a small normal effect arising from the displacement reaction that is occurring at C-5.

In summary, we have four pieces of isotopic information on the enzyme-catalyzed rearrangement of chorismate to prephenate: the solvent deuterium effect, and tritium effects at C-4, C-5, and C-9. These data, along with results from the non-enzymic reaction and from the use of chorismate analogues, limit the mechanistic possibilities for the chorismate mutase reaction. Thus we can eliminate those pathways (a) that involve a conformational isomerization of bound pseudo-diequatorial substrate, (b) that exploit the C-4 hydroxyl group to yield a carbonium ion at that position (**7**), (c) that proceed via an oxirinium ion intermediate (**8**), and probably (d) that involve anionic participation of the C-4 oxygen (**12**). The results are best accommodated by a pathway (Figure 2) in which the rate-limiting heterolytic cleavage of the ether bond of chorismate is assisted by attack of an enzymic nucleophile, to give an intermediate that collapses in an S_N2' process to yield the product prephenate.

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Communications to the Editor

Stereochemistry and Mode of Intermolecular Si-H Unsaturated Carbene Insertions†

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Unsaturated carbenes, like their saturated congeners, undergo four basic types of reactions: (a) additions; (b) insertions; (c) ylide formations; (d) rearrangements.[1] Recent, concomitant theoretical and experimental studies[2,3] have clearly established the exact manner of alkylidenecarbene–olefin interactions and concurrent transition-state geometries, whereas the mode of carbene insertion reactions in general, and unsaturated carbenes in particular, is much less understood.

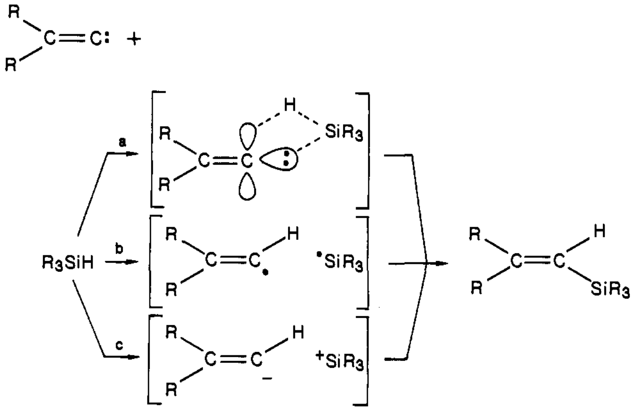
In a recent, elegant investigation, Gilbert and co-workers[4] established that the 1,5-intramolecular C–H insertion of alkylidenecarbenes occurs with retention of configuration, most likely via a concerted process involving a nonlinear transition state. Few examples of intermolecular C–H unsaturated carbene insertions are known.[1] However, these species readily insert into Si–H bonds.

A priori, intermolecular Si–H unsaturated carbene insertions may be envisioned to proceed by (a) a concerted, three-centered process or (b) a homolytic or (c) heterolytic hydrogen abstraction–recombination pathway (Scheme I).

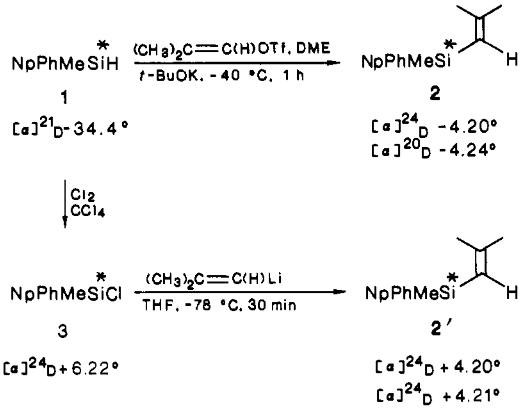
A concerted, three-centered process would require retention of chirality during the course of reaction with a chiral silane, whereas either of the abstraction–recombination pathways would predict loss of chirality. During the course of our investigations, Gilbert and Giamalva[5] predicted, by means of the temperature *independence* of the kinetic deuterium isotope effect [$(CH_3)_2C{=}C$: + $Et_3SiH(D)$], a concerted process, via a nonlinear transition state, as the most likely pathway for such intermolecular Si–H insertions. This transition state would require not only retention of chirality, but also *complete stereospecificity with retention of absolute configuration.*

