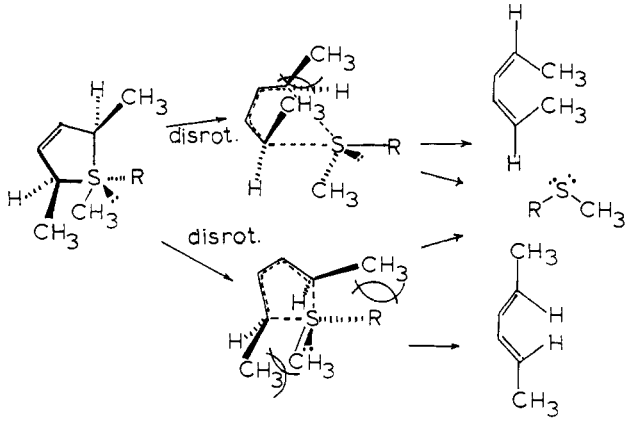
Path B accommodates all the experimental evidence. Assuming that the five-membered ring occupies an apical–basal orientation about sulfur, with the remaining basal ligands being the electron pair and the methyl group,[11] a disrotatory fragmentation to generate the cis,cis diene requires only that the methyl groups in the 2,5 positions be eclipsed as the carbon–sulfur bonds break (Scheme III).[12] However, the forming butyl

Scheme III. Proposed Stereochemistry of Sulfurane Decomposition



methyl sulfide experiences very little steric hindrance. On the other hand, in a disrotatory elimination leading to the all-trans isomer, the butyl methyl sulfide experiences a large interaction with both of the pseudoequatorial ring methyl groups as bond breaking commences.

It appears that this second interaction is slightly stronger, a fact which leads to a slight preponderance of cis,cis diene IX.

Acknowledgment. We wish to express our thanks to the National Institutes of Health and the National Science Foundation for their generous support of our program.

(11) (a) K. Mislow, *et al.*, *J. Amer. Chem. Soc.*, **91**, 7031 (1969); **91**, 564 (1969); (b) K. Mislow, *Accounts Chem. Res.*, **3**, 321 (1970), and references therein.

(12) It is difficult to visualize the developing eclipsing interactions depicted in Scheme III for each mode of disrotation without the aid of molecular models.

(13) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient.

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Competing Intramolecular Nucleophilic and General Base Catalysis in the Hydrolysis of Catechol Monosuccinates

Sir:

A recent communication[1] describing a possible case of intramolecular bifunctional catalysis (nucleophilic and general acid catalysis) in the hydrolysis of hexachlorophene monosuccinate (**1**) prompts us to report some results obtained from the hydrolysis of compounds belonging to a structurally similar system, the catechol monosuccinates (**2**). Here we find evidence for *competing* intramolecular nucleophilic and general base catalysis instead of cooperating bifunctional catalysis.

(1) T. Higuchi, H. Takechi, I. H. Pitman, and H. L. Fung, *J. Amer. Chem. Soc.*, **93**, 539 (1971).

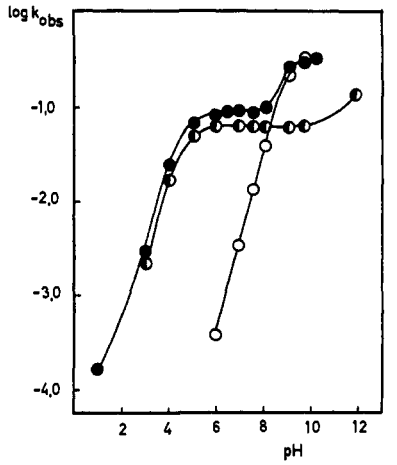
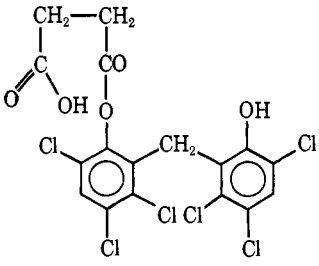
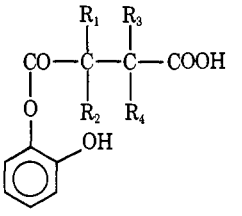


Figure 1. pH–rate profiles for catechol monosuccinate (**2a**, filled circles), *o*-methoxyphenyl hydrogen succinate (semifilled circles), and catechol monoacetate (**3**, open circles) at 25.0° in water containing 11% (by volume) acetonitrile.



