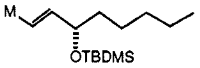
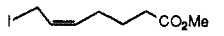
(ca. 1 mg of enzyme[9c]/g of **2**) provided monoacetate **4** (80%) which was oxidized with Jones reagent to enone (+)-**3** (95%, optical purity 98%).

The optically active ω side chain vinylstannane **6a** was prepared from the alkyne[10a] by the light-initiated addition of tributyltin hydride[10b] and was transmetalated with *n*-BuLi in THF at −78 °C to afford **3b**.[10c] A phosphine-stabilized organocopper reagent[11] was prepared from **6b**, copper(I) iodide/tributylphosphine complex (1.0 equiv), and tributylphosphine (1.0 equiv) in THF at −78 °C. Addition of this copper reagent (1.1 equiv) to (+)-**1** at −78 °C, followed by direct alkylation of the resulting enolate with iodide **7**[12] (1.5 equiv) in the presence of HMPA (2.0 equiv) at −30 °C for 3 h, resulted in a 53% yield of the trans vicinally disubstituted product **8a**.[13,14] Desilylation with aqueous HF and pyridine in acetonitrile yielded **8b** in 89% yield.[15a] Reduction with Al(Hg) in aqueous THF furnished (−)-PGE$_2$ methyl ester (**9a**), $[\alpha]^{25}_{D}$ −78.8° (*c* 1.25, MeOH) [lit.[2c] $[\alpha]^{25}_{D}$ −71.7° (*c*, 1.04, MeOH)], in 98% yield;[15b] no diastereomers of **9a** could be detected by high-field ^{1}H or ^{13}C NMR of the product. Ester **9a** has previously been converted to (−)-PGE$_2$ (**9b**) by enzymatic ester hydrolysis.[16] The 5,6-didehydro analogue **9c** was also synthesized in racemic form in a similar manner in 51% overall yield from **3**.



6a M = Bu$_3$Sn
b M = Li



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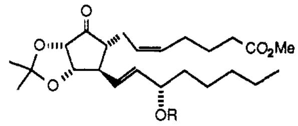
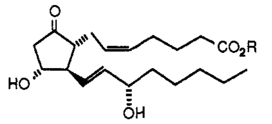


8a R=TBDMS
b R=H



9a R = Me
b R = H
c 5,6-didehydro (C≡C)

We anticipate that the optically pure synthon **3** and the concepts herein demonstrated involving the use of the acetonide grouping to mask an aldol will be applicable to the synthesis of a number of biologically interesting substrates. We are continuing to explore these matters.[17,18]

Acknowledgment. The developmental work on the enone was supported by a grant from the National Science Foundation and was based on studies by Dr. Kevin Kunnen whose contributions we gratefully acknowledge. The application of the chemistry to the synthesis of prostanoids was supported by a grant from the National Institutes of Health.

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(10) (a) 3(*S*)-[(*tert*-Butyldimethylsilyl)oxy]-1-octyne ($[\alpha]^{25}_{D}$ −47° (Et$_2$O)) was kindly provided by Dr. P. W. Collins, G. D. Searle and Co. (b) Collins, P. W.; Jung, C. W.; Gasiecki, A.; Pappo, R. *Tetrahedron Lett.* **1978**, 3187. (c) Stannane **6a** was obtained as an 85:15 mixture of *trans*- and *cis*-vinylstannanes. Only *trans*-**6a** was transmetalated to an appreciable extent under the reaction conditions (see ref 10b).

(11) Suzuki, M.; Suzuki, T.; Kawagishi, T.; Morita, Y.; Noyori, R. *Isr. J. Chem.* **1984**, *24*, 118.

(12) Prepared by the method of: Corey, E. J.; Sachdev, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 8483.

(13) The trans alkylation product was obtained in 46% yield along with 10% of the cis product, which was recycled to the desired **8a** by stirring with catalytic NaOAc in MeOH to provide **8a** in 53% overall yield. About 30% of product from addition of the lower side chain only was recovered from the reaction mixture; this material could be recycled to **8a** by treatment with LDA and **7**.

(14) All products were purified by "flash chromatography" on silica gel and gave satisfactory IR, ^{1}H NMR, ^{13}C NMR, exact mass, and/or elemental analysis.

(15) (a) Yield based on recovered starting material; isolated yield: 78%. (b) Yield based on recovered starting material; isolated yield: 89%.

(16) Sih, C. J.; Heather, J. B.; Sood, R.; Price, P.; Peruzzoti, G.; Lee, L. H.; Lee, S. S. *J. Am. Chem. Soc.* **1975**, *97*, 865.

(17) Since the submission of this manuscript, a convergent synthesis of PGE$_2$ based on oxime methodolgy has appeared (Corey, E. J.; Nimura, K.; Konishi, Y.; Hashimoto, S.; Hamada, Y. *Tetrahedron Lett.* **1986**, *27*, 2199).

