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(E,E)-1-METHOXY-4-TRIMETHYLSILYL-1,3-BUTADIENE:
A DIENE FOR THE DIELS-ALDER SYNTHESIS OF METHOXY-SUBSTITUTED ALLYL SILANES

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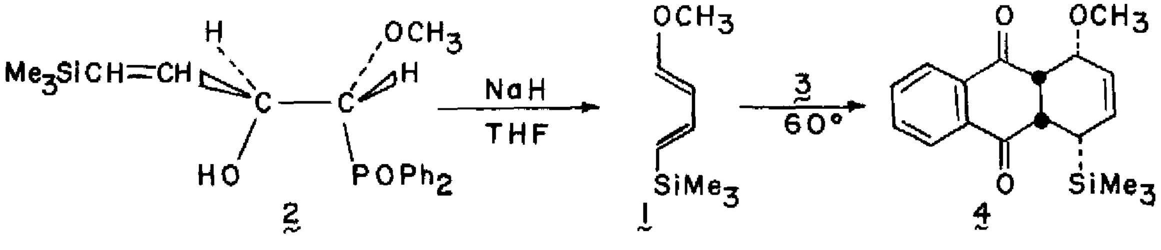
Summary: (E,E)-1-Methoxy 4-trimethylsilyl-1,3 butadiene (**1**) was prepared from the R,S and S,R adducts of methoxymethyldiphenylphosphine oxide with *trans*-trimethylsilylpropenal. The (E,E) diene (**1**) underwent facile Diels-Alder reaction with naphthoquinone and other dienophiles under mild conditions leading to *cis* 3-methoxy-6-trimethylsilylcyclohexene derivatives.

A recent interest in our laboratories has been the development of new heterosubstituted 1-trialkylsilyl 1,3-butadienes, and the investigation of their reactivities as Diels-Alder dienes.[1] The title diene was seen as valuable in the construction of anthracycline ring systems[2] which are often oxygenated. In addition the allylic trialkylsilyl functionality allows for a variety of synthetic transformations.[3]

After lithium diisopropyl amide (42mL, 2.0*M*) was added dropwise with stirring at 0° to methoxymethyldiphenylphosphine oxide[5] (17.4g) in THF (280mL), the solution was cooled to -78°, and *trans*-trimethylsilylpropenal[1,4] (6.08g) in THF (47mL) was added slowly. After allowing the mixture to warm to room temperature, saturated aqueous NH_4Cl and ether were added. The aqueous layer was extracted three times with ether. After the ether solution was dried and evaporated, the gum was chromatographed on 230-240 mesh silica gel (EtOAc), giving a mixture of diastereomers from which the RS,SR enantiomeric pair (2) crystallized out.[6] Fractional recrystallization gave 5.6g (32%) of the (RS,SR)-



1-diphenylphosphinoyl-1-methoxy-4-trimethylsilyl-3-buten-2-ol (**2**), mp 162-163°.[7] The other enantiomeric pair, which is RR,SS, was an oil (31%)

The adduct (**2**) (5.1g) in THF was treated with sodium hydride in THF-pentane overnight. After filtering through Celite, and washing with ether, the solvent was removed and the residue flash chromatographed (pentane). The pentane was distilled off leaving the pure diene (1), a liquid (2.0 g, 95%).[8]

Diene (**1**) reacted under mild conditions (60° for 50h) with naphthoquinone (3) giving *cis*-1-methoxy-4-trimethylsilyl-1,4,4a,9a-tetrahydro-anthraquinone(**4**) in 98% yield, mp 85-88°.[9,10] **1** also underwent Diels-Alder reaction with *N*-phenylmaleimide in 3h at 60° (100%), and with maleic anhydride in 12h at 60° (90%).

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REFERENCES AND NOTES:

1. J. J. Pegram and C. B. Anderson, *Tetrahedron Lett.*,**29**, 6719-20 (1988).
2. "Recent Aspects of Anthracyclinone Chemistry" Tetrahedron Symposia-In-Print No.17, T. Ross Kelly, Editor, *Tetrahedron*,**40**(22), 4537-4794 (1984).
3. G. Majetich, "Allylsilanes in Organic Synthesis" in *Organic Synthesis*, Vol. 1 pp 173-240, JAI Press, Inc. (1989); E.W. Colvin, *Silicon Reagents in Organic Synthesis*, Academic Press (1988), pp 25-30; E. W. Colvin, *Silicon in Organic Synthesis* (reprint), Krieger Publ. Co. (1985), pp 97-124.
4. T. K. Jones and S. E. Denmark, *Organic Syntheses*, A. S. Kende, Ed., Wiley, New York (1985) Vol. 64 pp 182-188.
5. C. Earnshaw, C. J. Wallis and S. Warren, *J. Chem. Soc. Perkin I*, 3099-3106 (1979).
6. This phenomenon was earlier noted in other systems, ref.5.
7. **2**-(RS,SR) ^{1}NMR ($CDCl_3$) 0.001 (s, 9H, $SiMe_3$), 3.22 (s, 3H, OCH_3), 3.74 (dd, 1H, J 8.65, 6.21 Hz, H-1), 4.40 (tdd, 1H, J 8.65, 3.54, 2.02 Hz, H-2), 4.46 (d, 1H, J 2.03 Hz, OH), 6.068 (s, 1H, H-4), 6.073 (d, 1H, J 3.5 Hz, H-3), 7.50 (m, 4H, Ar), 7.56 (m, 2H, Ar), 7.81 (m, 2H, Ar), 8.00 (m, 2H, Ar). Anal. Calcd. for $C_{20}H_{27}O_3PSi$, (SR,RS and SS,RR): C, 64.14; H, 7.27. Found: C, 63.80; H, 6.87.
8. **1** ^{1}H NMR ($CDCl_3$) 0.04 (s, 9H, $SiMe_3$), 3.57 (s, 3H, OCH_3), 5.56 (dd, 1H, J 12.52, 10.30 Hz, H-2), 5.59 (d, 1H, J 18.34 Hz, H-4), 6.38 (dd, 1H, J 18.34, 10.30 Hz, H-3), 6.65 (d, 1H, J 12.52 Hz, H-1). HRMS for $C_8H_{16}OSi$: Calcd 156.0970, found 156.0945.
9. **4** ^{1}H NMR ($CDCl_3$) 0.162 (s, 9H, $SiMe_3$), 0.172 (ddd, 1H, J 5.94, 2.94,2.02 Hz, H-4), 2.91 (s, 3H, OCH_3), 3.26 (dd, 1H, J 5.83, 4.19, Hz, H-9a), 3.45 (t, 1H, J 5.88, 5.83 Hz, H-4a), 3.98 (dd, 1H, J 4.58, 4.19 Hz, H-1), 5.92 (ddd, 1H, J 9.74, 4.58, 2.94 Hz, H-2), 6.01 (dd, 1H, J 9.74, 2.02 Hz, H-3), 7.66 (m, 2H, Ar), 7.92 (m, 1H, Ar), 8.05 (m, 1H, Ar). HRMS for $C_{18}H_{22}O_3Si$: calcd. 314.1338, found 314.1341.
10. More vigorous conditions cause isomerization to the vinyl silane. Very vigorous Diels-Alder conditions like 160° produces aromatization to 1-trimethylsilyl-9,10-anthraquinone.

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