1



2a, $R_{1-4} = H$
b, $R_{1,3} = H$; $R_{2,4} = Me(dl)$
c, $R_{1-4} = Me$

It is well established that aryl hydrogen succinates hydrolyze *via* an intramolecular nucleophilic attack by the carboxylate group on the ester carbonyl carbon atom with formation of succinic anhydride and the corresponding phenolate ion.[2,3] We have now investigated the hydrolysis of a series of catechol monosuccinates[4] (**2a–c**) which also hydrolyze *via* intramolecular carboxylate ion attack in the pH interval where only the carboxyl group is ionized. However, in the pH region where the phenolic hydroxyl group begins to ionize, one can also recognize a second mechanism, in which the phenolate group appears to act as a general base in competition with the nucleophilic attack by carboxylate ion. Thus, the pH–rate profile for **2a** shows an increase in rate at pH values above 7 (Figure 1) and a second plateau at pH > 9, which coincides with the plateau found in the pH–rate profile of catechol monoacetate (**3**) (Figure 1). The kinetic pK_{app} values for **2a** and **3** are identical within the limits of experi-

(2) (a) E. Gaetjens and H. Morawetz, *ibid.*, **82**, 5328 (1960); (b) T. C. Bruice and U. K. Pandit, *ibid.*, **82**, 5858 (1960); (c) T. C. Bruice and U. K. Pandit, *Proc. Nat. Acad. Sci. U. S.*, **46**, 402 (1960); (d) T. C. Bruice and W. C. Bradbury, *J. Amer. Chem. Soc.*, **87**, 4846 (1965).

(3) It has been shown (J. W. Thanassi and T. C. Bruice, *ibid.*, **88**, 747 (1966); L. Eberson, *Acta Chem. Scand.*, **18**, 2015 (1964); G. H. Hurst and M. L. Bender, *J. Amer. Chem. Soc.*, **93**, 704 (1971)) that the choice between participation of neighboring carboxylate or carboxyl group is governed by leaving group tendencies, good leaving groups being hydrolyzed *via* carboxylate group participation.

(4) Intermediates in the hydrolysis of cyclic succinoylcatechols; L. Eberson and L. Å. Svensson, work to be published.

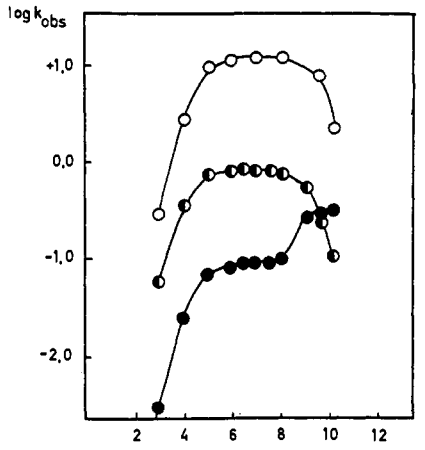


Figure 2. pH–rate profiles for catechol monosuccinate (**2a**, filled circles), catechol mono-*dl*-2,3-dimethylsuccinate (**2b**, semifilled circles), and catechol monotetramethylsuccinate (**2c**, open circles) at 25.0° in water containing 11% (by volume) acetonitrile.

mental error, which strongly supports the assumption that **2a** and **3** hydrolyze according to the same mechanism at pH > 8. Catechol monobenzoates **4** and **3** have previously been shown to undergo hydrolysis with intramolecular general base catalysis from the adjacent ortho phenolate group.[5] Furthermore, the solvent deuterium isotope effects for **2a** and **4** are identical (k_{H_2O}/k_{D_2O} = 1.8[6]), which points to a similarity in mechanism.

