**Egomaketone (23)**: IR (neat) 3140, 1675, 1560, 1508, 1155, 875, 788 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 1.68 (s, 3 H), 1.76 (s, 3 H), 3.45 (d, 2 H), 5.39 (t, 1 H), 6.77 (s, 1 H), 7.42 (s, 1 H), 8.02 (s, 1 H); MS, $m/z$ (rel intensity) 164 (M$^+$, 20), 95 (100). HRMS calcd for $C_{10}H_{12}O_2$, $m/z$ 164.0838; found, $m/z$ 164.0857. The spectral data are consistent with those reported.[13-15]

**Cyclic Voltammetry.** Cyclic voltammetry was carried out with a Nichia HP-E$_{500H}$ potentiostat at a sweep rate of 0.2 V s$^{-1}$ with a platinum disk electrode (1-mm diameter) in HMPA containing 0.1 M $Bu_4NClO_4$. The potential was measured in volts vs Ag/AgI.

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**Registry No.** **1a**, 503-60-6; **1b**, 870-63-3; **4a**, 4894-61-5; **4b**, 29576-14-5; **5**, 563-52-0; **6**, 19781-52-3; **7**, 19639-97-5; **8**, 19639-96-4; **9**, 36934-19-7; **10**, 14908-27-1; **11**, 2190-48-9; **12**, 25201-44-9; **13**, 75851-77-3; **14**, 75851-76-2; **15**, 27644-02-6; **16**, 27644-03-7; **17**, 1838-77-3; **18**, 64884-87-3; **19**, 64884-86-2; **20**, 498-60-2; **21**, 123030-45-5; **22**, 123030-46-6; **23**, 59204-74-9; TBAP, 1923-70-2; HMPA, 680-31-9; Pt, 7440-06-4; C, 7440-44-0; Zn, 7440-66-6; Ni, 7440-02-0; Al, 7429-90-5; Hg, 7439-97-6; $LiClO_4$, 7791-03-9; chlorotrimethylsilane, 75-77-4; pyridinium chlorochromate, 26299-14-9; acetone, 67-64-1; propanal, 123-38-6; benzaldehyde, 100-52-7.

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# Concerning the Mechanism of the Peterson Olefination Reaction

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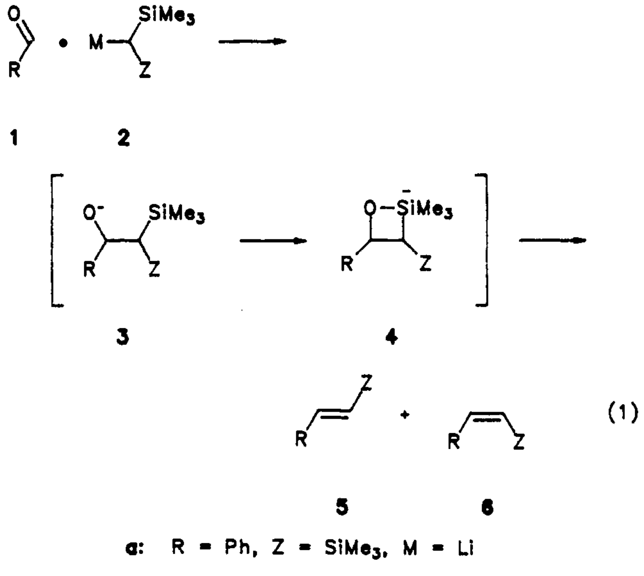
The Peterson olefination reaction of benzaldehyde with [bis(trimethylsilyl)methyl]lithium (**2a**) in THF/HMPA gives a 1.4:1 mixture of *trans-* and *cis*-vinylsilanes **5a** and **6a** [PhCH=CHSiMe$_3$] as reported by Gröbel and Seebach. In contrast, treatment of the corresponding $\beta$-hydroxysilane **13** [PhCHOHCH(SiMe$_3$)$_2$] with *t*-BuLi in THF/HMPA (or other bases) gives vinylsilane **5a**, which is >90% trans. Since the latter reaction must involve the $\beta$-oxidosilane **3a** [PhCHOLiCH(SiMe$_3$)$_2$], these results suggest that the Peterson olefination reaction may proceed, at least in part, by a pathway which does not involve this $\beta$-oxidosilane.

The Peterson olefination,[2,3] the reaction of an $\alpha$-silyl organometallic (usually organolithium) reagent with an aldehyde or ketone to yield an olefin (eq 1), is a useful alternative to the Wittig reaction. When carbanion-stabilizing groups (Z) are not present on the carbon-bearing silicon, $\beta$-hydroxysilanes are generally isolated; these can be converted to the olefin by treatment with either acid or base. However, when a carbanion-stabilizing group (Z) is present, the olefin (usually a trans-cis mixture) is generally isolated directly from the reaction; although it has usually not been possible to isolate the $\beta$-hydroxysilane,[4] the reaction has generally been assumed to take place via a $\beta$-oxidosilane intermediate (e.g. **3**). [By analogy to the Wittig reaction, the reaction pathway has been assumed to involve a 4-centered species (e.g. **4**).] We report here an example of a Peterson olefination which may *not* involve a $\beta$-oxidosilane intermediate, since it gives a stereochemical result that is different from that obtained from the corresponding $\beta$-oxidosilane generated by other methods.[5]



(1)

**a**: R = Ph, Z = SiMe$_3$, M = Li

**b**: R = p-tolyl, Z = SiMe$_3$, M = Li

In 1974 Gröbel and Seebach[6] reported the following example of the Peterson olefination reaction: the reaction

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[1] Current address: Department of Chemistry, Fitchburg State College, Fitchburg, MA 01420.

[2] (a) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780-784. For a review, see: (b) Ager, D. J. *Synthesis* **1984**, 384-398.

[3] The terms "Peterson olefination" and "Peterson reaction" have also been used to describe other olefin-forming elimination reactions of $\beta$-functional organosilicon compounds (for example, see ref 2b). We use these terms only for the reaction of an $\alpha$-silyl organometallic reagent with an aldehyde or ketone to yield an olefin. For studies relating to the mechanism of the Peterson olefination, see the following: (a) Trindle, C.; Hwang, J.-T.; Carey, F. A. *J. Org. Chem.* **1973**, *38*, 2664-2669. (b) Larchevêque, M.; Debal, A. *Chem. Commun.* **1981**, 877-878. (c) Bassindale, A. R.; Ellis, R. J.; Taylor, P. G. *Tetrahedron Lett.* **1984**, *25*, 2705-2708. (d) Boeckman, R. K., Jr.; Chinn, R. L. *Tetrahedron Lett.* **1985**, *26*, 5005-5008. (e) Bassindale, A. R.; Ellis, R. J.; Lau, J. C.-Y.; Taylor, P. G. *J. Chem. Soc., Perkin Trans. 2* **1986**, 593-597. See also: (f) Bassindale, A. R.; Ellis, R. J.; Lau, J. C.-Y.; Taylor, P. G. *Chem. Commun.* **1986**, 98-100.

