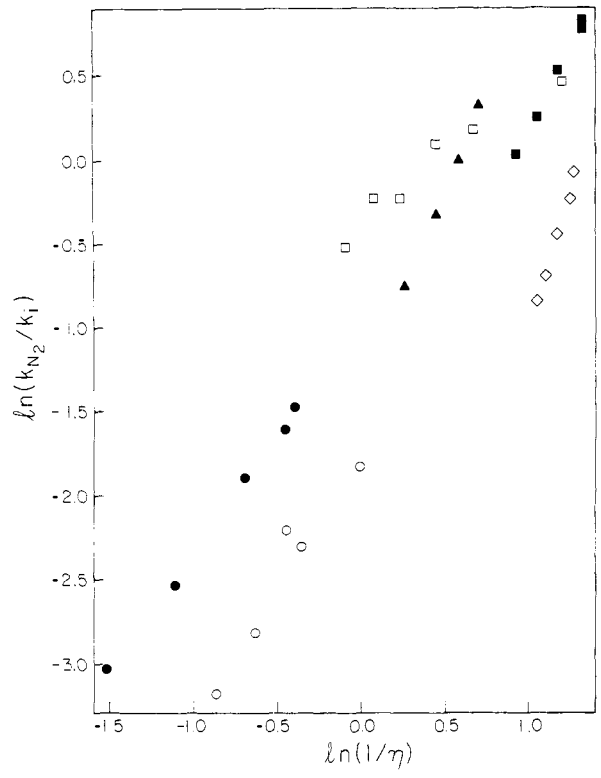

Figure 2. Viscosity dependence of ln (k_{N_2}/k_i); hexane (■), toluene (△), 2-propanol (●), acetone (◇), variable temperature;[4] hexane (□), ethanol (○), variable pressure.

scission,[10] recombination to give the stable trans isomers (k_{-1t}) should also be competitive.[11]

The smaller positive values of ΔV_i^* (Table I) are also consistent with this mechanism. On the basis of Scheme I, ΔV_i^* depends both on ΔV_1^* and the pressure dependences of the ratios k_{-1c}/k_{-1t} and k_{N_2}/k_i (eq 1).[12] The latter ratio decreases with increasing

$$\Delta V_i^* = \Delta V_1^* + RT\,(\partial \ln (1 + k_{-1c}/k_{-1t} + k_{N_2}/k_i)/\partial P) \quad (1)$$

pressure (Figure 1) while the ratio k_{-1c}/k_{-1t} is expected to remain constant or, perhaps, increase with pressure,[13] causing the differential term in eq 1 to be small. Thus, ΔV_i^* should be comparable to ΔV_1^* (ca. +5 cm^3/mol[10]), and this agrees with the data (Table I).[14] In contrast, Asano[15] has found that nonradical cis → trans isomerizations of azobenzenes give negative values of ΔV_i^*.

Decreases in k_{N_2}/k_i with increasing solvent polarity and decreasing temperature[4] have been explained in part by polar effects.[5,16] On the basis of Scheme I, k_{N_2}/k_i is equal to $(k_\beta + k_d)/k_{-1t}$, which is expected to decrease with solvent viscosity due to its effect on k_d. In fact, with the exception of the acetone data,[17] the values of ln (k_{N_2}/k_i), whether derived from *temperature variation*[4] in hexane, toluene, and 2-propanol or *pressure variation* in hexane and ethanol, show a rough linear correlation with ln $(1/\eta)$ (Figure 2),[18] consistent with our mechanism.

When diazenyl radicals are formed from *cis*-azoalkanes, we believe that they serve as isomerization intermediates (Scheme I).[19] However, not all *cis*-azoalkanes undergo deazatization (radical formation) competitively with isomerization.[4,5] In those cases, such as *cis*-azo-1-bicyclo[2.2.1]heptane and *cis*-azo-1-bicyclo[2.1.1]hexane, we agree that isomerization occurs by inversion at nitrogen. We also agree with Engel and Timberlake that increasing steric bulk of the R group increases the inversion rate.[4] However, we believe that isomerization via diazenyl radicals is a lower energy process for **1**, **2**, and the [2.2.2] isomer, for example, than isomerization via inversion.[20,21]

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Registry No. 1, 59388-63-5; **2**, 63561-19-3.

(10) See: Neuman, R. C., Jr.; Amrich, M. J., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 2730.

(11) While recognized as a possible mechanism,[4] lack of evidence for diazenyl radical intermediates made it unattractive.

