption band appeared at ~420 nm and its intensity increased with the progress of reaction. The band is characteristic of the former species.[8] In addition, *S*-(2,4-dinitrophenyl)-*N*-acetylcysteine is known to undergo a facile elimination reaction under alkaline conditions.[8] Anyway, the important thing is that the carboxylate group of **1a** renders the substrate susceptible only to the intramolecular rearrangement.

When the reaction medium is switched from methanol to DMF or $Me_2SO$, a drastic increase in the rearrangement rate of **1a** was observed. The reaction takes place instantaneously upon dissolving of the substrate even in the absence of base. Hence, only the final equilibrium mixture was seen by the conventional experimental technique. The molar ratio of **2a** to **1a** was estimated from the spectra to be 95:5 in both DMF and $Me_2SO$. Adding DBU to the mixture causes a time-dependent N → S Smiles rearrangement. Occurrence of the reverse rearrangement was further confirmed with the use of authentic **2a**. It should be noted that an intermediate was detected during this transformation in DMF but not in $Me_2SO$. A very broad absorption with a maximum at ~500 nm appeared instantaneously upon addition of DBU to the DMF solution (Figure 3). The band location is completely compatible with the structure of a σ complex like **6**, because similar




6

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anionic σ complex **7** has a strong absorption at ~510 nm[3,4] and the absorption maximum of the complex is insensitive to the nature of atoms directly linked to the phenyl ring.[11] The absorption due to the complex is greatest just after

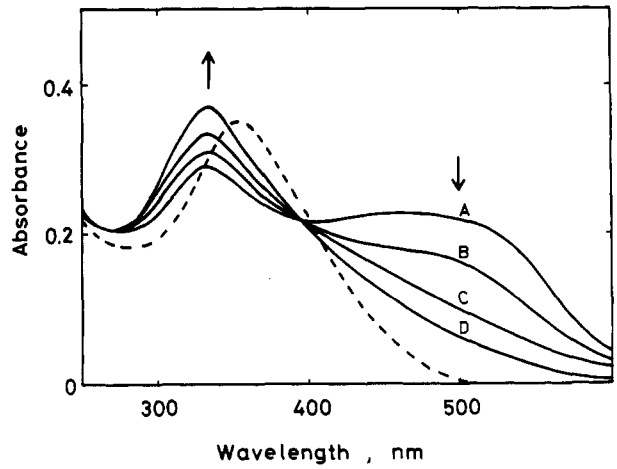



**Figure 3.** Spectroscopic observation of the rearrangement of **2a** into **1a** in DMF in the presence of DBU at 25.0 °C. Spectra were taken soon after addition of DBU (A) and at 10 (B), 30 (C), and 120 min (D). The broken line indicates the spectrum of **2a** before addition of DBU. Concentrations of **2a** and DBU were 2.13 × $10^{-5}$ and 9.8 × $10^{-4}$ M, respectively.

addition of the base and then decays slowly as shown in Figure 3. By reference to the known extinction coefficient for **7** (30 000),[2,3] the formation of **6** is estimated as ~30% at a maximum. The molar ratio of **2a** to **1a** was 1:9 for the final mixture in DMF.

When **1b** was employed as the substrate no spontaneous S → N rearrangement was observed either in DMF or $Me_2SO$, indicating that the carboxyl group in **1a** plays an essential role in the rearrangement in these solvents as well. In these solvents containing DBU, **1b** shows a complex spectral change similar to that observed in methanol. **2b** with DBU undergoes the slow N → S rearrangement through the same σ-complex intermediate, albeit its formation is not as extensive as that for **1b** (about one-fourth).

## Discussion

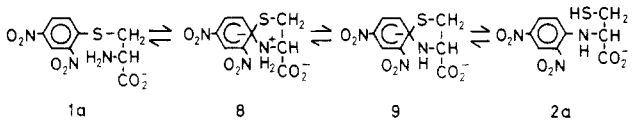
We have shown that the dinitrophenyl group linked to cysteine moves back and forth between sulfur and nitrogen atoms in polar organic solvents. Actually, **1a** and **2a** are present in equilibrium in these media and the equilibrium is dependent on the nature of solvent and whether base is present or not. Either isomer is more stable than the other by no greater than 2 kcal/mol under the conditions employed. Presumably this intrinsically small energy difference between the two isomers is responsible for the ready change in the relative populations depending on the medium.

In the present rearrangement reaction, the anionic σ-complex intermediate was spectroscopically detected in DMF. It has an absorption band at ~500 nm similar to the N,O-type σ complex **7**. This supports clearly that the reaction proceeds through such a complex. That the complex is observed only in DMF suggests that this solvent can somehow stabilize the unstable complex. Alternatively, the reaction mechanism may be regarded to be different among the solvents. But it is unlikely that a solvent such as $Me_2SO$, similar to DMF in many respects, affects the reaction mechanism in so drastically a different way. Many other S, N Smiles rearrangements have been known so far,[12-14] but in no case was a σ complex observed. This

(11) H. Hosoya, S. Hosoya, and S. Nagakura, *Theor. Chim. Acta*, **12**, 117 (1968).