[4] For an exception, see ref 3b.

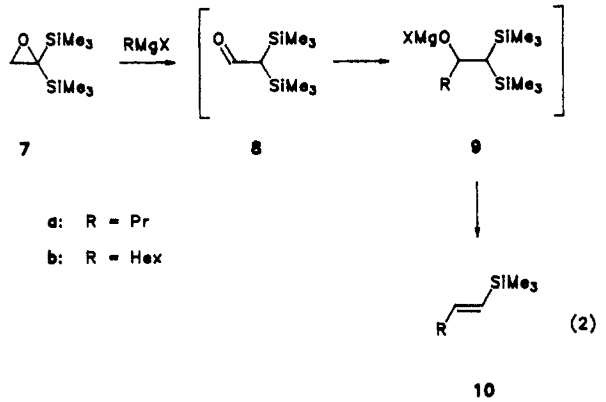
[5] Presented in part at the 8th International Symposium on Organosilicon Chemistry, St. Louis, MO, June 11, 1987. See also: Hudrlik, P. F.; Agwaramgbo, E. L. O. In *Silicon Chemistry*; Corey, E. R., Corey, J. Y., Gaspar, P., Eds.; Ellis Horwood, Ltd.: Chichester, 1988; pp 95-104.

[6] (a) Gröbel, B.-T.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 83-84. (b) Gröbel, B.-T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 852-866.

0022-3263/89/1954-5613$01.50/0

of benzaldehyde (**1a**) (and certain other carbonyl compounds) with [bis(trimethylsilyl)methyl]lithium (**2a**) in THF/HMPA to give a *mixture* of *trans*- and *cis*-vinylsilanes **5a** and **6a** (1.4:1 ratio) (eq 1a).[7] We have generated $\beta$-oxidosilane **3a**, the presumed intermediate in this reaction, by a number of different methods and find that it invariably yields the *trans*-vinylsilane **5a** in 90–99% isomeric purity.

Our interest in this topic grew out of some of our early work on the $\alpha$-opening of $\alpha,\beta$-epoxysilanes.[8,9] We found that the reaction of epoxide **7** with PrMgBr and with HexMgBr in THF (reflux) gave *trans*-vinylsilanes **10a** and **10b** in 97–98% isomeric purity as major products.[9] The formation of vinylsilanes was rationalized by the reaction pathway of eq 2, involving $\beta$-elimination of the $\beta$-oxidosilane **9**. The trans stereochemistry can be rationalized as follows: $\beta$-Hydroxysilanes have been shown to undergo $\beta$-elimination to form olefins by a syn pathway under basic conditions (and by an anti pathway under acidic conditions).[8a,10] Of the two conformations (A and B) of $\beta$-oxidosilane **9** which have the syn alignment of alkoxide and silicon, that (B) which would lead to the trans isomer is preferable on steric grounds.[7a,f,9] The contrast between the stereochemistry in this reaction and that of the Peterson olefination of eq 1 is striking, since both would be expected to involve a similar $\beta$-oxidosilane intermediate.

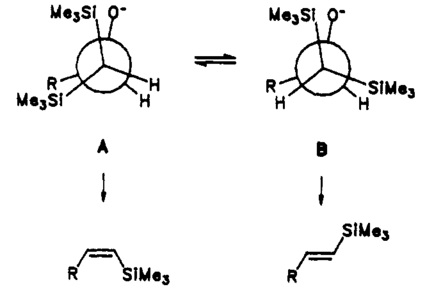


**7** **8** **9**

a: R = Pr

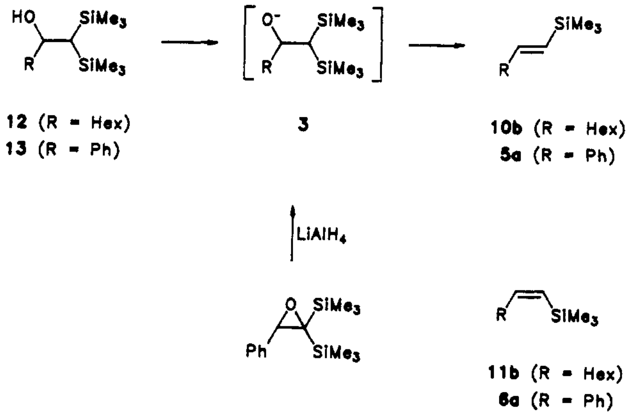
b: R = Hex

**10** (2)



**A** **B**

We therefore wished to prepare $\beta$-hydroxysilanes **12** and **13**, in order to study their $\beta$-elimination reactions under a variety of conditions. To prepare **12**, we repeated the reaction of eq 2 in ether instead of THF, reasoning that the $\beta$-elimination step would be slower in a less coordinating solvent. Treatment of **7** with HexMgBr in ether yielded $\beta$-hydroxysilane **12** in 60% yield. The base-promoted $\beta$-elimination of **12** gave *trans*-vinylsilane **10b**: When **12** was treated with KH in THF, **10b** was obtained in 95% yield, containing 1% or less of the cis isomer **11b**; similarly, treatment of **12** with NaH in THF gave **10b** in 92% yield, containing 1% or less of **11b**. These results lend support to the stereochemical rationale discussed above for eq 2. [In contrast, the acid-promoted $\beta$-elimination of **12** (with $BF_3$·$Et_2O$ in methylene chloride) gave a 40:53 mixture of **10b** and **11b** in 97% yield.]



**12** (R = Hex)
**13** (R = Ph)

**3**

**10b** (R = Hex)
**5a** (R = Ph)

**14**

**11b** (R = Hex)
**6a** (R = Ph)

To prepare $\beta$-hydroxysilane **13**, we first attempted the analogous reaction of epoxide **7** with PhMgBr in ether. This reaction was somewhat capricious, sometimes giving **13**, but frequently giving *trans*-vinylsilane **5a** as the major product (little or none of the cis isomer **6a** was observed). Subsequently, we found that **13** could be prepared more reliably by reduction of epoxide **14** with $LiAlH_4$ in ether. $\beta$-Hydroxysilane **13** appeared to be somewhat unstable to distillation and was generally used without purification.

