methylene group provides a further diagnostic method for differentiating the two isomers.

An application of the present method is determination of the erythro natures of compounds **13** and **14**. It was also employed in the recent determinations of the absolute configurations of ecdysone side chains[9] and the C_{18} juvenile hormone.[8]

Acknowledgments. We express our gratitude to Professor K. B. Sharpless, Massachusetts Institute of Technology, for gifts of samples and to Dr. H. Mori, Teikoku Hormone Co., for a gift of precursor to **11**. The work was supported by Public Health Service Grants AI 10187 (to K. N.) and GM 44322 (to D. A. S.), and by the Naito Foundation (to M. K.).

(8) For another example, see K. Nakanishi, D. A. Schooley, M. Koreeda, and J. Dillon, *J. Chem. Soc. D*, 1235 (1971).

(9) M. Koreeda, D. A. Schooley, K. Nakanishi, and H. Hagiwara, *J. Amer. Chem. Soc.*, **93**, 4084 (1971).

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α vs. β Scission in Reactions of Alkoxy and Thiyl Radicals with Diethyl Alkylphosphonites

Sir:

Previous work has indicated that reactions of alkoxy radicals with trialkylphosphines give mostly products of *displacement* of the attached alkyl substituent (product III in Scheme I). For example, *tert*-BuO· with n-Bu_3P at 130° gives a 4/1 displacement/oxidation ratio,[1] whereas at −90° with Et_3P, only esr signals resulting from Et· are noted.[2] The alkyl group displacement predominates despite the fact that it is *thermodynamically much less favored than oxygen transfer.*[3] On the other hand, in reactions of various trivalent phosphorus derivatives with thiyl radicals (RS·), no well-established examples of displacement exist.[6] Such reactions normally give exclusively *oxidation* products, II.

Scheme I

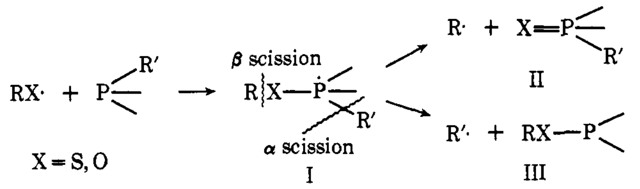
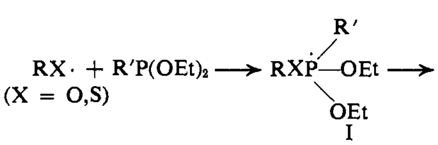


Table I. *α vs. β* Scission in the Reactions of Alkoxy and Thiyl Radicals with Diethyl Alkylphosphonites at 60° [a]



			$\frac{R'P(X)(OEt)_2}{RXP(OEt)_2}$[b]
1a	*tert*-BuO·	$PhCH_2$	0
1b	*tert*-BuO·	CH_3	0
1c	*tert*-BuO·	C_2H_5	0
1d	*tert*-BuO·	*tert*-C_4H_9	0
2	$PhCH_2O$·	$PhCH_2$	0.3
3	*i*-PrS·	$PhCH_2$	2[c]
4	*tert*-BuS·	$PhCH_2$	5[c]
5	$PhCH_2O$·	CH_3	4
6	*tert*-BuS·	C_2H_5	>20

[a] In degassed benzene except as noted. [b] Determined by vpc analysis of products (sensitivity corrected). RS· displacement products measured as $RSP(S)(OEt)_2$. [c] In *o*-dichlorobenzene. [d] From thermal decomposition of the hyponitrite, RON=NOR. [e] Azobisisobutyronitrile initiated reaction of RSH.

We present here results which show clearly that both oxidations and displacements can and do occur in reactions of RS· as well as those of RO· with alkyl-substituted trivalent phosphorus compounds. The oxidation/displacement ratio is found to be rather delicately balanced and to vary greatly with the nature of R and R′ (see Scheme I).

In Table I are compared the oxidation/displacement ratios, based on product analyses, for reactions of a series of RS· and RO· with various diethyl alkylphosphonites. Clearly, oxidation is generally more favorable with RS· than with RO·. (Compare reactions 1a and 2 with 3 and 4 as well as 5 with 6.) Further, for oxy radicals, the product ratio is dependent on the structure of RO·. Both oxidation and displacement are observed with $PhCH_2O$·, but only displacement is noted with *tert*-BuO· (reactions 1 *vs.* 2 and 5). A structural effect on the oxidation/displacement ratio is also seen on comparison of *i*-PrS· with *tert*-BuS· (reactions 3 and 4).