The absence of general acid catalysis in the hydrolysis of the catechol monosuccinates is evident from the small variation in the hydrolysis rates of the monosuccinates of phenol, *o*-methoxyphenol, and catechol (**2a**) (Table I). As can be seen from the pH–rate profiles of

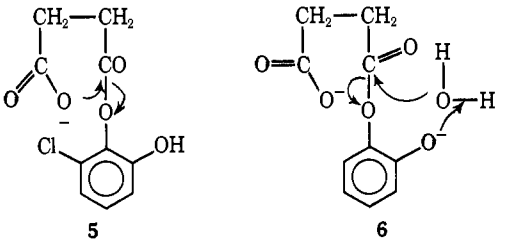
Table I. Values of k_α[a] for the Hydrolysis of Substituted Aryl Hydrogen Succinates

Ester	k_α, min^{-1}
2a	0.093 (0.076[b])
2b	0.84
2c	12.3
Phenyl hydrogen succinate	0.085[b]
o-Methoxyphenyl hydrogen succinate	0.065 (0.072[b])

[a] k_α is the rate constant for hydrolysis *via* intramolecular carboxylate ion attack, *i.e.*, at the plateau of the pH–rate profile. [b] Reference 2a.

esters **2b** and **2c** (Figure 2), methyl substitution in the succinic acid moiety increases the rate of the intramolecular carboxylate ion catalyzed reaction (k_α) and decreases the rate of the intramolecular general base catalyzed reaction (relevant rate constants are summarized in Table I). The increase in k_α is caused by the accommodation of alkyl substituents in the carbon chain, the geminate dimethyl effect, which operates strongly in the cyclization of succinic acid derivatives,[7] while the retardation of the second mechanism is due to increased steric hindrance for the general base catalyzed attack of a water molecule at the ester carbonyl carbon atom. In addition, the pH–rate profile for **2a** shows that the intramolecular carboxylate catalysis must be unimportant when intramolecular general base catalysis by the adjacent ortho phenolate group is operating. This is not unexpected in view of the electrostatic repulsion introduced in the dianion of **2a**. It is, however, possible that the degree of intramolecular carboxylate ion participation at pH >8 increases as the succinic acid moiety becomes more substituted, which of course will make the participation of the adjacent ortho phenolate group less efficient.

Thus, we have presented strong evidence for *competing* intramolecular nucleophilic and general base catalyzed mechanisms in the hydrolysis of catechol monosuccinates **2a**, **b**, and **c**. These mechanisms can be represented by formulas **5** and **6**. We believe that the difference in hydrolysis behavior between **1** and **2** can be rationalized in terms of a much weaker hydrogen bond between the free OH group and the ether oxygen of the ester group in **5** than in the corresponding anion of **1**.[8]



5 **6**

(5) B. Capon and B. C. Ghosh, *J. Chem. Soc. B*, 472 (1966).
(6) Ratio of the rate constants based on the concentration of the ionized forms of the esters.
(7) L. Eberson and H. Welinder, *J. Amer. Chem. Soc.*, in press, and references cited therein.
(8) M. Tichy, *Advan. Org. Chem.*, **5**, 115 (1965); V. S. Korobkov, *Russ. J. Phys. Chem.*, **38**, 795 (1964).

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Cyclobutenes by Ring Expansion of Cyclopropenes

Sir:

We wish to report a new and general cyclobutene synthesis, in which lithium aluminum hydride mixed with aluminum chloride reductively expands the ring of readily accessible cyclopropenes. Our approach complements the known methods for obtaining cyclobutenes.[1] The following synthesis of 1,2-dipropyl-

(1) One such scheme depends on the availability of properly substituted acylcyclopropanes, the tosylhydrazones of which are heated with alkoxide [*cf.* C. D. Gutsche and D. Redmore "Carbocyclic Ring Expansions," Academic Press, New York, N. Y., 1968, p 111; I. D. R. Stevens, H. M. Frey, and C. L. Bird, *Angew. Chem., Int. Ed. Engl.*, **7**, 646 (1968)]. Another preparation requires 1,3-butadienes, which can be photochemically cyclized [*cf.* K. J. Crowley, *Tetrahedron*, **21**, 1001 (1965); W. G. Dauben, R. L. Cargill, R. M. Coates, and J. Saltiel, *J. Amer. Chem. Soc.*, **88**, 2742 (1966); H. M. Frey, *Trans. Faraday Soc.*, **59**, 1619 (1963)]. Other useful though less general methods have also been reported [*cf.* R. Fuks and H. G. Viehe in "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, p 435].