(12) Equation 1 is derived from Scheme I by recognizing that (a) $\Delta V_i^* = -RT(\partial \ln k_i/\partial P)$; (b) $\Delta V_1^* = -RT(\partial \ln k_1/\partial P)$; (c) $k_i = k_1[k_{-1t}/(k_{-1c} + k_{-1t} + k_d + k_\beta)]$; (d) $k_{N_2} + k_i[(k_\beta + k_d)/(k_{-1c} + k_{-1t} + k_d + k_\beta)]$, and (e) $k_{N_2}/k_i = (k_\beta + k_d)/k_{-1t}$.

(13) Geminate recombination to give *cis*-**1** or -**2** should be pressure accelerated. Formation of *trans*-**1** or -**2** (k_{-1t}) involves bond formation but also demands pressure-retarded rotational diffusion of the caged radicals.

(14) $\Delta V^*_{N_2} = \Delta V_1^* + RT(\partial \ln (1 + k_{-1c}/(k_\beta + k_d) + k_i/k_{N_2})/\partial P)$;[12] *both* rate constant ratios in this differential term *increase* with pressure causing $\Delta V^*_{N_2} \gg \Delta V^*_1$.[10]

(15) (a) Asano, T.; Okada, T.; Shinkai, S.; Shigematsu, K.; Kusano, Y.; Manabe, O. *J. Am. Chem. Soc.* **1981**, *103*, 5161. (b) Asano, T.; Yano, T.; Okada, T. *Ibid.* **1982**, *104*, 4900.

(16) (a) Schulz, A.; Rüchardt, C. *Tetrahedron Lett.* **1976**, 3883. (b) Duismann, W.; Rüchardt, C. *Chem. Ber.* **1978**, *111*, 596.

(17) The acetone data[4] are less accurate than those for the other solvents.

(18) (a) Since solvent internal pressure and viscosity are related, this supports earlier proposals of internal pressure effects by Snyder.[17b] (b) Olsen, H.; Snyder, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 285.

(19) However, if $(k_\beta + k_d) \gg k_{-1t}$ (e.g. azo-2-methyl-2-propane), isomerization could be undetectable.[4,5]

(20) See ref 4, Figure 3; the log k_{rel} vs. E_s correlation could be fit with two lines, one through **1** and [2.2.2] and the other through [2.2.1] and [2.1.1].

(21) (a) Dannenberg[21b] calculates that *cis*-azoethane decomposes by one-bond scission: (b) Dannenberg, J., private communication.

An Incremental Approach to Hosts That Mimic Serine Proteases[1]

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The design and synthesis of enzyme-mimicking host compounds remains one of the challenging and stimulating problems of organic chemistry. We chose to study serine protease mimics because the structure and mechanism of action of these enzymes have been so thoroughly studied. Their active sites contain a complexing cavity, an acyl-receiving and -releasing hydroxymethylene group, and a proton-transfer system that is organized to complement the structures of certain amide and ester substrates.[2] The naturally occurring cyclodextrins neatly combine a complexing cavity with primary hydroxyl groups (nucleophiles), and they have been successfully modified to provide systems that exhibit some of the features of the serine proteases.[3]

The structures of two totally unknown systems, **1** and **2** (Chart I), have been designed with CPK molecular models to combine in a cooperative arrangement similar to that of the proteases a binding site, a primary hydroxyl, an imidazole, and a carboxyl group. These two "ultimate target" hosts have in common with simpler host **3** the same organization of binding site and hydroxyl nucleophile. We report here the synthesis of **3**, its binding

(1) We thank the Public Health Service for Grant GM 12640, which supported this research.

(2) (a) Blow, D. M.; Birktoft, J. J.; Hartley, B. S. *Nature (London)* **1969**, *103*, 337-340. (b) Hamilton, S. E.; Zerner, B. *J. Am. Chem. Soc.* **1981**, *103*, 1827-1831 and references therein.

(3) (a) Trainor, G. L.; Breslow, R. *J. Am. Chem. Soc.* **1981**, *103*, 154-158 and references quoted therein. (b) Bender, M. L.; Komiyama, M. "Cyclodextrin Chemistry"; Springer-Verlag: New York, 1977; pp 1-79, and references quoted therein.

