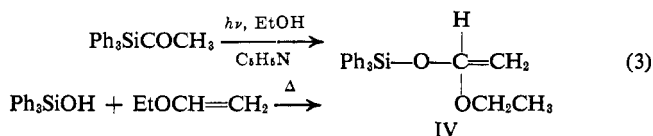ployed a 100-w lamp.[4] Using 0.5-g quantities of ketone in 10–15 ml of solvent, complete reaction was accomplished within 15–45-min exposure, as evidenced with benzoylsilanes by the fading of the originally yellow solution to colorless. After removal of the solvent under reduced pressure, the resulting material was examined by nmr spectroscopy, which allowed determination of the compounds present and of their proportions. This was of considerable assistance since most of the products were liquids, and some were relatively unstable.

The compounds formed under slightly basic conditions are of particular interest. Thus photolysis of benzoyltriphenylsilane in methanol gave α-methoxy-α-triphenylsiloxytoluene (IIIa) (benzaldehyde methyl triphenylsilyl acetal), as an unstable oil, identified by analysis, by its infrared absorption at 3.52 (O–Me), 6.9 (C–Ph), 7.0 and 9.0 (Si–Ph), and 9.4 μ (Si–O–C), and by its nmr spectrum which consisted of a 1-proton singlet at δ 5.87 ppm, assigned to the alkyl proton deshielded by two adjacent oxygen atoms, a 3-proton singlet at 3.0 ppm for the methoxyl group, and a 20-proton aromatic multiplet from 7.1 to 7.9 ppm. Similarly the oil isolated from photolysis of acetyltriphenylsilane in ethanol was assigned the structure 1-ethoxy-1-triphenylsiloxyethane (IV), based on its spectral properties and its independent synthesis from triphenylsilanol and ethyl vinyl ether, based on the procedure of Shostakovskii, et al.[5]
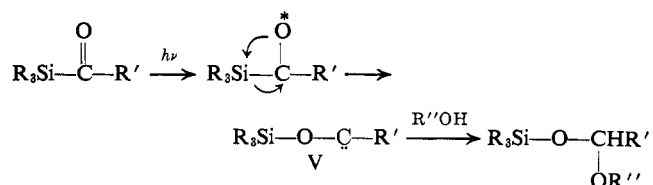
$$Ph_3SiCOCH_3 \xrightarrow[C_5H_5N]{h\nu,\ EtOH} Ph_3Si{-}O{-}\overset{\overset{\displaystyle H}{|}}{C}{=}CH_2 \quad (3)$$
$$Ph_3SiOH + EtOCH{=}CH_2 \xrightarrow{\Delta} \underset{\displaystyle \overset{|}{OCH_2CH_3}}{} $$
$$\text{IV}$$

Two other results are also of particular interest. When optically active (+)-benzoylmethyl-α-naphthylphenylsilane, $[\alpha]D$ +6.05°, of known absolute configuration[6] was photolyzed in neutral methanol, the predominant product found was (−)-methyl-α-naphthylphenylmethoxysilane, $[\alpha]D$ −8.0°, having a rotation corresponding to 78% net retention of configuration.[7]

On photolysis in methanol containing a trace of pyridine, (+)-benzoylsilane, $[\alpha]D$ +6.18°, gave α-(methyl-α-naphthylphenylsiloxy)-α-methoxytoluene (IIIb) as the major product, as indicated by its nmr spectrum: δ 0.73 (s, 3 H, Si–Me), 3.05 (s, 3 H, O–Me), 5.75 (s, 1 H, C–H), and 7.1–8.2 (m, 17 H, ArH) ppm. The acetal was immediately reduced with lithium aluminum hydride in dibutyl ether, reaction conditions known to involve retention of configuration,[8] giving 77% of (−)-methyl-α-naphthylphenylsilane, (−)R$_3$-Si*H, with $[\alpha]D$ −25.1°, corresponding to 90% over-all retention of configuration. Thus both photochemical

pathways (eq 1 and 2) involve significantly stereoselective processes.

