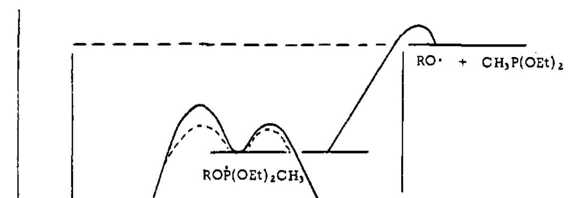

Figure 1. Energy diagram for α *vs.* β scission for the reaction of the *tert*-butoxy radical with diethyl methylphosphonite.[3b]

thermodynamically. With *tert*-BuO· it appears that P–O π-bond formation, which ultimately accounts for the greater exothermicity of the oxidation step, is not well enough advanced at the transition state[12] to compensate for the relatively strong C–O bond being simultaneously broken. But, as the C–X bond in I is weakened by substitution of PhCH$_2$ for *tert*-Bu or replacement of O by S, β scission becomes increasingly important and ultimately dominant. The effect of R· stability on the β scission is noted as well in comparing the *tert*-BuS· and *i*-PrS· reactions with PhCH$_2$P(OEt)$_2$.[13] Effects of temperature change on the α/β scission ratios of reactions 3 and 4 show E_a(displacement) > E_a(oxidation), although by less than 1 kcal/mol. If E_a(displacement) is assumed essentially constant, then E_a for sulfur transfer from *i*-PrS· is greater than that from *tert*-BuS·.

The α/β ratio is also affected in reactions 4 and 6 by weakening of the P–R′ bond in response to increased stability of R·′. This also is consistent with the idea that the α/β ratio is determined *primarily* by the relative strengths of the R–S and P–R′ bonds. A similar conclusion is reached from comparison of experiments 2 and 5.

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[12] Figure 1 shows that $\Delta H_r°$ for the β cleavage must be at least 40 kcal/mol exothermic.

[13] Estimates of the C–S dissociation heat for R–S· of 63 and 65 kcal/mol have been made for R = *tert*-Bu and *i*-Pr, respectively (H. Mackle, *Tetrahedron*, **19,** 1159 (1963)).

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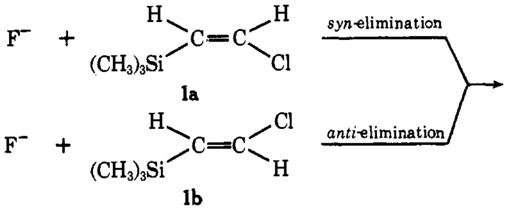
β Elimination of Unsaturated Silanes. Acetylene *via* Dechlorosilylation

Sir:

Although facile β elimination of saturated β-haloalkylsilanes leading to alkenes (eq 1) is a well-documented phenomenon,[1] corresponding β-haloalkenylsilanes (R$_3$SiCH=CHX) are not known to undergo elimination to alkynes under similar conditions.[2]

$$\mathrm{N} + \mathrm{R_3SiCH_2CH_2X} \longrightarrow \mathrm{H_2C{=}CH_2} + \mathrm{R_3SiN} + \mathrm{X} \quad (1)$$

More vigorous treatment of a variety of haloalkenylsilanes with concentrated aqueous or alcoholic alkali results in the displacement of the halovinyl moiety from silicon.[3] In contrast to this behavior, we wish to report that potassium fluoride (KF) in dimethyl sulfoxide (DMSO) effects the smooth β elimination of both *cis*- and *trans*-β-chlorovinyltrimethylsilane (**1a** and **1b**, respectively) under mild conditions (eq 2). This observation thus represents an unambiguous indication that elimination reactions of vinyl halides have a counterpart in organosilicon chemistry.



$$\mathrm{HC{\equiv}CH} + \mathrm{(CH_3)_3SiF} + \mathrm{Cl^-} \quad (2)$$

Treatment of a *cis*- and *trans*-β-chlorovinyltrichlorosilane mixture[4] with methylmagnesium bromide afforded, after spinning band distillation, **1a**[5] (bp 106.5°; pmr[6,7] δ 5.89 and 6.71 (AB pattern, J = 9 Hz)) and **1b**[5] (bp 112°; pmr[6,7] δ 6.10 and 6.28 (AB pattern, J = 15 Hz); ir 10.6 μ (*trans*-CH=CH)).