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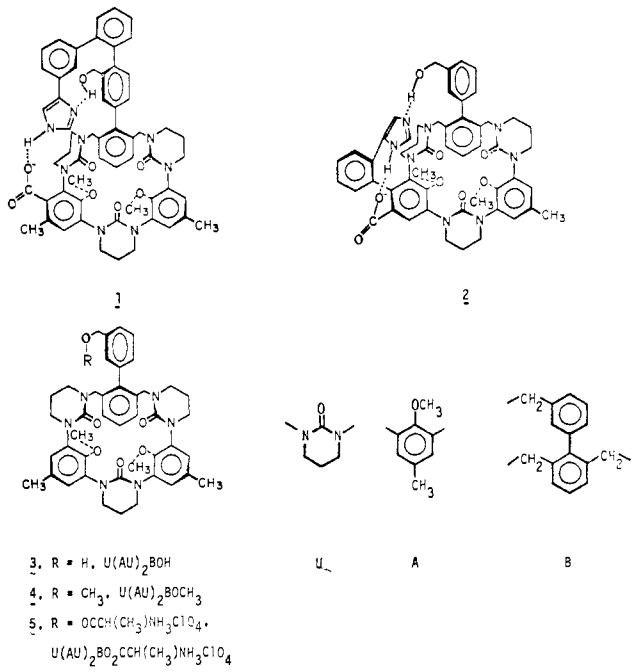
Chart I



properties, and its promising behavior as an acyl acceptor of an amino ester salt. Host **3** and its precursors will be represented by sequences of capital letters (see Chart I), each standing for the structural units indicated.

The critical ring-closing reaction to form $U(AU)_2BOCH_3 \cdot H_2O$[4] (**4**, 60%, mp 200 °C, phase change) involved condensation of HUAUAUH[5] with $(Br)_2BOCH_3$[6] ($(CH_2)_4O$–NaH, high dilution, −78 to 25 °C, 40 h). The cycle was purified by gel permeation chromatography of its NaBr complex, which was decomplexed by heating with methanol–water, the process being driven by crystallization of the insoluble free cycle.[5] Treatment of $U(AU)_2BOCH_3$ with HBr–AcOH (25 °C, 20 m) followed by hydrolysis (aqueous Na_2CO_3, 100 °C) gave $U(AU)_2BOH \cdot 2H_2O$[4] (**3**, 60%, mp 250 °C dec). The $-\Delta G°$ values for complexation of **3** with Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, $CH_3NH_3^+$, and *t*-$BuNH_3^+$ picrates in $CDCl_3$ saturated with D_2O at 25 °C[5] were found to be 12.2, 15.0, 15.4, 12.6, 11.8, 13.6, 12.7, and 10.6 kcal mol^{-1}, respectively. Those for **4** complexing Rb^+ and $CH_3NH_3^+$ picrates were 13.7 and 13.6 kcal mol^{-1}, respectively. The similarity of values for the two hosts indicates that if any intramolecular hydrogen bonds must be broken during complexation of **3**, the cost is only ~1 kcal mol^{-1}. When equal molar quantities of $U(AU)_2BOH \cdot 2H_2O$ (**4**) and L-alanyl *p*-nitrophenyl ester perchlorate[4] (prepared by standard methods, mp 197–198 °C) were dissolved in CH_2Cl_2–pyridine at 25 °C (2 days), the corresponding ester complex $U(AU)_2BO_2CCH(CH_3)NH_3ClO_4 \cdot H_2O$ was formed (**5**, 84%, glass).[4]

Table I. Rate Factors for Acyl Transfer from L-Alanyl *p*-Nitrophenyl Ester Perchlorate to U(AU)BOH (**3**) vs. **6**[a]

run no.	nucleophile kind	nucleophile concn, M	R_3N concn, M	10^3k, m^{-1}[b]	rate factor[c]
1	**6**	0.016	0.006	<0.01	
2	**6**	0.032	0.006	<0.01	1
3	**3**	0.0014	0.001	2.8	
4	**3**	0.0014	0.003[d]	2.2	
5	**3**	0.0014	0.003	9.1	
6	**3**	0.0014	0.006	17[e]	≈10^{11}
7	**3**	0.0014	0.010	24	
8	**3**	0.0007	0.006	19[e]	≈10^{11}
9[f]	**3**	0.0016	0.006	0.43	≈10^9

[a] Concentration of ester, 0.0001 M; of R_3NHClO_4, 0.001 M, unless otherwise specified. [b] *k*'s obtained from plots of ln $(A_\infty - A_t)$ vs. $t(m)$, where A_∞ is absorbance units at time infinity and A_t at time *t*. [c] See footnote 11 for calculation. [d] R_3NHClO_4, 0.003 M. [e] Triplicate or duplicate runs. [f] Complexed **3**, $U(AU)_2BOH \cdot NaClO_4$, used in place of **3**.