(12) W. J. Evans and S. Smiles, *J. Chem. Soc.*, 181 (1935).
(13) S. Ghisla, W. C. Kenney, W. R. Knappe, W. McIntire, and T. P. Singer, *Biochemistry*, **19**, 2537 (1980).
(14) Y. Maki, T. Hiramitsu, and M. Suzuki, *Tetrahedron*, **36**, 2097 (1980).

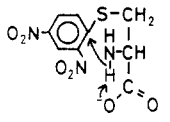
Scheme I



1a 8 9 2a

might be due to the fact that the mechanism is different from that of **1a**, because the reaction mechanism is dependent much on the nature of a migrating aromatic ring.[2] It is, however, conceivable that a complex was not detected because of an unfit choice of solvent. We believe that the reaction mechanism of the Smiles rearrangement could be better understood, at least partly, by a suitable choice of solvents.

In summary, the mechanism of the present Smiles rearrangement may be illustrated as in Scheme I. Formula **9** is assigned to the anionic $\sigma$ complex observed in DMF, since it should be more stable than 8 under alkaline conditions.[15] As shown in the Results section the carboxylate group of **1a** plays an essential role in the formation of the $\sigma$ complex and its replacement by the carboxamide made the substrate unreactive. Since there is not a large difference in both the electronic effect and the steric bulkiness between the two groups, the observed difference in the reactivity may be explained in terms of the neighboring participation of the carboxylate in the reaction through space. This is accomplished presumably by intramolecular proton abstraction from **1a** to form the key intermediate **9** as shown in **10**. The positive effect of added bases is



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consistent with this hypothesis. Although intramolecular catalysis is well documented in many organic reactions,[16] this is the first explicit example of such catalysis in Smiles rearrangements.

**Registry No. 1a**, 23815-63-6; **1b**, 76466-52-9; **2a**, 35749-09-8; **2b**, 76466-53-0; **3a**, 23067-16-5; **3b**, 76479-86-2; L-cysteinamide, 758-90-7; 2,4-dinitrofluorobenzene, 70-34-8.

(15) C. F. Bernasconi, C. L. Gehriger, and R. H. de Rossi, *J. Am. Chem. Soc.*, 98, 8451 (1976).

(16) W. P. Jencks, "Catalysis in Chemistry and Enzymology", Chapter 1, McGraw-Hill, New York, 1969.

# Mechanism of Hydrolysis of Hydroxy Thiolesters in the Presence of Boric Acid

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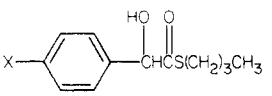
*Received November 13, 1980*

The catalytic effect of boric acid on the hydrolysis of *S*-butyl 2-hydroxy-2-phenylthioacetate (thiomandelate, **1**) and 3-hydroxy-3-phenylthiopropionate (**2**) has been investigated in aqueous solution. The catalytic constants increased sigmoidally with increasing pH, the p$K_a$ of the curve being 9.2 for both **1** and **2**. Approximate Hammett $\rho$ values were 1.2 and 0.6 for the alkaline and borate-catalyzed hydrolyses of ring-substituted derivatives of **1**, respectively. Boric acid did not show any specific influence on the hydrazinolysis of **1**. These results lead to the conclusion that the borate catalysis occurs through an intramolecular transfer of the boron-coordinated hydroxide ion to the carbonyl carbon within a borate–substrate complex.

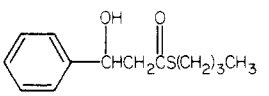
It has long been known that boric acid easily forms chelate complexes with polyols[1,2] and $\alpha$-hydroxy carboxylic acids.[3,4] These complexes equilibrate very rapidly in aqueous solution as temperature-jump experiments demonstrated.[5-7]

Capon and Ghosh[8] on the other hand found that hydrolysis of phenyl salicylate is accelerated in borate buffers and considered that the acceleration was due to the transient formation of a borate complex with the substrate. Similar observations were made during the hydrolysis of salicylideneaniline.[9] However, the speculative mechanism presented for the borate catalysis was later criticized by Tanner and Bruice,[10] who investigated kinetically the formation and hydrolysis of boric acid esters of salicylamides.

In this paper we describe an investigation of the mechanism of boric acid catalysis of the hydrolysis of thiolesters of $\alpha$- and $\beta$-hydroxy carboxylic acids. The substrates examined include *S*-butyl 2-hydroxy-2-phenylthioacetates (thiomandelates, **1a–c**), 3-hydroxy-3-phenylthiopropionate (**2**), and thioacetate (**3**).



1a, X = H
b, X = $CH_3$
c, X = Cl



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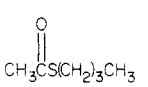

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