We consider it probable that the mixed acetals III arise from a photochemical isomerization of the silyl ketone to a siloxycarbene V, which then inserts into

$$\underset{\text{O}}{\overset{\displaystyle \parallel}{R_3Si{-}C{-}R'}} \xrightarrow{h\nu} R_3Si{-}\overset{\overset{\displaystyle *}{\overset{\displaystyle \curvearrowleft O}{}}}{\underset{\curvearrowright}{C}}{-}R' \longrightarrow$$
$$R_3Si{-}O{-}\underset{\text{V}}{C}{-}R' \xrightarrow{R''OH} R_3Si{-}O{-}\underset{\displaystyle \overset{|}{OR''}}{\overset{\displaystyle H}{\underset{}{C}}HR'}$$

the OH bond of the alcohol.[9] Photochemical formation of oxacarbenes from ketones have been reported recently by several workers,[10] and Quinkert[11] has established that in such processes an adjacent asymmetric center retains its stereochemical configuration, as observed here. Retention of configuration at an asymmetric silicon center involved in silicon–oxygen bond formation and silicon–carbon bond rupture has been observed previously.[6,12]

At present we do not understand the role of base in apparently changing the course of the photochemically catalyzed alcoholysis in neutral or acidic media to that described above. Preliminary rate studies suggest that the rate of conversion of mixed acetals of type III to alkoxysilanes I and aldehyde acetals II in alcohol medium having comparable acid concentrations is much slower than the direct rate of photolysis of ketone to I and II. In addition the displacement of alkoxide from asymmetric silyl ethers by alcohol, catalyzed either by base or acid, is known to involve inversion of configuration[13] at silicon.

Based on this evidence it is unlikely that the formation of I and II arises from an acid-catalyzed displacement on III by alcohol followed by acid-catalyzed acetal formation. Further studies are in progress.

(9) Unpublished studies from this laboratory strongly indicate the intermediacy of a siloxycarbene in the photochemical reactions of diphenylsilacyclohexanone: A. G. Brook and J. B. Pierce, *J. Org. Chem.*, **30**, 2566 (1965).

(10) P. Yates and L. Kilmurry, *Tetrahedron Letters*, 1739 (1964); *J. Am. Chem. Soc.*, **88**, 1563 (1966); H. V. Hosteller, *Tetrahedron Letters*, 687 (1965); R. F. C. Brown and R. K. Solly, *ibid.*, 169 (1966); H. A. Staab and J. Ipaktschi, *ibid.*, 583 (1966).

(11) G. Quinkert, G. Cimballek, and G. Burn, *ibid.*, 4573 (1966).

(12) A. G. Brook and C. M. Warner, *ibid.*, **18**, 815 (1962).

(13) R. Baker, R. W. Bott, C. Eaborn, and P. W. Jones, *J. Organometal. Chem.* (Amsterdam), **1**, 37 (1963).

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(4) General Electric "PAR-38" spot lamp, color temperature 2700°K.

(5) M. F. Shostakovskii, D. A. Kochkin, I. A. Shikhiev, and V. M. Vlasov, *J. Gen. Chem. USSR.*, **25**, 593 (1955); *Chem. Abstr.*, **50**, 3270 (1956).

(6) A. G. Brook and W. W. Limburg, *J. Am. Chem. Soc.*, **85**, 832 (1963).

(7) The relative and absolute configurations of a wide variety of methyl-α-naphthylphenylsilyl derivatives have been unambiguously established from stereochemical and X-ray studies.[6] See also L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

(8) L. H. Sommer, C. L. Frye, and G. A. Parker, *J. Am. Chem. Soc.*, **86**, 3276 (1964).
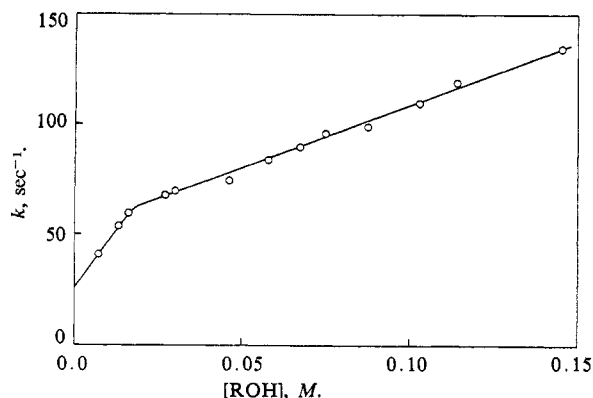
Direct Observation of Intermediates in the Chromic Acid Oxidation of Secondary Alcohols[1]

Sir:

Although the oxidation of secondary alcohols has been postulated to proceed *via* the series of steps[2]

(1) This investigation was supported by the National Science Foundation.