The rates of acylation by L-alanyl *p*-nitrophenyl ester perchlorate of host $U(AU)_2BOH \cdot 2H_2O$ (**3**) and of the noncomplexing model compound 3-phenylbenzyl alcohol[4,8] (**6**) were followed through 5–8 half-lives with 9–18 points at 24.0 ± 0.1 °C by observing the absorbance at 350 nm of the *p*-nitrophenol liberated.[9] The medium was $CDCl_3$ containing diisopropylethylamine–perchlorate salt buffer (R_3N and R_3NHClO_4, respectively) and ~0.5% of $(CH_3)_2NCHO$ by volume. Formation of $U(AU)_2BO_2CCH(CH_3)NH_3ClO_4$ (**5**) in the kinetic medium was verified by its ^1H NMR spectrum. The concentration of ester (10^{-4} M) was exceeded by that of **3** by factors of 7–16 and by that of **6** by factors of 160–320. The concentration of R_3NHClO_4 was held at 0.001 M except in run 4 when it was 0.003 M. The reactions followed pseudo-first-order kinetics (correlation coefficients of 0.997–0.980) whose rate constants (k) and conditions are summarized in Table I.[9]

Runs 3–7 indicate the reaction to be first order in buffer ratio (over a ratio change of 1 order of magnitude), which indicates that CH_2O^- is the active nucleophile in the transacylation. Thus the complexation of $CH_3CH(CO_2R)NH_3^+$ to $U(AU)_2BOH$ (**3**) is strong enough to resist proton transfer from NH_3^+ to R_3N at buffer ratios high enough to provide kinetically controlling concentrations of CH_2O^-. In the absence of complexation, the pK_a of the NH_3^+ group of the amino ester is 7,[10a] that of R_3NH^+ is 10.8,[10b] and that of $ArCH_2OH$ is about 15.4 in water.[10c] Thus the pK_a of the complexed amino ester NH_3^+ proton must be raised by several units, a hypothesis compatible with the 12.7 kcal mol^{-1} binding free energy of **3** by $CH_3NH_3^+$ picrate in $CDCl_3$ saturated with water.

The rate factors of Table I refer to solutions of $CH_3CH(CO_2R)NH_3ClO_4$, $U(AU)_2BOH$, and **6** as the standard states for the reactants that were mixed to cause the reactions whose kinetics were followed. The treatment[11] compares the nucleophilicity of

(4) These new compounds gave C and H analyses within 0.30% of theory and ^1H NMR spectra and mass spectra consistent with their assigned structures.

(5) Cram, D. J.; Dicker, I. B.; Knobler, C. B.; Trueblood, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 6828–6830. Procedures for similar ring closures are recorded here, as well as ^1H NMR spectra and binding free energies for similar compounds.

(6) The synthesis of Br_2BOCH_3 is outlined here. The Grignard reagent prepared from 3-bromotoluene was added to 1,3-bis(4,4-dimethyl-2-oxazolin-2-yl)-2-fluorobenzene[4,7] ($(CH_2)_4O$, 25 °C, 18 h) to produce 2,6-bis(4,4-dimethyl-2-oxazolin-2-yl)-3′-methyl-1,1′-biphenyl[4] (oil, 96%). This substance was N-methylated with CH_3I in CH_3NO_2, the product was hydrolyzed with NaOH, and the salt was acidified to produce 3′-methyl-1,1′-biphenyl-2,6-dicarboxylic acid[4] (mp 214–215 °C, 73%). This diacid was converted to its dimethyl ester (CH_2N_2), whose arylmethyl was monobrominated with *N*-bromosuccinimide. The crude product was converted with $NaOCH_3$ to dimethyl 3′-(methoxymethyl)-1,1′-biphenyl-2,6-dicarboxylate[4] (oil, 54%). This diester was reduced with $LiAlH_4$–ether to the corresponding diol, which was treated with PBr_3 in CH_2Cl_2–C_6H_6 to give Br_2BOCH_3[4] (mp 52–53 °C, 67%).

(7) M. P. de Grandpre and D. J. Cram, unpublished preparation, based on analogous work: Meyers, A. I.; Gabel, R.; Mikelich, E. D. *J. Org. Chem.* **1978**, *43*, 1372–1379.