(18) The chemistry herein described is the subject of a patent application by Wayne State University.

Simplest Chloronium Radical. A Neutralization–Reionization Mass Spectrometry Study

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The hydrogen + chlorine chain reaction has been an exemplar in the development of the kinetics of elementary gas-phase reactions.[1] The barrier heights of the chain propagating step $Cl^{\bullet} + H_2$ and of the symmetric atom-exchange $H'^{\bullet} + H''Cl \rightarrow H'Cl + H''^{\bullet}$ have been the subject of numerous recent experimental and theoretical investigations.[1c–e] An important intermediate in these reactions is the prototype chloronium radical, $H_2Cl^{\bullet}$, for which semiempirical calculations[1b] indicate that Cl–H–H structures are dynamically more stable than H–Cl–H structures. Here we report the preparation of stable (~10^{-6} s) $H_2Cl^{\bullet}$ by neutralization[2–5] of fast gaseous H_2Cl^+ ions, with the surprising apparent lifetimes HDCl ≫ H_2Cl > D_2Cl. In contrast, Porter has found[2] that the analogous $H_4N^{\bullet}$, $H_3O^{\bullet}$, and $H_2F^{\bullet}$ survive for ~10^{-6} s only if they are perdeuterated.

To produce the neutralization–reionization (NR) mass spectra[2–5] (Figure 1),[6] 10-keV mass-selected $H_2{}^{37}Cl^+$ ions[7] are neutralized by Hg vapor (30% transmittance),[4b] residual ions are deflected electrostatically, and the resulting beam of fast neutrals is ionized by collision with He (90% or 30% transmittance).[4c] The presence of m/z 39 (40,41) proves that a substantial portion of the H_2Cl (HDCl, D_2Cl) neutrals formed upon Hg neutralization has survived undissociated, a lifetime >0.8 μs under our experimental conditions.[3c] Interaction times are ~10^{-15} s, precluding bimolecular reactions.[2–5] Unexpectedly,[2] the reionization abundances show $[HDCl^+] \gg [H_2Cl^+] > [D_2Cl^+]$ (Figure 1, parts A, E, I). Further, these abundances decrease with increasing ion source pressure (Figure 1, parts A, E, I vs. parts C, G, K, respectively). The average bond lengths in H_2Cl^+ should be substantially less than those in $H_2Cl^{\bullet}$, causing an unfavorable Franck–Condon factor for the vertical transition $H_2Cl^+ \rightarrow H_2Cl^{\bullet}$.[3d] Collisional cooling of the H_2Cl^+ ions (which should be formed with ~12 kcal mol^{-1} excess energy)[7,8] should thus decrease the proportion of ions which produce $H_2Cl^{\bullet}$ below the dissociation threshold. As a possible explanation of the isotope effects, the Franck–Condon overlap in neutralization could be decreased with deuterium, but this should be much less than the order of magnitude decrease caused by collisional cooling. Similarly, although deuterium substitution should stabilize the resulting chloronium

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(6) Full experimental details are published.[3,4]

(7) H_2Cl^+ is produced in a chemical ionization ion source from $HCl^{\bullet+}$ + HCl → H_2Cl^+ + $Cl^{\bullet}$, and D_2Cl^+ and $DHCl^+$ from DCl and DCl + HCl.

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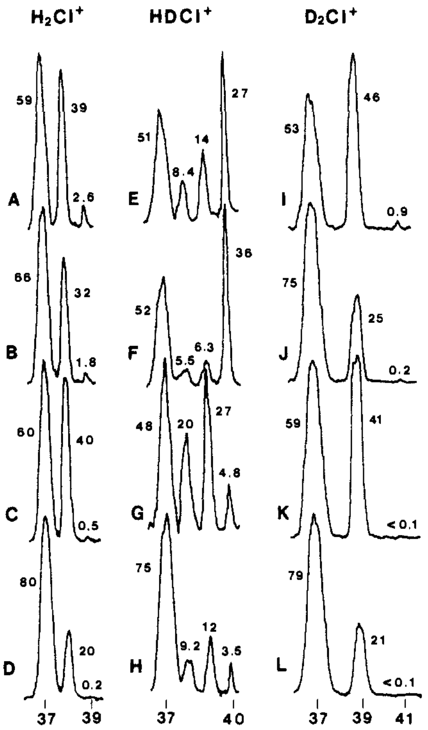