Treatment of $\beta$-hydroxysilane **13** with a variety of bases led to *trans*-vinylsilane **5a**. With NaH or KH in THF, **5a** was obtained in 96–99% isomeric purity; in a preparative experiment, the reaction of **13** with KH in THF gave **5a** in 45% yield and 96% isomeric purity. In order to duplicate the base–solvent system used by Gröbel and Seebach (eq 1a),[6] $\beta$-hydroxysilane **13** was treated with *t*-BuLi and with (i-Pr)$_2$NLi, each at −78 °C in THF/HMPA. In both cases, *trans*-vinylsilane **5a** was formed in over 90% isomeric purity, although the overall purity of the vinylsilanes was lower than in the reactions of **13** with NaH and with KH.

When $\beta$-hydroxysilane **13** was treated with 1.15 equiv of *t*-BuLi (THF/HMPA, −78 °C, 2 h) a product mixture

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[7] For other Peterson olefinations involving two silicons (leading to vinylsilanes and substituted vinylsilanes), see ref 3d and the following: (a) Sakurai, H.; Nishiwaki, K.-I.; Kira, M. *Tetrahedron Lett.* **1973**, 4193–4196. (b) Hartzell, S. L.; Rathke, M. W. *Tetrahedron Lett.* **1976**, 2737–2740. (c) Carter, M. J.; Fleming, I. *Chem. Commun.* **1976**, 679–680. (d) Sachdev, K. *Tetrahedron Lett.* **1976**, 4041–4044. (e) Seebach, D.; Bürstinghaus, R.; Gröbel, B.-T.; Kolb, M. *Liebigs Ann. Chem.* **1977**, 830–845. (f) Seyferth, D.; Lefferts, J. L.; Lambert, R. L., Jr. *J. Organomet. Chem.* **1977**, *142*, 39–53. (g) van der Leij, M.; Zwanenburg, B. *Tetrahedron Lett.* **1978**, 3383–3386. (h) Isobe, M.; Kitamura, M.; Goto, T. *Tetrahedron Lett.* **1979**, 3465–3468. (i) Fleming, I.; Pearce, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2485–2489. (j) Carter, M. J.; Fleming, I.; Percival, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2415–2434. (k) Sato, Y.; Takeuchi, S. *Synthesis* **1983**, 734–735. (l) Ager, D. J. *J. Org. Chem.* **1984**, *49*, 168–170. (m) Inoue, S.; Sato, Y. *Organometallics* **1986**, *5*, 1197–1201. (n) Terao, Y.; Aono, M.; Takahashi, I.; Achiwa, K. *Chem. Lett.* **1986**, 2089–2092. (o) Marchand, A. P.; Huang, C.; Kaya, R.; Baker, A. D.; Jemmis, E. D.; Dixon, D. A. *J. Am. Chem. Soc.* **1987**, *109*, 7095–7101. (p) Kira, M.; Hino, T.; Kubota, Y.; Matsuyama, N.; Sakurai, H. *Tetrahedron Lett.* **1988**, *29*, 6939–6942. (q) Bates, T. F.; Thomas, R. D. *J. Org. Chem.* **1989**, *54*, 1784–1785. See also (r) Fleming, I.; Floyd, C. D. *J. Chem. Soc., Perkin Trans. 1* **1981**, 969–976.

[8] (a) Hudrlik, P. F.; Peterson, D.; Rona, R. J. *J. Org. Chem.* **1975**, *40*, 2263–2264. (b) Hudrlik, P. F.; Misra, R. N.; Withers, G. P.; Hudrlik, A. M.; Rona, R. J.; Arcoleo, J. P. *Tetrahedron Lett.* **1976**, 1453–1456. (c) Hudrlik, P. F.; Arcoleo, J. P.; Schwartz, R. H.; Misra, R. N.; Rona, R. J. *Tetrahedron Lett.* **1977**, 591–594. (d) Hudrlik, P. F.; Hudrlik, A. M.; Rona, R. J.; Misra, R. N.; Withers, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1993–1996. (e) Hudrlik, P. F.; Hudrlik, A. M.; Misra, R. N.; Peterson, D.; Withers, G. P.; Kulkarni, A. K. *J. Org. Chem.* **1980**, *45*, 4444–4448. (f) Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *Tetrahedron Lett.* **1985**, *26*, 139–142.

[9] (a) Hudrlik, P. F.; Withers, G. P., unpublished results. (b) Withers, G. P. Ph.D. Thesis, Rutgers University, New Brunswick, NJ, 1978.

[10] See also: Hudrlik, P. F.; Peterson, D. *J. Am. Chem. Soc.* **1975**, *97*, 1464–1468.

was obtained containing *trans*- and *cis*-vinylsilanes **5a** and **6a** in a 91/9 ratio. However, the overall VPC purity for the vinylsilanes was only 52%, with a major impurity at higher retention time. When only small amounts of *t*-BuLi were added to **13**, the vinylsilanes were obtained together with the starting material (**13**) as the only major impurity. For example, when *t*-BuLi was added to **13** in increments of $\sim ^1/_3$ equiv, *trans*-vinylsilane **5a** was observed in 94–97% isomeric purity after each increment, with **13** as the only major impurity after the first increment (−78 °C, 10 min), but with unidentified byproducts observed after the later increments. To determine whether the byproducts might arise from reaction of *t*-BuLi with the vinylsilanes, **5a** and **6a** were each treated with *t*-BuLi. In both cases, little starting material remained. The major product from the reaction of *trans*-vinylsilane **5a** with *t*-BuLi was identical by VPC retention time and GC–mass spectrum to the major unidentified byproduct from the reaction of β-hydroxysilane **13** with *t*-BuLi.

The reaction of **13** with $(i\text{-Pr})_2NLi$ in THF/HMPA gave **5a** and **6a** in ratios between 92:8 and 94:6; in a reaction at −78 °C for 2 h, the vinylsilanes were obtained in 68% yield with an overall VPC purity of 91%.

We briefly studied the β-elimination reaction of β-hydroxysilane **13** under acidic conditions. Treatment of **13** with $BF_3{\cdot}Et_2O$ ($CH_2Cl_2$, 0 °C) gave predominantly **5a** together with a small amount of styrene. To test whether styrene was being formed selectively from either **5a** or **6a**, a mixture of **5a** and **6a** was treated with $BF_3{\cdot}Et_2O$ ($CH_2Cl_2$, 0 °C); both were found to be slowly consumed at similar rates to give styrene.