(8) Hammond, G. S.; Reeder, C. E. *J. Am. Chem. Soc.* **1958**, *80*, 573–575.

(9) Separate stock solutions of diisopropylethylamine and its perchlorate salt were prepared in 25 mL of $CDCl_3$ at concentrations of 0.080 M. Solid **6** was weighed and directly added to the reaction mixture. Host **3** or its $NaClO_4$ complex (run 9) was added as a 0.0040 M stock solution in $CDCl_3$. The amino ester perchlorate (0.050 mmol) was dissolved in 0.50 mL of $(CH_3)_2NCHO$, and $CDCl_3$ was added to provide 5 mL total volume. Aliquots were transferred with Pasteur pipettes. No solution was stored more than 24 h. Reactions were run in quartz UV cells (2.5 mL) with Teflon stoppers in cell holders immersed in a constant-temperature bath. Absorbances (A) were measured periodically at 350 nm with a Beckman DU quartz spectrophotometer (Guilford digital readout). Initial readings were 0.050–0.100, and final readings (A_∞) were 0.400–0.500 and stable.

(10) (a) Hay, R. W.; Morris, R. J. *J. Chem. Soc. B* **1970**, 1577–1582. (b) Werber, M. W.; Shalitin, Y. *Bioorg. Chem.* **1973**, *2*, 202–220. Williams, A. W.; Young, G. T. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1194–1200. (c) Murto, J. *Acta Chem.. Scand.* **1964**, *18*, 1043–1053.

uncomplexed $U(AU)_2BOH$ with that of *uncomplexed* **6** toward *uncomplexed* ester. The much greater rates of reaction of $U(AU)_2BOH$ compared to **6** are interpreted in terms of all effects associated with $U(AU)_2BOH$ complexing $CH_3CH(CO_2R)NH_3^+$ in its transition state for transacylation (both $NH_3^+\cdots O$ and $O-C-O^-$ as binding sites) as compared to **6** complexing $CH_3CH(CO_2R)NH_3^+$ (only $O-C-O^-$ as a binding site) in its transition state for transacylation. The rate factor estimated in runs 6 and 8 is $\approx 10^{11}$. Although this value is approximate and subject to uncertainties,[11] there is no doubt that the rate factor associated with all of the effects of complexation is very large indeed, probably within a few powers of ten of that estimated. The high magnitude of this value provides an indication of the importance of collection and orientation[12] by complexation to the rate accelerations. The crystal structure of the complex $U(AUCH_2)_2A\cdot(CH_3)_3CNH_3^+ClO_4^-$ indicates it to be highly structured by three $N^+-H\cdots O=C$ hydrogen bonds in a nearly perfect tripod-type arrangement.[5] In molecular models a similar structure for $U(AU)_2BOH\cdot CH_3CH(CO_2R)NH_3^+$ places the CO_2R carbonyl group of the guest beautifully oriented for attack by the CH_2O^- group of the host. This high rate acceleration further confirms the validity of combining the techniques of host design, synthesis, crystal structure determination, and kinetic studies of structural recognition in complexation.[13]

Sodium ion in a concentration equal to that of **3** acted as a competitive inhibitor of complexation and, therefore, of acylation in run 9. The estimated acceleration rate factor fell by 2 orders of magnitude in run 9 as compared to run 6, in which Na^+ was absent. This degree of inhibition is consistent with expectations based on the $-\Delta G°$ values of binding of 15.0 kcal mol^{-1} by $U(AU)_2BOH$ for Na^+ vs. 12.7 kcal mol^{-1} for $CH_3NH_3^+$.

We were encouraged to do this work by the success of our first use of a thiol chorand as a host for transacylation of amino ester salts[14] and by the subsequent findings by others that two other thiol chorand hosts behaved similarly.[15] Unlike the earlier studies, the current one involves an incremental approach to serine protease-mimicking host systems. Compounds **1** and **2** in molecular models contain what in principle are all the features needed to approach the catalytic activities of the enzymes, but their syntheses represent a substantial effort. Accordingly, the synthesis of hemispherand $U(AUCH_2)_2A$ was developed, it was found to bind $CH_3NH_3^+$ and Na^+ much better than the chorands, and its complexes were found to provide the anticipated structures.[5] In $U(AU)_2BOH$ (**3**) described herein, the binding site and nucleophile are combined and are found to act cooperatively. In future studies, the imidazole and carboxylates of **1** and **2** will be added sequentially to **3** in the hope of making the proton transfers intramolecular, which with **3** are intermolecular parts of the transacylation processes.

