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ANTI STEREOCHEMISTRY IN PROTODESILYLATION OF AN OPTICALLY ACTIVE ALLYLSILANE WITH TRIFLUOROACETIC ACID-*D*[1]

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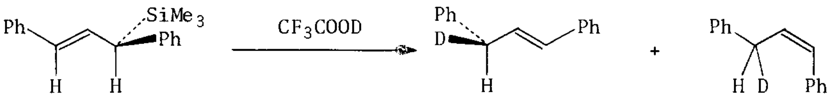
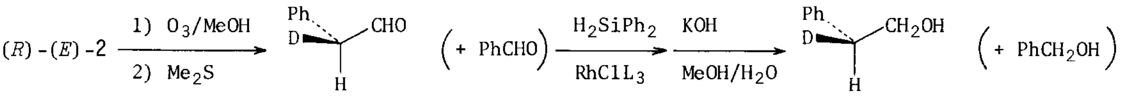
Summary: S_E' reaction of (*R*)-(*E*)-1,3-diphenyl-3-trimethylsilylpropene with trifluoroacetic acid-*d* proceeded with *anti* stereochemistry to give (*R*)-(*E*)-1,3-diphenylpropene-*3-d*.

Protodesilylation of allylsilanes leading to olefins with a net shift of the double bond has been of synthetic and mechanistic interest for years.[2] Fleming has reported[3] that proton attacks the same face of a double bond as a leaving silyl group (*syn* attack) in the reaction of an allylsilane with bicyclo[3,2,0]heptenone framework, where the stereochemistry may be controlled not by the inherent nature of the allylsilane but by the exo bias in the bicyclic system. We report that the protodesilylation in an unbiased acyclic system proceeds with *anti* stereochemistry.

(*R*)-(*E*)-1,3-Diphenyl-3-trimethylsilylpropene (**1**), which was prepared by an asymmetric Grignard cross-coupling in the presence of a chiral ferrocenylphosphine-palladium catalyst[4] and had $[\alpha]_D^{20}$ -43.3° (*c* 0.9, benzene) indicating 94% optical purity, was allowed to react with an excess of trifluoroacetic acid-*d* without solvent at ambient temperature for 20 h. Addition of aqueous sodium bicarbonate, extraction with ether, and a short silica gel column chromatography gave 77% yield of 1,3-diphenylpropene-*3-d* (**2**) (>96% deuterated) which consisted of *E* and *Z* isomers[5] in 85 : 15. The isomers were separated by MPLC (silica gel/hexane) and the *E* isomer **2**, showing a slightly negative optical rotation, was converted into known 2-phenylethanol-*2-d*[6] (**4**) by way of aldehyde **3**. Thus, ozonolysis of (*E*)-**2** followed by treatment with dimethyl sulfide gave

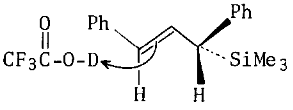


(*R*)-(*E*)-**1** (*R*)-(*E*)-**2** (*Z*)-**2**

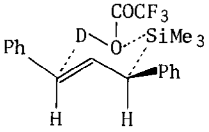


(*S*)-**3** (*S*)-**4**

a mixture of phenylethanal-*2-d* (3) and benzaldehyde. Since the aldehyde 3 is unstable and was expected to racemize readily, the aldehydes were not isolated but the mixture was subjected immediately to reduction by rhodium-catalyzed hydrosilylation.[7] After the usual work-up and distillation of a mixture of alcohols, isolation by preparative GLC (Silicone DC550) gave 2-phenylethanol-*2-d* (4) (98% deuterated) in 41% overall yield from (*E*)-2. The alcohol 4 showed $[\alpha]_D^{20}$ -1.47° (neat)[8] and is determined to be an *S* isomer of ∿96% enantiomeric purity.[6] Consequently, (*E*)-2 obtained in the deuterodesilylation of 1 must have *R* configuration of ∿96%. These results indicate that the deuterium cation attacked the double bond selectively *anti* with respect to the leaving trimethylsilyl group. The *anti* stereochemistry may be best illustrated by linear transition state A rather than cyclic one B.[9]



A



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4. T. Hayashi, M. Konishi, H. Ito, and M. Kumada, *J. Am. Chem. Soc.*, in press.
5. ^{1}H NMR (CCl_4/TMS): (*E*)-2, 3.50 (broad d, *J* = 5 Hz, 1H), 6.36 (ABX, *J* = 5 and 16 Hz, Δν = 9 Hz, 2H), 7.1-7.4 (m, 10H). (*Z*)-2, 3.59 (broad d, *J* = 7 Hz, 1H), 5.81 (double d, *J* = 7 and 11 Hz, 1H), 6.55 (double d, *J* = 11 and 2 Hz, 1H), 7.1-7.4 (m, 10H).
6. R. L. Elsenbaumer and H. S. Mosher, *J. Org. Chem.*, **44**, 600 (1979).
7. Homogeneous hydrosilylation with $RhCl(PPh_3)_3$ catalyst is the best method so far reported for the reduction of optically active aldehydes to alcohols without racemization. See, T. Hayashi, M. Konishi, M. Fukushima, T. Mise, M. Kagotani, M. Tajika, and M. Kumada, *J. Am. Chem. Soc.*, 104, 180 (1982).
8. The alcohol 4 (174 mg) was diluted to 1 ml with $PhCH_2CH_2OH$, showing α_D^{20} -0.255° (1 dm).
9. Protodestannylation of an indenyl-organotin compound has been reported to proceed with *anti* stereochemistry: A. N. Kashin, V. N. Bakunin, V. A. Khutoryanskii, I. P. Beletskaya, and O. A. Reutov, *J. Organometal. Chem.*, 171, 309 (1979).

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