Two additional methods to generate β-oxidosilane **3a** were briefly investigated. The reaction of epoxide **14** with $LiAlH_4$ was run in THF, giving a mixture of *trans*- and *cis*-vinylsilanes **5a** and **6a** in a 89.5/10.5 ratio with an overall VPC purity of 88%.[11] In a preliminary reaction, bis(trimethylsilyl)acetaldehyde (**8**)[8b,9b] was treated with PhLi in THF/HMPA (−78 °C, 1 h). A product mixture containing *trans*-vinylsilane **5a** contaminated with considerable amounts of biphenyl and small amounts of unidentified compounds was obtained; not more than 1% of *cis*-vinylsilane **6a** was present. These experiments confirm the results of the elimination experiments which suggested that β-oxidosilane **3a** decomposes to give primarily *trans*-vinylsilane **5a**.

We have repeated the Peterson olefination reaction of Gröbel and Seebach (eq 1a)[6,13] a number of times, obtaining *trans*- and *cis*-vinylsilanes **5a** and **6a** in ratios of 1.3:1 to 2:1, and we have also treated *p*-tolualdehyde (**1b**) with [bis(trimethylsilyl)methyl]lithium (**2a**) under similar conditions, giving a 64% yield of vinylsilanes **5b** and **6b** in a ratio of 1.4:1 (eq 1b).

To test for the possibility that the *trans*-vinylsilane (**5**) isomerizes to the cis (**6**) under the reaction conditions, we carried out the reaction of **1b** with **2a** in the presence of *trans*-vinylsilane **5a**. VPC analysis of the crude product at various reaction times from 1 min to 1 h showed *trans*- and *cis*-vinylsilanes **5b** and **6b** (~1.7:1 ratio) together with *trans*-vinylsilane **5a**; little or no *cis*-vinylsilane **6a** was observed, indicating that trans → cis isomerization does not occur.

We have also carried out the reaction of benzaldehyde with **2a** in THF-$d_8$/HMPA in an NMR tube in a 200-MHz NMR spectrometer at −60 °C. Although the initial purpose of the experiment was to look for CIDNP (none was observed), we did see peaks assigned to the trans and cis vinyl hydrogens of vinylsilanes **5a** and **6a** (in an approximate ratio of 1.3:1), ruling out the possibility that the trans–cis mixture could have resulted from β-elimination of **13** during workup.

A number of conceivable mechanisms for the Peterson olefination reaction can be postulated. Those involving initial C–C bond formation (whether preceded by single-electron transfer or not) lead to a β-oxidosilane; since the stereochemical results described above indicate that β-oxidosilane **3** may *not* be involved, at least in the major pathway, we considered the possibility that C–C bond formation and Si–O bond formation are concerted, or that Si–O bond formation precedes C–C bond formation. To shed light on the latter possibility, we carried out the Peterson olefination of benzaldehyde with [(*tert*-butyldimethylsilyl)(trimethylsilyl)methyl]lithium (i.e. **2**, Z = $SiMe_2t$-Bu). Since a *tert*-butyl group is known to retard the rate of some intermolecular displacement reactions at silicon by a factor of about $10^4$ relative to methyl,[14] a reaction involving initial Si–O bond formation would be expected to lead to *tert*-butyldimethylvinylsilanes in preference to trimethylvinylsilanes. In a preliminary experiment, we treated the lithium reagent from (*tert*-butyldimethylsilyl)(trimethylsilyl)methane[15] with benzaldehyde under the conditions used for the reaction of **2a** with benzaldehyde and with tolualdehyde and obtained a mixture of four compounds, assigned as *trans*- and *cis*-vinylsilanes **5a** and **6a**, and the corresponding *tert*-butyldimethylsilyl compounds, **5** and **6** (Z = $t$-$BuMe_2Si$, R = Ph),[16] in a 2:1:3:1 ratio by VPC. These results are not those expected from initial Si–O bond formation.

In order to investigate the generality of the stereochemistry of these Peterson olefination reactions, it would be desirable to study the reaction of **2a** with saturated aldehydes such as heptanal and to compare the results with the base-induced elimination reactions of β-hydroxysilane **12** (which gave *trans*-vinylsilane with KH and NaH). Reaction of **2a** with enolizable aldehydes was reported to give only low yields of vinylsilanes due to competing abstraction of an α hydrogen; however, the NMR spectrum of the product of butanal and **2a** indicated the presence of both cis and trans isomers, although the ratio was not specified.[6b]

In conclusion, the base-induced β-elimination reactions of β-hydroxysilanes **12** and **13**, which most certainly proceed via a β-oxidosilane intermediate, as well as the reactions of epoxide **14** with $LiAlH_4$ in THF and of silyl

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[11] When the reaction mixture was not cooled before the addition of aqueous $NaHCO_3$, 1-phenyl-2-(trimethylsilyl)ethane[12] was a major product.

[12] Weber, W. P.; Felix, R. A.; Willard, A. K. *Tetrahedron Lett.* **1970**, 907–910. Weber, W. P.; Willard, A. K.; Boettger, H. G. *J. Org. Chem.* **1971**, *36*, 1620–1626.

[13] Fleming and Pearce (ref 7i) used the reaction of benzaldehyde (**1a**) with **2a** in TMEDA to prepare trans vinylsilane **5a**.

[14] (a) Åkerman, E. *Acta Chem. Scand.* **1956**, *10*, 298–305. (b) Åkerman, E. *Acta Chem. Scand.* **1957**, *11*, 373–381. (c) Shirai, N.; Moriya, K.; Kawazoe, Y. *Tetrahedron* **1986**, *42*, 2211–2214. See also: (d) Stork, G.; Hudrlik, P. F. *J. Am. Chem. Soc.* **1968**, *90*, 4464–4465. (e) Hudrlik, P. F.; Feasley, R. *Tetrahedron Lett.* **1972**, 1781–1784. (f) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190–6191.

[15] Gornowicz, G. A.; West, R. *J. Am. Chem. Soc.* **1968**, *90*, 4478–9. West, R.; Gornowicz, G. A. *J. Organomet. Chem.* **1971**, *28*, 25–35.

[16] Two components were assigned as **5a** and **6a** by comparison of their VPC retention times and GC–mass spectra as well as the NMR spectrum of the product mixture with those of authentic samples. A third component was assigned as *cis*-vinylsilane **6** (Z = $SiMe_2t$-Bu, R = Ph) by a similar comparison with the compound prepared by treatment of $PhC{\equiv}CSiMe_2t$-Bu[17] with DIBAL followed by protonolysis. The fourth component was assumed to be the *trans*-vinylsilane **5** (Z = $SiMe_2t$-Bu, R = Ph) from the similarity of its GC–mass spectrum to that of the cis compound and from the NMR spectrum of the product mixture.