In this paper, we wish to report the results of our investigation of the interaction of both $(CH_3)_2C{=}C$: and $(CH_3)_2C{=}C{=}C{=}C$: with chiral, optically pure (*S*)-α-NpPhMeSi*H (**1**).[6]

Scheme I



Scheme II



Optically pure (*S*)-α-NpPhMeSi*H (**1**) was prepared according to the procedure of Corriu and Moreau.[7] Interaction of the triflate-derived[1] $(CH_3)_2C{=}C$: with **1** in glyme (duplicate runs) gave the insertion product **2** in 78% yield with $[\alpha]_D$ −4.20° and

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† Dedicated to Professors W. von E. Doering and A. Streitwieser, Jr., on the occasion of their 70th and 60th birthdays, respectively.

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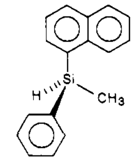
[6] (*S*)-α-NpPhMeSi*H =



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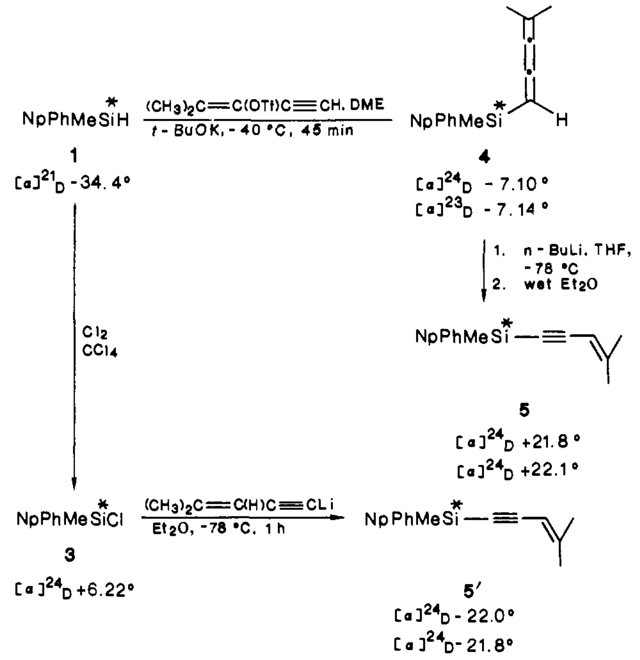
Scheme III



−4.24° (Scheme II). Conversion of the optically pure **1** to the chloride **3** is known to proceed with complete retention of configuration.[8] Interaction of chlorosilane **3** with a variety of alkyllithium compounds is known[9] to occur with complete inversion of configuration, yielding tetrasubstituted silanes. Therefore, we treated chloride **3** with $(CH_3)_2C=C(H)Li$ to obtain "authentic" adduct[10] **2′** of known optical purity and configuration. As seen in Scheme II, duplicate runs gave, within experimental error, an $[\alpha]_D$ of *identical magnitude but opposite sign* to the carbene insertion product. Since the anionic route involves one retention and one inversion, this establishes that the carbene insertion must proceed by complete stereospecificity with retention of configuration.

Likewise, duplicate runs of the reaction of **1** with triflate-derived $(CH_3)_2C=C=C=C$: gave adduct **4**.[11] Unfortunately, as cumulenyl anions are unknown, we were unable to prepare authentic **4** to establish its configuration via a direct procedure. However, adduct **4** readily undergoes a base-promoted rearrangement to enynylsilane **5** (Scheme III). Since this rearrangement does not involve any bonds to the chiral silicon, neither the configuration nor the enantiomeric purity of the product should be affected. Reaction of silane-derived chloride **3** with $(CH_3)_2C=C(H)C\equiv CLi$ in duplicate runs (Scheme III) gave "authentic"[12] **5′** with an $[\alpha]_D$ of *identical magnitude but of opposite rotation* to the carbene insertion derived, rearranged, tetrasubstituted silane **5**. Since the halide displacement reaction is known[9] to involve inversion of configuration, this establishes that the $(CH_3)_2C=C=C=C$:/Si—H insertion also must proceed by complete stereospecificity with retention of configuration.