(2) F. H. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943); F. H. Westheimer and N. Nicolaides, *J. Am. Chem. Soc.*, **71**, 25 (1949); F. Holloway, M. Cohen, and F. H. Westheimer, *ibid.*, **73**, 65 (1951);
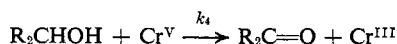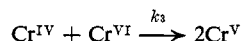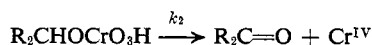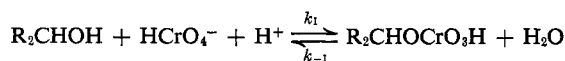
Figure 1. Rate of appearance of chromate esters as a function of isopropyl alcohol concentration. [Cr(VI)] = 1.03 × 10⁻³M, [H⁺] = 1.25 × 10⁻² M, μ = 0.183 M.

$$R_2CHOH + HCrO_4^- + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_2CHOCrO_3H + H_2O$$

$$R_2CHOCrO_3H \xrightarrow{k_2} R_2C{=}O + Cr^{IV}$$

$$Cr^{IV} + Cr^{VI} \xrightarrow{k_3} 2Cr^V$$

$$R_2CHOH + Cr^V \xrightarrow{k_4} R_2C{=}O + Cr^{III}$$

the individual steps have not been observed in the study of any one substrate. The steps are of considerable importance since the separation of the equilibrium constant for the first reaction from the rate constant of the second would allow a more meaningful interpretation of substituent effects[3] and since little is known about the last reaction even though it is the major contributor to product formation.
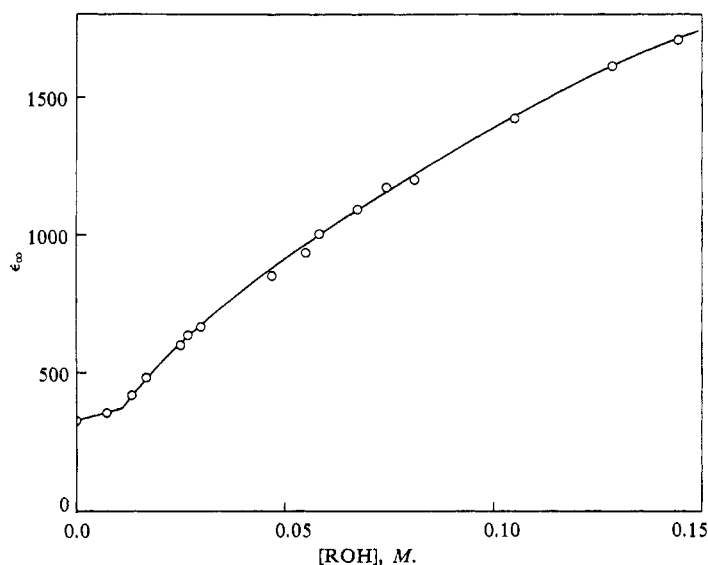

Figure 2. Dependence of equilibrium absorbance on isopropyl alcohol concentration.

We wish to report that we have been able to observe spectrophotometrically a series of consecutive reactions. In 97% aqueous acetic acid as solvent we found a very rapid reaction (τ 5–10 msec) which occurs prior to

J. Rocek, F. H. Westheimer, A. Eschenmoser, L. Moldovanyi, and J. Schreiber, Helv. Chim. Acta., 45, 2554 (1962).

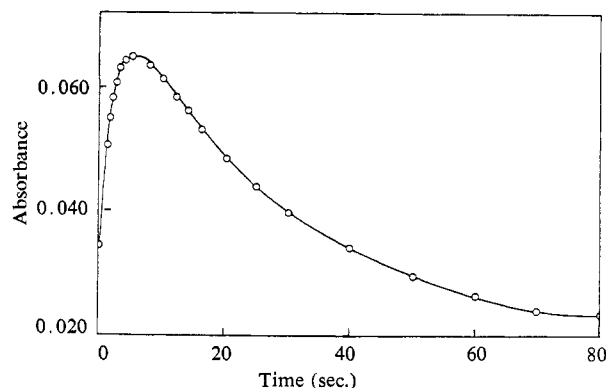(3) H. Kwart and P. S. Francis, J. Am. Chem. Soc., 77, 4907 (1955).