[17] Fallon, G. D.; Fitzmaurice, N. J.; Jackson, W. R.; Perlmutter, P. *J. Chem. Soc., Chem. Commun.* **1985**, 4–5. Fitzmaurice, N. J.; Jackson, W. R.; Perlmutter, P. *J. Organomet. Chem.* **1985**, *285*, 375–81.

aldehyde **8** with PhLi, give predominantly *trans*-vinylsilane **5a**. In contrast, the corresponding Peterson olefination (eq 1a) gives a cis–trans mixture. *These results suggest that β-oxidosilane **3a** is not a major intermediate in the Peterson olefination reaction, at least in this particular case, and suggest that the reaction of **1** and **2** may involve nearly simultaneous formation of C–C and Si–O bonds to give oxasiletane anion **4** directly.* This is analogous to some Wittig reactions, for which evidence has been found for oxaphosphetanes, but not for betaines.[18]

Although it is conceivable that the β-oxidosilane is generated but the elimination step is affected by various factors such as the degree of aggregation, ion pairing, or solvation, it should be noted that routes to the β-oxidosilane involving different cations and solvents gave similar results. It is also possible that the β-oxidosilane is generated but the elimination is faster than conformational change. In any event, it is clear that the Peterson olefination reaction is not as closely related to the base-induced β-elimination reactions of β-hydroxysilanes as had been previously assumed.

## Experimental Section

**General.** All reactions were carried out under nitrogen or argon. The verb "concentrated" means removal of solvent using a rotary evaporator. Infrared (IR) spectra were obtained using a Perkin-Elmer 1320 infrared spectrophotometer. Proton nuclear magnetic resonance (NMR) spectra were obtained as 60-MHz spectra using a Hitachi Perkin-Elmer R-600 spectrometer unless otherwise stated; 200-MHz spectra were taken on a Nicolet NT-200 instrument. Chemical shifts were measured relative to chloroform, δ 7.28. Mass spectra were obtained using a Finnigan 3200 E automated gas chromatograph–mass spectrometer (GC–MS). Vapor-phase chromatography (VPC) analyses were carried out on a Varian Aerograph Model 90-P instrument (SE-30 and Carbowax columns) or on a Shimadzu Model GC-9A instrument (OV-101 column) using helium as the carrier gas; in many cases, the retention time of a hydrocarbon standard under the given conditions is included. The following columns were used: SE-30 (10% SE-30 on 60–80 mesh Chromosorb W, 10 ft × 0.25 in. aluminum column), Carbowax (25% Carbowax 20M on 60–80 mesh Chromosorb W, 20 ft × 0.25 in. aluminum column), OV-101 (3% OV-101 on 100–120 mesh Supelcoport, glass column). Unless otherwise indicated, the OV-101 column was used with the following temperature program: 100 °C (2 min), 100–250 °C (10 °C/min); under these conditions, tetradecane had a retention time of 7.7 min.

Anhydrous ether and tetrahydrofuran (THF) were distilled from sodium and benzophenone. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride. Boron trifluoride etherate ($BF_3 \cdot Et_2O$) was distilled under reduced pressure. Comparison samples of **5a** and **6a** were prepared according ref 19. Comparison samples of **10b** and **11b** were available.[20]

**1,1-Bis(trimethylsilyl)-2-octanol (12).** To an ice-cooled solution of 1.04 g (5.52 mmol) of epoxide **7**[8b] in 40 mL of anhydrous ether was added 4.4 mL of hexylmagnesium bromide (from 1.44 g (59 mmol) of magnesium turnings and 3.3 g (20 mmol) of hexyl bromide in 8 mL of ether). The reaction mixture was stirred at ice temperature for 1 h and at room temperature for 20 h. Aqueous $NH_4Cl$ (30 mL) was added, and the organic layer was washed with saturated $NaHCO_3$. The combined aqueous layers were extracted with ether (2 × 20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated. Kugelrohr distillation (110 °C, oil pump vacuum) gave 0.91 g (60% yield) of **12** as a colorless liquid: IR (film) 3600, 3400, 2940, 2920, 2840, 1240, 835 $cm^{-1}$; 200-MHz NMR ($CDCl_3$) δ 0.10 (s, 18 H), 0.29 (d, 1 H, $J$ = 5.9 Hz), 0.85–1.68 (m, 13 H), 3.85–4.03 (m, 1 H), 4.75 (s, 1 H, disappears on addition of $D_2O$); mass spectrum $m/z$ (rel intensity) 256 ($M^+ - H_2O$, <0.1), 189 (5), 169 (42), 147 (73), 75 (37), 73 (100); exact mass 189.1094 ($M^+$ – Hex, calcd for $C_8H_{21}OSi_2$: 189.1131) and 169.1409 ($M^+$ – 105, calcd for $C_{10}H_{21}Si$: 169.1413). VPC analysis (SE-30, 170 °C, hexadecane = 4.3 min) showed the major peak (97.5%) at 4.5 min.

**Elimination Reaction of β-Hydroxysilane 12 Using KH: *trans*-1-(Trimethylsilyl)-1-octene (10b).** Potassium hydride (0.2 g of a 22% slurry in oil, 1.1 mmol) was stirred with two portions of pentane, and each time the liquid was removed with a pipet. To the residue was added 10 mL of THF and 0.091 g (0.33 mmol) of β-hydroxysilane **12**. The resulting mixture was stirred at room temperature for 1.5 h. The reaction mixture was added to 25 mL of 10% $NH_4Cl$ overlaid with ether. The organic layer was dried ($MgSO_4$) and concentrated. Kugelrohr distillation (50 °C, oil pump vaccum) gave 0.058 g (95% yield) of **10b** as a colorless liquid. The IR and NMR spectra were identical with those of an authentic sample.[20] VPC analysis (Carbowax, 140 °C, decane = 4.3 min) showed the major peak (96.8%) at 5.6 min; a peak at 6.3 min (1% or less) corresponded to **11b**.

**Elimination Reaction of β-Hydroxysilane 12 Using NaH: *trans*-1-(Trimethylsilyl)-1-octene (10b).** By a procedure similar to that for the reaction of **12** with KH, 0.27 g (1 mmol) of **12** was treated with pentane-washed sodium hydride (from 0.096 g of a 50% slurry in oil, 2 mmol) in 30 mL of THF (20 h, room temperature). Kugelrohr distillation (50 °C, oil pump vaccum) of the crude product gave 0.17 g (92% yield) of **10b** as a colorless liquid. The IR and NMR spectra were identical with those of an authentic sample.[20] VPC analysis (Carbowax, 140 °C, decane = 4.3 min) showed the major peak (98%) at 5.6 min; a peak at 6.3 min (1% or less) corresponded to **11b**.