In terms of phosphoranyl radical intermediate I,[7] these results seem best interpreted by referral to Figure 1. Reactions of RO· and RS· with PXYZ are generally very rapid with activation energies in the range 1–4 kcal/mol.[10] Both oxidation and displacement, as shown for *tert*-BuO· in Figure 1, are very exothermic processes overall,[3b] and it is quite likely that the α and β scissions are also highly favorable

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(1) S. A. Buckler, *J. Amer. Chem. Soc.*, **84**, 3093 (1962).

(2) J. K. Kochi and P. J. Krusic, *ibid.*, **91**, 3944 (1969).

(3) (a) Based on $\Delta H_f°$ (g, 298) for $(C_2H_5O)_3P$ and $(C_2H_5O)_3PO$ of −195.9 and −284.5 kcal/mol[4] and *D*(*tert*-BuO· → *tert*-Bu· + O) of 90.5 kcal/mol,[5] $\Delta H_r°$ for *tert*-BuO· + $P(OC_2H_5)_3$ → *tert*-Bu· + $OP(OC_2H_5)_3$ of −57 kcal/mol is calculated. For the reaction *tert*-BuO· + $P(CH_3)_3$ → *tert*-$BuOP(CH_3)_2$ + CH_3·, $\Delta H_r°$ of −17 kcal/mol can be estimated. Such a value is based on $\bar{D}_{PC}$ for $(CH_3)_3P$ of 67 kcal/mol and $\bar{D}_{PO}$ of 84 kcal/mol. These values can be calculated from the standard heats of formation of trimethylphosphine[4] and triethyl phosphite[4] and those[5] for CH_3·, C_2H_5O·, and P. (b) The above $\Delta H_r°$ values are used as estimates for the reactions depicted in Figure 1.

(4) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970.

(5) From $\Delta H_f°$ data in J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

(6) A possible exception is the photochemically induced reaction of Et_2PPEt_2 with MeSSMe to give Et_2PSMe (identified as $Et_2P(S)Me$): Yu. N. Shlyk, G. M. Bogolyubov, and A. A. Petrov, *J. Gen. Chem. USSR*, **38**, 194 (1968). However, the mechanistic details of this reaction have not been established.

(7) Considerable esr[2,8] and chemical[9] evidence for the intermediacy of phosphoranyl radicals of the type $(RO)_xPR'_{4-x}$ has been recently presented.

(8) (a) A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem.*, **83**, 800 (1971); (b) P. J. Krusic, W. Mahler, and J. K. Kochi, private communication.

(9) W. G. Bentrude and R. A. Wielesek, *J. Amer. Chem. Soc.*, **91**, 2406 (1969); W. G. Bentrude and T. B. Min, *ibid.*, **94**, 1025 (1972).

(10) *E.g.*, in ref 8a for the reaction of *tert*-BuO· with $(C_2H_5)_3P$, E_a for the overall rate constant is estimated to be 2.2 kcal/mol. E_a for the β scission is estimated to be 9 kcal/mol. For the reaction[11] of Ph· with $(CH_3O)_3P$ to yield $PhP(O)(OCH_3)_2$ + CH_3·, E_a is about 3–4 kcal/mol (W. G. Bentrude, J.-j. L. Fu, and C. E. Griffin, paper submitted for publication).

(11) W. G. Bentrude, J.-j. L. Fu, and C. E. Griffin, *Tetrahedron Lett.*, 6033 (1968).

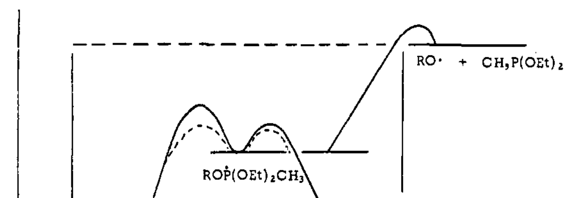

Figure 1. Energy diagram for α *vs.* β scission for the reaction of the *tert*-butoxy radical with diethyl methylphosphonite.[3b]

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.

Acknowledgment. This work was supported by a grant the Petroleum Research Fund administered by the American Chemical Society (2439A4).

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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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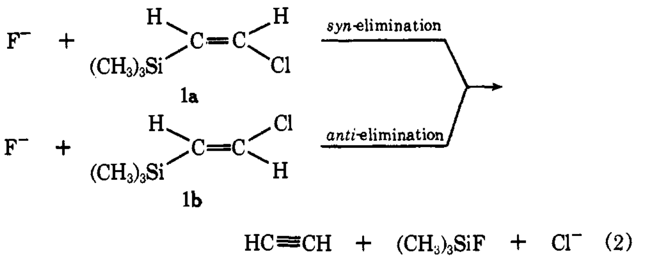
β Elimination of Unsaturated Silanes. Acetylene *via* Dechlorosilylation

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]

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

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.



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.