Although it is conceivable, it is extremely unlikely that either the radical pairs[13] or the ion pairs in Scheme I would have a sufficiently short lifetime to undergo recombination faster than loss of chirality. Hence, we have established that alkylidenecarbenes, as well as the more extended members of the unsaturated carbene family, undergo intermolecular Si–H insertion via a concerted, three-centered transition state (albeit perhaps with some polar character) in accord with Gilbert's predictions[5] and in contrast to Newman's[15] original proposal involving ion pairs. These results are in concord with the observations of Sommer and coworkers[16] on the stereospecific insertion of Br_2C: and Cl_2C: into chiral NpPhMeSi*H.

Acknowledgment. We are grateful to the NSF (CHE 84-19099) for financial support and to Professor G. L. Larsen for a batch of chiral silane **1**.

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[10] The two vinylsilanes **2** and **2′** prepared by the carbene insertion and the anion route were identical in all respects, IR, NMR, GC retention, etc., but for the direction of rotation. For **2**: IR (neat) 1619 (C=C), 1440, 1429, 1250, 1103, 732 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.6 (m, 12), 5.73 (s, 1), 1.97 (s, 3), 1.65 (s, 3), 0.82 (s, 3); ^{13}C NMR ($CDCl_3$) δ 155.02, 138.08, 136.84, 135.67, 135.05, 134.69, 133.31, 129.91, 128.81, 128.73, 127.71, 125.41, 125.20, 125.02, 120.76, 29.73, 23.85, −0.75; mass spectrum, EI, *m/z* (relative intensity) 302 (M^+, 92), 287 (100), 259 (20), 247 (33), 233 (23).

[11] For **4**: IR (neat) 2028 (C=C=C=C), 1428, 1250, 1210, 785 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.6 (m, 12), 5.92 (sept, 1, J = 1.05 Hz), 1.92 (d, 3, J = 1.05 Hz), 1.68 (d, 3, J = 1.05 Hz), 0.84 (s, 3); ^{13}C NMR ($CDCl_3$) δ 173.64, 157.28, 136.93, 135.38, 134.66, 134.06, 133.27, 130.30, 129.14, 128.82, 128.69, 127.74, 125.56, 125.31, 124.98, 124.04, 25.61, −2.11; mass spectrum, FAB, *m/z* 327 (MH^+), 247, 169.

[12] The two enynylsilanes **5** and **5′** were identical in all respects, IR, NMR, GC retention, etc., but for the *direction* of rotation. Both **2** and **5** gave satisfactory C and H analyses. For **5**: *IR* (neat) 2120 ($C\equiv C$), 1428, 1250, 1106, 785 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.6 (m, 12), 5.38 (sept, 1, J = 0.97 Hz), 1.94 (d, 3, J = 0.97 Hz), 1.82 (d, 3, 0.97 Hz), 0.86 (s, 3); ^{13}C NMR ($CDCl_3$) δ 151.37, 136.60, 135.94, 135.21, 134.44, 133.27, 132.88, 130.56, 129.37, 128.69, 128.62, 127.83, 125.63, 125.37, 124.96, 107.32, 105.47, 92.78, 24.95, 21.43, −0.56; mass spectrum, EI, *m/z* (relative intensity) 326 (M^+, 89), 311 (100), 284 (11), 271 (16), 247 (16), 231 (23).

[13] Although there is evidence[14] for the existence of chiral NpPhMeSi•, in no instance has there been complete stereospecificity observed in these radical reactions. Moreover, radical traps such as galvinoxyl, O_2, and *t*-BuNO did not affect our insertion reactions.

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Kinetics of Hexafluorobenzene Decomposition on a Pt Surface

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Kinetics of gas-solid heterogeneous reactions are usually monitored by means of mass spectrometric techniques, in which the probe can be ions (secondary ion mass spectrometry—SIMS),[1] thermal energy (thermal desorption spectrometry-TDS),[2-4] and lasers (laser-induced desorption),[5-7] or by means of electron spectroscopic techniques.[8] In this communication we present a novel technique (direct recoil spectrometry—DRS)[9] for monitoring surface kinetics which provides direct time-resolved compositions of surface constituents. Application to decomposition of hexafluorobenzene (HFB) on platinum has found that carbon is deposited on the surface while fluorine is evolved, the kinetics follow a second-order rate law with a 4-kcal/mol activation energy, and a proposed mechanism involving migration of surface fluorine is the rate-limiting step.

The DRS technique, which has been described elsewhere,[9] has been used for monitoring chemisorption and for studying ion-

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