**Elimination Reaction of β-Hydroxysilane 12 Using $BF_3 \cdot Et_2O$.** To an ice-cooled solution of 0.274 g (1 mmol) of β-hydroxysilane **12** in 20 mL of dichloromethane was added 0.5 mL (4 mmol) of $BF_3 \cdot Et_2O$. The resulting mixture was stirred at ice temperature for 1.5 h and was then added to saturated $NaHCO_3$ and dichloromethane. The organic layer was dried ($MgSO_4$) and concentrated. Kugelrohr distillation (50 °C, oil pump vaccum) gave 0.18 g (97% yield) of a mixture of **10b** and **11b** as a colorless liquid. The IR and NMR spectra were consistent with a mixture of trans and cis vinylsilanes **10b** and **11b**.[20] VPC analysis (Carbowax, 140 °C, decane = 4.3 min) showed the major peaks at 5.8 min (40%, **10b**), 6.6 min (53%, **11b**), and 8.1 min (5%).

**2,2-Bis(trimethylsilyl)styrene Oxide (14).** To an ice-cooled mixture of 3.0 g (14 mmol) of *m*-chloroperbenzoic acid (80–85%), 2.7 g (19 mmol) of $Na_2HPO_4$, and 60 mL of dichloromethane was added 2.5 g (10.1 mmol) of β,β-bis(trimethylsilyl)styrene.[6b] The ice bath was removed, and the reaction mixture was stirred for 18 h. A slurry of $NaHSO_3$ in water was added and stirred for 2 h, a solution of 10% NaOH was added, and the resulting mixture was stirred for another 2 h. The organic layer was washed with aqueous $NaHCO_3$. The bicarbonate layer was extracted with ether. The combined organic layers were dried ($MgSO_4$) and concentrated. Kugelrohr distillation (110 °C, oil pump vacuum) gave 1.5 g (56% yield) of **14** as a colorless liquid: IR (film) 2959, 2902, 1382, 1251, 939–698 (several peaks) $cm^{-1}$; NMR ($CDCl_3$) δ 7.51 (s, 5 H), 4.3 (s, 1 H), 0.37 (s, 9 H), 0.00 (s, 9 H); mass spectrum $m/z$ (rel intensity) 264 ($M^+$, 1), 147 (32), 73 (100), 45 (30); exact mass 264.1353 (calcd for $C_{14}H_{24}OSi_2$: 264.1366). VPC analysis (OV-101) showed the major peak at 8.9 min (98%).

**Reaction of Epoxide 14 with $LiAlH_4$ in Ether: β-Hydroxysilane 13.** To 0.46 g (12 mmol) of $LiAlH_4$ in 60 mL of anhydrous ether cooled in an ice bath was added 1.05 g (3.97 mmol) of epoxide **14**, and the reaction mixture was allowed to warm to room temperature with stirring for 2.25 h. The mixture was cooled in a dry ice/acetone bath, and cold aqueous $NaHCO_3$ was added dropwise. Ether was added, the layers were separated, and the aqueous layer was extracted with ether (2 × 30 mL). The

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combined organic layers were dried ($MgSO_4$) and concentrated to give 0.68 g (64% crude yield) of **13** as a colorless liquid: IR (film) 3569, 3452, 2954, 1251, 1042, 872, 842, 759, 701 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.26–7.58 (5 H), 5.1–5.4 (b m, 1 H), 1.4–1.8 (m, 1 H), 0.8 (d, 1 H, $J$ = 5 Hz), 0.2 (s, 9 H), 0.1 (s, 9 H). The GC–MS showed two peaks on the GC in the approximate ratio of 1:30. The mass spectrum of the larger peak showed $m/z$ (rel intensity) 251 (0.02), 187 (4), 176 (21), 161 (100), 147 (63), 75 (47), 73 (67). The smaller peak was identified as **5a** by the mass spectrum and VPC retention time. VPC analysis (OV-101) showed peaks at 4.5 min (1.1%, **6a**), 5.6 min (4%, **5a**), 10.3 min (4.2%, unidentified), and 11.2 min (85.8%, **13**). This product was used for the elimination reactions (below) without further purification.

**Elimination Reaction of $\beta$-Hydroxysilane 13 Using KH: *trans*-$\beta$-(Trimethylsilyl)styrene (5a).** By a procedure similar to that for the reaction of **12** with KH, 0.2 g (0.7 mmol) of **13** was treated with pentane-washed potassium hydride (from 0.2 g of a 22% slurry in oil, 1 mmol) in 10 mL of THF (1 h, room temperature). After aqueous workup with $NH_4Cl$, Kugelrohr distillation (80 °C, oil pump vacuum) gave 0.06 g (45% yield) of **5a** as a colorless liquid. The IR and NMR spectra were in agreement with those of an authentic sample[19] except for a moderate OH peak in the IR spectrum. VPC analysis (OV-101) showed the major peak (96%) at 5.49 min (**5a**) and a peak at 4.36 min (4.0%) corresponding to **6a**.

**Elimination Reaction of $\beta$-Hydroxysilane 13 Using *t*-BuLi.** To a solution of 0.266 g (1.0 mmol) of $\beta$-hydroxysilane **13** in 5 mL of THF and 1 mL of HMPA cooled to −78 °C was added 0.2 mL (0.3 mmol) of *t*-BuLi (1.5 M in hexane). After 10 min at −78 °C, an aliquot was taken and added to saturated $NaHCO_3$ overlaid with pentane. VPC analysis (OV-101) of the organic layer showed the major peaks at 4.5 min (3.9%, **6a**), 5.6 min (68.5%, **5a**), and 11.1 min (23.5%, **13**). Another 0.2 mL of the *t*-BuLi was added, and an aliquot taken after 10 min showed by VPC analysis major peaks at 4.5 min (5.5%, **6a**), 5.6 min (78.8%, **5a**), 7.6 min (2.7%), 9.2 min (4.4%), and 11.1 min (7.3%, **13**). Another 0.2 mL of the *t*-BuLi was added, and an aliquot taken after 5 min showed by VPC analysis as above, major peaks at 5.6 min (32.8%, **5a**), 7.6 min (10.3%), 9.2 min (42.5%), 14.3 min (4.4%), and 16.9 min (3.9%); a small peak at 4.5 min (1.0%) corresponded in retention time to **6a**.