When 0.018 mol of a 1:2 mixture of **1a** and **1b** in 15 ml of anhydrous[8] DMSO saturated with 0.027 mol of KF[9] was heated at 100° for 16 hr, total conversion of substrate occurred to a mixture of acetylene and fluorotrimethylsilane.[10] No other volatile or nonvolatile organic products were observed, either by glpc or by subsequent work-up of the DMSO solution. The salts recovered by filtration showed a weight increase of 0.30 g, corresponding to an exchange of 0.018 equiv of chloride ion for fluoride. In separate runs on isomerically pure **1a** and **1b**, respective AgCl yields of 88 and 96% were obtained from the residual salts upon AgNO$_3$ treatment.

Eliminations monitored at lower temperatures showed good stereoselectivity. For example, when 0.002 mol

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[1] For a recent review, see A. W. P. Jarvie, *Organometal. Chem. Rev. A*, **6,** 153 (1970).

[2] (a) L. H. Sommer, D. L. Bailey, G. M. Goldberg, C. E. Buck, T. S. Bye, F. J. Evans, and F. C. Whitmore, *J. Amer. Chem. Soc.*, **76,** 1613 (1954); (b) E. T. McBee, C. W. Roberts, and G. W. R. Puerckhauer, *ibid.*, **79,** 2329 (1957), and references therein.

[3] β,β-Dichlorovinyltrichlorosilane, for example, yields α,α-dichloroethylene: H. Wagner and A. N. Pines, *ibid.*, **71,** 3567 (1949). An explosive material presumed to be chloroacetylene was also formed in this reaction. See also ref 2b.

[4] R. F. Cunico, *J. Org. Chem.*, **36,** 929 (1971).

[5] *Anal.* Calcd for C$_5$H$_{11}$ClSi: C, 44.59; H, 8.24. Found (**1a**): C, 44.54; H, 8.52. (**1b**): C, 44.27; H, 8.36. The n^{25}D value for **1a** was 1.4317; for **1b**, 1.4340. The authors thank Mr. J. C. Camp for the characterization of **1a** and **1b**.

[6] Pmr data obtained at 60 MHz from CCl$_4$ solutions containing HCCl$_3$ as internal standard.

[7] See also H. Bock and H. Seidl, *J, Organometal. Chem.*, **13,** 87 (1968).

[8] Typical runs on this scale were shown to contain no more than 3 × 10^{-4} mol of water by Karl Fischer titration.

[9] All runs were heterogeneous because of undissolved KF. The solubility of KF at 25° was determined by flame emission photometry to be 8 mg/100 g of DMSO.

[10] Volatile products were trapped and identified by ir comparison after low-temperature fractionation.

each of **1a** and **1b** was treated with 0.005 mol of KF in 10 ml of DMSO at 25°, only 10% of **1a** had reacted after 20 hr, but 95% of **1b** had undergone elimination.[11] The reaction also displayed significant stereoselectivity at 70°, consuming 86% of **1b**, but only 25% of **1a**, within 75 min.

Fluoride ion in solution appears to be critical to the reaction and is presumably the species engaged in attack upon substrate. Both **1a** and **1b** are stable to DMSO or KF alone under the conditions employed for elimination and were unaffected by either hot (70–90°) slurries of KCl or KI in DMSO or by hot solutions of tetrabutylammonium chloride or bromide in DMSO. Although it has been reported that tetraethylammonium fluoride generates the methylsulfinyl carbanion in DMSO,[12] we found no evidence (*via* benzophenone trapping) that KF behaves in a similar fashion.

Given the premise that fluoride ion in aprotic solvents is strongly nucleophilic toward silicon as well as toward hydrogen and carbon,[13] at least four mechanisms for elimination are, in principle, possible: (a) attack of fluoride ion at silicon in a concerted, bimolecular dechlorosilylation (E2-Si), (b) attack of fluoride ion at silicon to form the chlorovinyl carbanion followed by collapse to acetylene (Elcb-Si), (c) vicinal dehydrochlorination of substrate to trimethylsilylacetylene (**2**) followed by acid-assisted cleavage to products, and (d) geminal dehydrochlorination followed (or accompanied) by rearrangement to **2** and subsequent cleavage to products. Omitting unstable intermediates, mechanisms a and b are represented by eq 2 and mechanisms c and d by eq 3 plus 4.