Figure 1. Hg/He neutralization–reionization (NR) mass spectra of H_2Cl^+ (A–D), $DHCl^+$ (E–H), and D_2Cl^+ ions (I–L) at lower ion source pressures ($[H_2Cl^+]/[HCl^{\bullet+}] = 0.04$; A, E, I, B, F, J) or higher source pressures ($[H_2Cl^+]/[HCl^{\bullet+}] = 3.1$; C, G, K, D, H, L). He reionization was achieved at transmittances of the neutral beams of 90% (A, E, I, C, G, K) and 30% (B, F, J, D, H, L). The figures adjacent to the peaks give peak areas in percent of the spectrum total. The absolute abundances of the reionized precursors (percent of the precursor ions collected without ion deflection): spectra B and D, m/z 39, 0.00032 and 0.00004; spectra F and H, m/z 40, 0.017 and 0.0015; spectra J and L, m/z 41, 0.000 04 and <0.000 02.

radical, it seems surprising that these effects combined would give the observed difference of ~400 × (Figure 1, part F vs. part J).[2,3d]

A possible alternative explanation is that the H–Cl+–H structure initially formed[9] rearranges in the absence of thermalizing collisions to a more stable isomer; for this the structure Cl–H+–H would be consistent with production on neutralization of the more stable[1b] Cl–H–H structure, for which various geometries are conceivable. The 12 kcal mol^{-1} exothermicity of H_2Cl^+ formation[7,8] would approximate the maximum activation energy for H–Cl+–H → Cl–H+–H. If this involves migration of one hydrogen, the isomerization would be slowed substantially be perdeuteration but little by monodeuteration. On the other hand, for the Cl–H–H product the isotope effect should reduce the dissociation of either Cl–D–H or Cl–D–D. Thus the HDCl observable would be favored over either H_2Cl or D_2Cl.

Consistent with these structural postulates, neutralization of the supposed Cl–D+–H (Figure 1E, low source pressure) gives $[Cl^+] > [(H,D)Cl^{\bullet+}]$,[10] while that of D–Cl+–H (Figure 1G, higher source pressure) gives equivalent abundances, with Cl+ formed in substantial part from $HCl^{\bullet+}$ dissociation (vide infra). Rearrangement is required for formation of $Cl^\bullet + H_2$ from H–Cl–H[10] but not from Cl–H–H. A surprisingly high stability of $H_2Cl^\bullet$ for collisional dissociation[10] is also indicated. Increasing the He pressure from 90% to 30% transmission increases the average number of collisions for affected precursors from 1.06 to 2.12.[11] The NR spectrum of D_2Cl^+ under high ion source pressures shows only DCl^+ and Cl^+ (Figure 1K); increasing the helium pressure causes substantial collisional dissociation of DCl and $DCl^{\bullet+}$ (Figure 1L). However, increasing the helium collision pressure under conditions giving high formation of HDCl (Figure 1E) shows (Figure 1F) a much greater reduction in $[HCl^{\bullet+}]$ and $[DCl^{\bullet+}]$ than in $[HDCl^+]$. Sophisticated ab initio studies of the potential energy surfaces of both H_2Cl^+ and $H_2Cl^\bullet$ should be helpful in the further understanding of these systems.

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[10] $\Delta H_f°$ (products) = 30 kcal mol^{-1} for $H^\bullet$ + HCl, and 29 kcal mol^{-1} for $H_2 + {}^\bullet Cl$.[8]

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Surface Metal Ion Enhancement of Thermally Treated Zeolites[†]

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During the past several years the area of zeolite science has received increasingly intense attention owing to the preparation of new molecular sieves[1] and the availability of modern spectroscopic methods for the study of these materials.[2] The majority of spectroscopic studies of zeolites have focused on measurements of bulk magnetic, electronic, and structural properties, but few surface studies have been reported.[3,5,6] Surface-inhomogeneous aluminum and silicon species have recently been reported by Barr and co-workers.[3] In this study we have heated metal ion containing zeolites under controlled conditions in order to probe interactions between the zeolite and the metal ion. Here we present preliminary results for Ag^+/NaY and Cs^+/NaY zeolites studied by X-ray photoelectron spectroscopy (XPS), static secondary ion mass spectrometry (SSIMS), and ion scattering spectroscopy (ISS).

Zeolites Ag^+/NaY and Cs^+/NaY were prepared by ion-exchange procedures. After exchange both samples were filtered, washed with distilled deionized water, and dried at room temperature in a vacuum line at a pressure of 1×10^{-4} kPa. The silver sample was prepared in the absence of light. Samples were pressed into pellets and then mounted in a Leybold-Heraeus spectrometer for surface studies. The bulk concentrations of these materials were obtained by a combination of atomic absorption and thermogravimetric analysis. The resulting approximate emperical formulas are $Na_{3.1}Ag_{52.9}Al_{56}Si_{136}O_{384}\cdot 213H_2O$ and $Na_{18.9}Cs_{37.1}$-

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[*] To whom correspondence should be addressed.

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