In a separate experiment where *t*-BuLi was added in one portion [0.14 g (0.53 mmol) of **13**, 5 mL of THF, 1 mL of HMPA, 0.4 mL (0.6 mmol) of *t*-BuLi, (1.5 M), −78 °C, 2 h], the product (0.1 g after Kugelrohr distillation) contained vinylsilanes **5a** and **6a** (91:9 ratio) as 52% of the product mixture, with the major impurities coming at 7.4 min (6%) and 9.0 min (36%) by VPC analysis under the above conditions. In another experiment [0.133 g (0.5 mmol) of **13**, 5 mL of THF, 1 mL of HMPA, 0.2 mL (0.3 mmol) of *t*-BuLi (1.5 M), −78 °C, 2 min], VPC analysis of the crude product (OV-101) showed the major peaks at 4.5 min (5.3%, **6a**), 5.6 min (68.1%, **5a**) and 11.1 min (23.1%, **13**). In one experiment (using 8:1 THF/HMPA), the crude product contained about 90% of *trans*-vinylsilane **5a** and about 5% of *cis*-vinylsilane **6a** by VPC, and the IR and NMR spectra were in agreement with those of authentic samples of the vinylsilanes. We were not able to achieve the disappearance of **13** again without producing significant amounts of the higher retention time byproducts. The differences in these results may arise from use of different batches of *t*-BuLi, from difficulties in measuring precise amounts of *t*-BuLi, or from different batches of **13**, which, as mentioned above, was used without purification.

The vinylsilanes were each treated with *t*-BuLi to determine whether the high retention time byproducts might arise from their reaction with *t*-BuLi. From **5a** [0.18 g (1.02 mmol) of **5a**, 5 mL of THF, 1 mL of HMPA, 0.8 mL (1.1 mmol) of *t*-BuLi (1.4 *M* in hexane), −78 °C, 20 min], VPC analysis of the crude product (OV-101) showed major peaks at 5.6 min (**5a**, 9.5%), 7.5 min (10.5%), 9.2 min (48.8%), and 14.2 min (7.0%). A similar reaction of **6a** with *t*-BuLi showed a similar GC, although with a major peak at 16.8 min, which had been present only in minor amounts in the previous mixture. GC–mass spectra were taken of the product mixtures from the reactions of **13** and of **5a** and **6a** with *t*-BuLi. The assignments of the vinylsilanes **5a** and **6a** and of **13** in the product mixtures were confirmed by comparison with authentic samples (mass spectra **5a** and **6a** were essentially identical), but structures were not assigned for the other products. The mass spectra of the major impurity (~9-min retention time) from the elimination reactions was equivalent to that of the major product from the reaction of **5a** with *t*-BuLi. (The mass spectra of some of the other products were not very informative.)

**Elimination Reaction of $\beta$-Hydroxysilane 13 Using $BF_3{\cdot}Et_2O$: *trans*-$\beta$-(Trimethylsilyl)styrene (5a).** By a procedure similar to that for the reaction of **12** with $BF_3{\cdot}Et_2O$, 0.16 g (0.6 mmol) of **13** was treated with 0.2 mL (1.6 mmol) of $BF_3{\cdot}Et_2O$ in 5 mL of dichloromethane (0 °C, 5 min). After aqueous workup with $NH_4Cl$, Kugelrohr distillation (80 °C, oil pump vacuum) gave 0.07 g (66% yield) of **5a**. The IR and NMR spectra were in agreement with those of an authentic sample[19] except for a trace of an impurity peak in the NMR at $\delta$ 1.5 (s, 1 H). VPC analysis (OV-101) showed the major peak (90.5%) at 5.5 min and peaks at 1.3 min (5.6%, styrene) and 4.4 min (2.9%, **6a**).

In a separate experiment, in which the crude product was not concentrated, the VPC (OV-101) showed three peaks at 1.22 min (12%), 4.3 min (3%), and 5.6 min (76%), which were identified as styrene, **6a**, and **5a**, respectively, by GC–MS.

**Reaction of [Bis(trimethylsilyl)methyl]lithium with *p*-Tolualdehyde: Vinylsilanes 5b and 6b.** To a solution of 2.8 mL (2.1 g, 13 mmol) of bis(trimethylsilyl)methane in 30 mL of THF was added 10 mL of HMPA. The reaction mixture was cooled to −78 °C, and 10.0 mL (16.5 mmol) of *t*-BuLi (1.65 M in pentane) was added slowly dropwise. After 15 min, the reaction mixture was warmed to −40 °C and stirred for 7.5 h at −40 °C in a dry ice/acetonitrile bath. The reaction mixture was then cooled to −78 °C and 1.1 mL (1.12 g, 9.3 mmol) of *p*-tolualdehyde (**1b**) was added. The solution turned dark brown. After 1 h at −78 °C, the reaction was quenched by adding aqueous $NaHCO_3$, and the resulting mixture was poured into a solution of $NaHCO_3$ overlaid with pentane. The organic layer was washed with water (2 × 20 mL). The combined aqueous layers were extracted with pentane. The combined organic layers were dried ($MgSO_4$) and concentrated. Kugelrohr distillation (60 °C, oil pump vacuum) gave 1.13 g (64% yield) of a mixture of **5b** and **6b** as a colorless liquid: IR (film) 2958, 1609, 1509, 1249, 987, 869, 788 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 0.00 (s, $Me_3Si$ of **6b**, (minor)), 0.15 (s, $Me_3Si$ of **5b**, (major)), 2.3 (s, $ArCH_3$), 5.71 (d, $J$ = 15 Hz, **6b**), 6.33 (d, $J$ = 19 Hz, **5b**), 6.95–7.35 (m). The 200-MHz NMR spectrum ($CDCl_3$) showed a pair of doublets ($J$ = 19 Hz) at $\delta$ 6.33 and 6.78 (assigned to the major isomer **5b**) and a smaller doublet ($J$ = 15 Hz) at $\delta$ 5.71 (assigned to the minor isomer **6b**). The GC–mass spectrum showed two peaks on the GC in the approximate ratio of 1:2. The mass spectrum of the larger peak (**5b**) showed $m/z$ (rel intensity) 190 ($M^+$, 43), 175 (100), 159 (60), 149 (35), 115 (15), 73 (12), 59 (45); the mass spectrum of the smaller peak (**6b**) was very similar; exact mass 190.1173 (calcd for $C_{12}H_{18}Si$: 190.1178). VPC analysis (OV-101, temperature programming: 80 °C (2 min), 80–200 °C (10 °C/min)) showed the major peaks at 8.2 min (42%, **6b**) and 10.2 min (57%, **5b**), respectively.