Figure 3. Absorbance change during chromic acid oxidation of isopropyl alcohol. λ 510 mμ, [Cr(VI)] = 1.03 × 10⁻³ M, [H⁺] = 1.25 × 10⁻² M, [ROH] = 0.124 M, μ = 0.183.
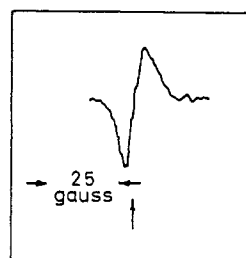

Figure 3.

Figure 4. Esr spectrum of chromium(V) formed during the chromic acid oxidation of isopropyl alcohol. The center of the band corresponds to g = 1.9805.

oxidation. At 385 mμ a fairly large increase in absorbance with time is noted, and the change is unaffected by deuterium substitution in the α position of the alcohol. This reaction is probably ester formation.[4] Plots of rate constants against alcohol concentration (Figure 1) and of final absorbance for this step against alcohol concentration (Figure 2) indicate two reactions are occurring. These are presumably the formation of the monoester and the diester, respectively. From these data, both the equilibrium constants and the rate constants for ester formation were obtained for various secondary alcohols, and these data will be reported in detail subsequently.

At 510 mμ, one obtains kinetic curves such as that in Figure 3. The absorbance first increases and then decreases to the value expected for chromium(III). The rate constants for the two successive reactions could be obtained using the procedure described previously.[5] The rates of both processes were decreased by deuterium substitution in the alcohols, indicating that both reactions involve oxidation of the alcohol.

The nature of the intermediate chromium species is indicated by the esr spectrum (Figure 4). The signal can only be due to chromium(V) since neither chromium(IV) nor chromium(III) would be expected to give a relatively sharp signal. The intensity of this signal reaches a maximum at the same time the absorbance of the reaction mixtures reaches a maximum. Thus, the second step can only be oxidation by chromium(V).

(4) Ester formation has been observed spectrophotometrically in aqueous solution: U. Kläning, Acta Chem. Scand., 11, 1313 (1957); 12, 576 (1958). However, under these conditions, ester formation proceeds to only a small extent, and rate constants for its formation were not obtained.

(5) K. B. Wiberg and P. A. Lepse, J. Am. Chem. Soc., 86, 2612 (1964).

This observation permits one to study directly the kinetic isotope effect, effects of substituents, and other kinetic parameters for chromium(V). These data have been obtained and will be reported in detail subsequently. Similar behavior also has been observed using aldehydes as substrate.

Thus, the spectrophotometric study provides confirmation for the Westheimer mechanism and permits one to examine all of the steps in the reaction with the exception of the very rapid electron transfer between chromium(VI) and chromium(IV).

Acknowledgment. We are indebted to Professor J. M. Sturtevant for the use of his stopped-flow apparatus and to Professor J. H. Wang for the use of his esr spectrometer.

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2-Naphthoic Acid Derivatives as Models for the Isocarbostyril Substrates of α-Chymotrypsin (CHT)[1]

Sir:

Several efforts have been made to define that conformation (the "reactive" conformation) of methyl acetyl-L-phenylalaninate (L-APME) which is most susceptible to hydrolysis by ChT, using as a first approximation the relatively rigid geometry of D-3-carbomethoxydihydroisocarbostyril (D-CDIC).[2–5] Detailed understanding of what structural features are primarily responsible for the rapid hydrolysis of D-CDIC by ChT should greatly assist these efforts. Study of the rates of hydrolysis of **1–6** (Figure 1) by ChT may, for example, provide insight into the importance of the amide group in determining the reactivities of D- and L-CDIC and CIC toward the enzyme.

Table I displays the results of such a study[6–8] and reveals that the ease of hydrolysis[9] of **1–6** by ChT varies by more than 10^3 and is highly dependent on the nature of the ring bearing the ester groups. Particularly interesting is the observation that hydrolysis of **6** occurs with great rapidity both in an absolute sense and relative to **5**, although **5** and **6** lack the acylamino group characteristic of "specific" substrates of ChT. Ester **6** is estimated to be as reactive[9] as the *p*-nitrophenyl esters of D-3-carboxydihydroisocarbostyril or acetyl-L-

(1) Supported by Grant AM 08005-03 of the U. S. Public Health Service.

(2) G. Hein and C. Niemann, *Proc. Natl. Acad. Sci. U.S.*, **47**, 1341 (1961); *J. Am. Chem. Soc.*, **84**, 4487, 4495 (1962).

(3) E. S. Awad, H. Neurath, and B. S. Hartley, *J. Biol. Chem.*, **235**, PC35 (1960).