(11) Calculation of the rate factors of Table I involve the following definitions and reasonable assumptions about mechanistic schemes. The reaction of $CH_3CH(CO_2C_6H_4\text{-}p\text{-}NO_2)NH_3ClO_4$ (gL) with **3** (hOH) to give **5** (gOh) and $p\text{-}NO_2C_6H_4OH$ (HL) is presumed to involve an overall bimolecular rate constant k_a but to go by the following mechanism in which [B] is the concentration of R_3N:

$$gL + hOH \xrightarrow{k_a} gOh + LH$$

$$gL + hOH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} gL\cdot hOH \qquad K_1 = k_1/k_{-1}$$

$$gL\cdot hOH + B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} gL\cdot hO^-\cdot BH^+ \qquad K_2 = k_2/k_{-2}$$

$$gL\cdot hO^-\cdot BH^+ \xrightarrow{k} gOh + LH + B$$

Experimentally [hOH] and [B] are constant, K_1 is very high valued, and k_{-1} is expected to be $> k$. Thus, the observed first-order kinetics (k_{obsd}) for the appearance of LH can be decribed by eq 1. With the reasonable assumption

$$k_{obsd} = [B]K_2k \ m^{-1} \tag{1}$$

$$k_a = [B]K_1K_2k \ M^{-1} \ m^{-1} \tag{2}$$

$$k_a = K_1k_{obsd} \ M^{-1} \ m^{-1} \tag{3}$$

that $k_{-1} > k_2[B]$, the second-order rate constant (k_a) for acylation of hOH by gL can be expressed by eq 2, which when combined with eq 1 gives eq 3. The value of K_1 for $CH_3CH(CO_2C_6H_4\text{-}p\text{-}NO_2)NH_3ClO_4$ complexing **3** is presumed to be within a few orders of magnitude of K_1 for CH_3NH_3 picrate complexing **3** ($2 \times 10^9 \ M^{-1}$). This assumption is supported by the following facts. With chorand hosts, $t\text{-}BuNH_3ClO_4$ gave K_1 values $\sim$60 times those of $t\text{-}BuNH_3$ picrate (Moore, S. S.; Tarnowski, T. L.; Newcomb, M.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 6398-6405). The K_1 values for **3** complexing Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, $CH_3NH_3^+$, and $t\text{-}BuNH_3^+$ picrates vary only from extremes of 10^8 to $10^{11} \ M^{-1}$, suggesting that the value for the alanyl ester picrate should fall in this range.

The reaction of gL with 3-phenylbenzyl alcohol (bOH) to give acylated product gOb and HL is presumed to involve an overall bimolecular rate constant k_b and to go by the following mechanism:

$$gL + bOH \xrightarrow{k_b} gOb + HL$$

$$bOH + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} bO^-\cdot HB^+ \qquad K = k_1/k_{-1}$$

$$gL + bO^-\cdot HB^+ \xrightarrow{k'} gOb + HL + B$$

With [bOH] > [gL] and [B] constant, $[mO^-\cdot HB^+]$ is constant, and the reaction should follow the first-order kinetics ($k_{obsd}{}^b$) of eq 4. Equation 5

$$k_{obsd}{}^b = k'[mO^-\cdot HB^+] \ m^{-1} \tag{4}$$

$$k_b = [B]k_1k'(k' + k_{-1}) \ M^{-1} \ m^{-1} \tag{5}$$

$$k_b = k_{obsd}{}^b/[bOH] \ M^{-1} \ m^{-1} \tag{6}$$

$$k_a/k_b = K_1k_{obsd}[bOH]/k_{obsd}{}^b \tag{7}$$

expresses k_b as a function of k_1, k_{-1}, k', and [B]. Since $k_{-1} > k_1$, eq 5 reduces to eq 6. The rate factor due to all effects of complexation is k_a/k_b, whose values at constant [M] can be estimated through eq 7. We warmly thank Professors R. L. Schowen and F. A. L. Anet for very helpful suggestions regarding this kinetic treatment.

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Dimerization and Cycloaddition Reactions of a Carbomethoxy-Substituted Cyclopropene

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Suitably substituted cyclopropenes suffer the ene reaction[1-3] and also readily undergo dimerization,[4] cycloaddition[5] and complexation with transition metals[6] as a means of releasing strain. During the course of our studies dealing with the excited-state behavior of cyclopropenes, we have uncovered a novel dimerization reaction that differs significantly from previously reported examples.[7] We report here the results of these studies.

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