**Reaction of [Bis(trimethylsilyl)methyl]lithium with *p*-Tolualdehyde in the Presence of Vinylsilane 5a.** To a solution of 1.5 mL (1.13 g, 7 mmol) of bis(trimethylsilyl)methane in 10 mL of THF was added 2 mL of HMPA. The reaction mixture was cooled to −78 °C, and 3.8 mL (5.7 mmol) of *t*-BuLi (1.5 M in hexane) was added slowly dropwise. The reaction mixture was warmed to −40 °C and stirred for 7.5 h at −40 °C in a dry ice/acetonitrile bath, and 0.34 g (1.9 mmol) of vinylsilane **5a** and 0.26 g of *m*-*tert*-butyltoluene (internal standard) were added. The resulting mixture was cooled to −78 °C, and an aliquot was taken and quenched in aqueous $NaHCO_3$ overlaid with pentane. VPC analysis of the organic layer (OV-101, temperature programming: 80 °C (7 min), 80–250 °C (20 °C/min)) showed major peaks at 6.3 min (40.1%, *m*-*tert*-butyltoluene) and 10.5 min (39.8%, **5a**). Then 0.6 mL (0.6 g, 5 mmol) of *p*-tolualdehyde (**1b**) was added. Aliquots were taken at 1, 5, 15, 30, and 60 min, were quenched by adding them to standard $NaHCO_3$ overlaid with pentane, and were each analyzed by VPC under the above conditions. VPC analysis of the organic layer of the aliquot taken after 1 min showed major peaks at 6.4 min (17.4%, *m*-*tert*-butyltoluene), 10.5 min (17.2%, **5a**), 10.7 min (15.5%, **6b**), and 11.6 min (27.9%, **5b**). VPC analysis of the organic layer of the aliquot taken after 1 h showed major peaks at 6.4 min (18.0%, *m*-*tert*-butyltoluene), 10.5 min (17.9%, **5a**), 10.7 min (16.4%, **6b**), and

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11.6 min (28.7%, **5b**). In three of the aliquots (1 min, 15 min, 1 h), a small peak (<1%) was detectable at 9.3 min, corresponding in retention time to *cis*-vinylsilane **6a**; in the other two aliquots, no peak was detectable at 9.3 min.

A separate reaction without the internal standard gave similar results.

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# *Notes*

## Fluoromalonaldehyde Bis(dialkyl acetals): Synthesis by Carbene Condensation and Transformation to Dialkyl Fluoromalonates and Fluorinated Heterocyclic Compounds

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Fluoromalonaldehyde (**1**) has been used as a fluorinating building block for synthesis of various fluorine-substituted carbocyclic and heterocyclic compounds.[1] To date, only one preparation of **1** has been reported.[2] This useful reagent was prepared by Vilsmeier formylation of sodium fluoroacetate followed by alkaline hydrolysis of the 2-fluoro-3-(dimethylamino)acrolein so obtained. The toxicity of the starting material and the poor overall yield (15%) limited the interest for this fluorinating building block.

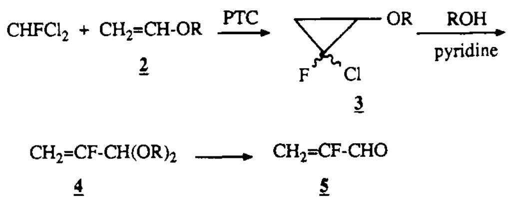
OCH-CHF-CHO

**1**

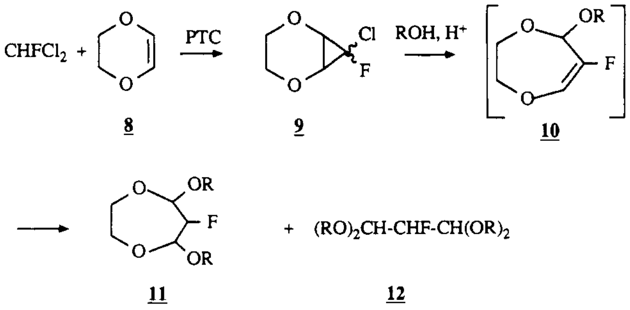
We report here an easy two-step synthesis of acetals of fluoromalonaldehyde starting from dichlorofluoromethane and dioxene. Then we will show how these new compounds can be used as starting material in place of **1** to get fluorinated heterocyclic compounds and for a new and convenient way to dialkyl fluoromalonates.[3]

Some years ago we developed a carbene process for the synthesis of 2-fluoroacrolein (**5**).[4] Chlorofluorocarbene generated from dichlorofluoromethane was condensed on enol ether **2**. Phase-transfer catalysis (PTC) was used, and these mild conditions permitted isolation of the dihalocyclopropane **3**.[4,5] The following step for the synthesis of 2-fluoroacrolein (**5**) was the conversion of **3** to the acetal **4** by refluxing it in pyridine and alcohol (Scheme I).

**Scheme I**



**Scheme II**



**a** : R = $CH_3$ ; **b** : R = $C_2H_5$

The application of this method to 1,2-dialkoxyethylene **6** should lead in two steps to the acetal **7**, a masked form of fluoromalonaldehyde. Reagent **6** ought to be readily available to make this synthetic pathway attractive. Among compounds of type **6**, only 2,3-dihydro-*p*-dioxin (dioxene) (**8**) could be easily prepared on a large scale from diethylene glycol.[6]

RO-CH=CH-OR　　　RO-CH=CF-CH$(OR)_2$

**6**　　　**7**

### Results and Discussion

**Carbene Condensation.** Condensation of dioxene (**8**) with chlorofluorocarbene under phase-transfer conditions led to 7-chloro-7-fluoro-2,5-dioxabicyclo[4.1.0]heptane (**9**) (Scheme II). Liquid–liquid PTC (50% aqueous sodium hydroxide–dichloromethane–benzyltriethylammonium chloride) at 5–10 °C gave **9** in 91% isolated yield. A mixture of cis (**9c**) and trans (**9t**) isomers was obtained in the ratio 58/42. These configurations were determined on the basis of the $^{19}$F NMR chemical shifts and coupling constants in **9c** ($\delta = -145$ ppm, $J_{HF} = 14$ Hz) and in **9t** ($\delta = -170$ ppm, $J_{HF} = 0$ Hz).[7,8]

A much simpler solid–liquid PTC procedure[9] using tris(3,6-dioxaheptyl)amine (TDA-1)[10] was also tried, giving

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