(4) I. B. Wilson and B. F. Erlanger, *J. Am. Chem. Soc.*, **82**, 6422 (1960).

(5) M. S. Silver, *ibid.*, **88**, 4247 (1966).

(6) The substrates were prepared by conventional methods and gave satisfactory microanalyses. Rotations for 1% solutions of the optically active compounds in CHCl₃ were as follows: acid precursor of **5**, $[\alpha]^{25}D$ +259.6° (lit.[7] +158.7°); acid precursor of **6**, $[\alpha]^{26}D$ −282.5°; **5**, $[\alpha]^{21}D$ +171.4°; **6**, $[\alpha]^{25}D$ −197.5°. The kinetic behavior of **5** and **6** shows that **6** is only 82% (−) isomer, so either the acid was not completely resolved or extensive racemization occurred in the preparation of the ester. The hydrogenation experiment described later suggests that the latter may be correct. The ease of racemization and rearrangement of 1,2-dihydro-2-naphthoic acid derivatives probably explains the low rotation of the (+)-acid isolated by Pickard and Yates.[7]

(7) R. H. Pickard and J. Yates, *J. Chem. Soc.*, **95**, 1011 (1909).

(8) The kinetic methods employed were identical with those of ref 5.

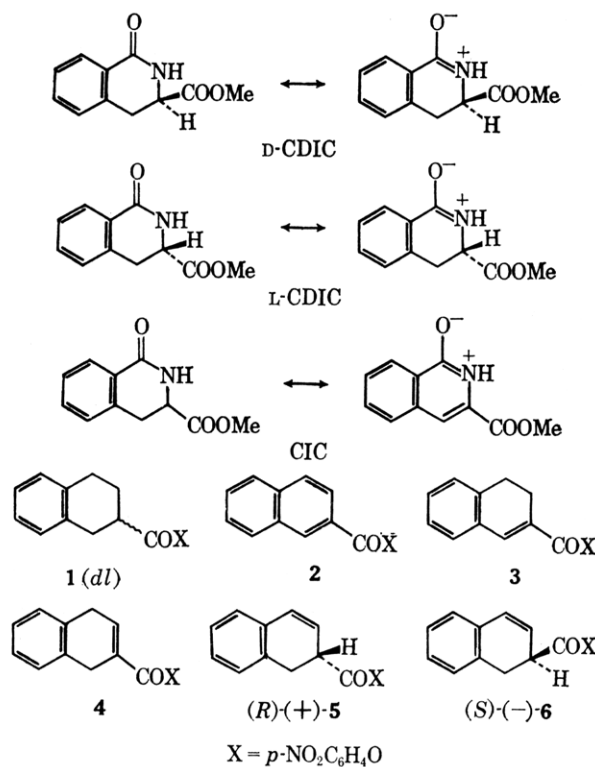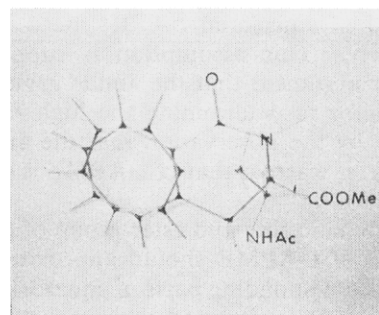(9) All comparisons of reactivity in this communication are based on k_0/K_0.

Figure 1.

Figure 2. Photograph of Drieding models illustrating a possible reactive conformation of L-APME superimposed on equatorial D-CDIC.

phenylalanine (L-APNPE) would be under similar experimental conditions (Table I).[10] The data show that possession of a 1,2-dihydro-2-naphthoic acid-like skeleton of correct configuration is sufficient to cause the ready hydrolysis of an ester by ChT and suggest that the amido group is only a minor contributor to the reactivity of D-CDIC. Two facts other than the ease of hydrolysis of **6** support the use of **6** as a model for D-CDIC: (a) indole competitively inhibits the hydrolysis of **6** and D-CDIC, and (b) the behavior of **6** relative to **5** resembles that of D-CDIC relative to L-CDIC.

The purpose of these experiments is to define the geometry of the reactive conformation of L-APME. Figure 2 illustrates a proposed geometry which enjoys appreciable experimental support and which was obtained from the study of molecular models viewed in

(10) Detailed comparisons of k_0 and K_0 await data for the methyl esters analogous to **5** and **6** and for the *p*-nitrophenyl esters analogous to D- and L-CDIC. We believe these data will support the substance of our argument.