$$\mathbf{1a,b} + F^- \longrightarrow \underset{\mathbf{2}}{(CH_3)_3SiC{\equiv}CH} + HF + Cl^- \qquad (3)$$

$$\mathbf{2} + HF \longrightarrow HC{\equiv}CH + (CH_3)_3SiF \qquad (4)$$

Since **2** was found to react rapidly (total consumption in 5–10 min) with anhydrous potassium bifluoride (KHF_2) in DMSO—conditions which approximate intermediate stages of c and d—to give trimethylfluorosilane and acetylene,[14] the observed absence of **2** during eliminations of either **1a** or **1b** is mechanistically inconclusive. As a result of indirect evidence, however, we tend at the present time to favor an E2-Si process (a) in which anti dechlorosilylation is more facile than syn elimination.[15] Only a few proven examples of an Elcb-H mechanism have been reported in the vinylic series, and all involve carbanions stabilized by resonance[16] or inductive[17] effects of α substituents. Heterolytic rupture of the carbon–silicon bond in either **1a** or **1b** (mechanism b) would generate a chlorovinyl carbanion lacking such stabilization. Pathway c, proceeding by way of vicinal dehydrochlorination as the rate-determining step, would require that syn, rather than anti, dehydrochlorination be faster. The reverse is instead true for analogous substrates not containing silicon.[16] Finally, vinyl chloride was found to be inert to KF in DMSO under conditions (100°, 4.5 hr) which serve to completely convert **1a** or **1b** to products, evidence which mitigates against pathways c and d.[18]

We are currently investigating the nature of this and similar eliminations from the standpoints of substrate type and reaction conditions.[19]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant No. PRF 4535-ACl, 3), for support of this work.

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[11] Eliminations were followed by glpc (10-ft SE-30 column) using the internal standard method.

[12] J. Hayami, N. Ono, and A. Kaji, *Tetrahedron Lett.*, 1385 (1968).

[13] A. J. Parker, *Advan. Org. Chem.*, **5**, 1 (1965).

[14] Trimethylsilylacetylene is easily cleaved by KF in the presence in a proton donor: C. S. Kraihanzel and J. F. Poist, *J. Organometal. Chem.*, **8**, 239 (1967). We found **2** to be stable to KF in DMSO for at least 120 hr at 25°.

[15] A preference for anti dechlorometalation is also indicated for some other β-chlorovinyl metalloids. See A. N. Nesmeyanov, A. E. Borisov, and I. S. Savel'eva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 286 (1968); C. L. Hewett, *J. Chem. Soc.*, 1203 (1948).

[16] G. Modena, *Accounts Chem. Res.*, 4, 73 (1971).

[17] S. I. Miller, and W. G. Lee, *J. Amer. Chem. Soc.*, **81**, 6313 (1959).

[18] J. T. Maynard, *J. Org. Chem.*, **28**, 112 (1963), has reported that vinyl chloride affords acetylene in indefinite yield upon treatment with KF in *N*-methyl-2-pyrrolidone at 200°.

[19] Preliminary results indicate that tetraethylammonium fluoride and metal alkoxides are potent reagents for such eliminations when employed in homogeneous solutions of aprotic solvents.

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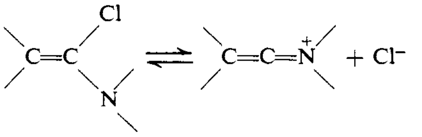
Electrophilic Aminoalkenylation of Aromatics with α-Chloroenamines

Sir:

The simultaneous presence of an electron-donating substituent and a good leaving group on a sp^2 carbon atom has been shown[1] to confer versatile chemical behavior to the readily available alkyl- or aryl-substituted α-chloroenamines.



Like enamines they react at the β-carbon atom with various electrophilic reagents.[1,2] Furthermore, in contrast to ordinary vinylic halides, they show a remarkably high reactivity toward nucleophilic reagents.[1,3] The nucleophilic substitutions are accelerated by the addition of silver ions[4,5] and considerably retarded (or suppressed) by the presence of electron-withdrawing substituents in the β position.[5] These results are best explained by a prior ionization to a keteneimmonium chloride followed by attack of the nucleophile.

We wish now to report that alkyl-substituted α-chloroenamines react readily with electron-rich aromatics in electrophilic substitutions, *without the need of an acid catalyst.* The α-chloroenamines **2a–c** were obtained

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[1] L. Ghosez, B. Haveaux, and H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, 6, 454 (1969).

[2] T.-F. Lin, unpublished results.

[3] M. Rens and L. Ghosez, *Tetrahedron Lett.*, 3765 (1970).

[4] (a) The addition of silver tetrafluoroborate to alkyl-substituted α-chloroenamines at −60° gives the keteneimmonium salts and silver chloride. J. Marchand-Brynaert and L. Ghosez, *J. Amer. Chem. Soc.*, **94**, 2870 (1972). (b) Recently, H. Weingarten, *J. Org. Chem.*, **35**, 3970 (1970), described the pmr spectrum of tetramethylketeneimmonium hexafluorophosphate.

[5] B. Haveaux, M. Rens, and J. Marchand-Brynaert, unpublished results.