

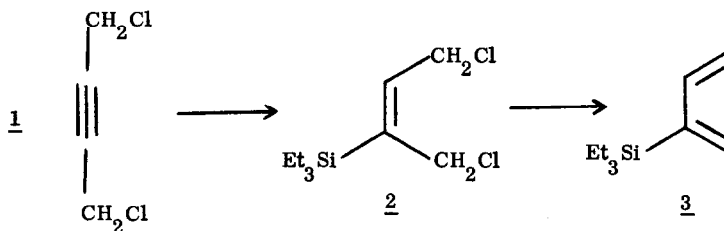
SYNTHESIS AND CYCLOADDITION REACTIONS OF 2-TRIETHYLSILYL-1,3-BUTADIENE

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Diels-Alder reactions of trans-1-trialkylsilylbutadienes with reactive dienophiles produce cyclohexenylsilanes which are of broad utility in the construction of functionalized six-membered rings.^{3,4} However the corresponding 2-silylated butadienes have not been characterized in the literature⁵ nor their reactivity investigated.⁶ We describe here a simple two-step synthesis of the title compound 3 and report its participation in a variety of representative cycloadditions.

Catalytic hydrosilylation of commercially available 1,4-dichloro-2-butyne 1 with triethylsilane (.01 mole % anhydrous H_2PtCl_6 , neat, 100°) produces 2 quantitatively. This vinylsilane may be distilled, bp 83° (.9 mm) [NMR δ ($CDCl_3$) 6.10 (t, 1H, $J=7$), 4.20 (d, 2H, $J=7$), 4.15 (s, 2H), 0.5-1.1 (m, 15H)] but the crude product is usually reduced directly with excess zinc dust in absolute ethanol (reflux, 1-2h) to afford diene 3 directly as a colorless liquid, bp 30-33° (.7 mm), in 55-65% overall yield from 1 [NMR δ ($CDCl_3$) 6.45 (dd, 1H, $J=10, 18$ Hz), 5.82 (d, 1H, $J=3$ Hz), 5.39 (d, 1H, $J=3$ Hz), 5.23 (dd, 1H, $J=1, 18$ Hz), 4.98 (dd, 1H, $J=1, 10$ Hz); IR λ_{max} (film) 6.20 μ ; UV λ_{max} (hexane) 224 nm ($\epsilon=10,200$); mass spectrum m/e 168 (M^+), 111 (base)].

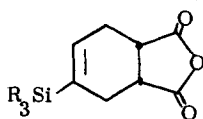
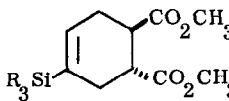
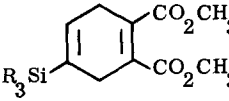
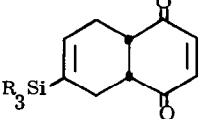
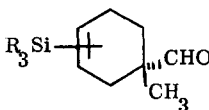
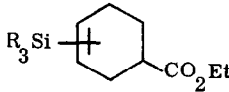


Cycloadditions of 3 (1 equiv) with common dienophiles are summarized in the Table and indicate that this diene is considerably more reactive than its 1-substituted isomer. Pure adducts with sym-

metrical dienophiles are readily obtainable in which the alkenyltriethylsilane group masks numerous latent functional groups.⁷ Fleming and Percival have noted that the silyl substituents in 1-trimethylsilylbutadiene and 2-trimethylsilylcyclopentadiene exhibit only weak directing effects in reactions of those diene systems with unsymmetrical olefins. Diene 3 behaves similarly although the 3.3:1 ratio of para:meta-substituted isomers with ethyl acrylate becomes 7.3:1 in the presence of 20 mole %

$\text{BF}_3 \cdot \text{Et}_2\text{O}$ (90% yield).

TABLE

Dienophile	Conditions	Product (Yield) ^a	Physical Data
maleic anhydride	rt, neat, 3h	 (75%)	NMR δ 6.30 (m, 1H, vinyl); IR 5.44, 5.64 μ diacid mp 139.8-140.6° ^b
dimethyl fumarate	1:1 O_2 : CHCl_3 reflux, 10h		NMR 5.95 (m, 1H), 3.69 (s, 6H) IR 5.79 μ ; mp 69-70° ^b (81%)
dimethyl acetylenedicarboxylate	O_2 , reflux 10h		(87%) oil; NMR 6.00 (s, 1H), 3.70, 3.69 (2s, 3H each), 2.98 (s, 4H); IR 5.83 μ
benzoquinone	O_2 , reflux 6h		(85%) oil; NMR 6.65 (s, 2H), 5.93 (m, 1H), 3.1-3.25 (m, 2H); IR 5.95 μ
methacrolein	CHCl_3 , reflux 18h		(69%) oily mixture: HPLC (μ -porasil) shows two overlapping regioisomers. NMR 9.46 (s, 1H), 5.95 (m, 1H).
ethyl acrylate	O_2 , reflux 6h		(77%) oily mixture: 3.3:1 <u>p</u> : <u>m</u> by HPLC NMR 6.00 (m, 1H), 4.15 (q, 2H), 1.39 (t, 3H); IR 5.77 μ

(a) Unless otherwise noted, reported yields are for crystalline or chromatographically homogeneous substances. (b) Satisfactory elemental analysis was obtained for this compound.

References and Footnotes

- (1) NSF Predoctoral Fellow (2) Fellow of the A. P. Sloan Foundation, 1978-1980
- (3) S. I. Sadykh-Zade, A. D. Petrov, *Zhur. obshechi Khim.*, **28**, 1591 (1958)
- (4) I. Fleming, A. Percival, *J. Chem. Soc. Chem. Commun.*, 178 (1978); 681 (1976)
- (5) A mixture of 1 and 2-(butadienyl)diethylmethylsilanes has been prepared from chloroprene but not characterized: L. L. Shchukovskaya, A. D. Petrov, A. N. Lazarev, *Proc. Acad. Sci. USSR, Chem. Sect. (Eng.)* **135**, 1395 (1960).
- (6) For 3-trimethylsilyl-1,5,5-trimethylcyclohexa-1,3-diene see A. R. Chamberlin, J. E. Stemke, F. T. Bond, *J. Org. Chem.*, **43**, 147 (1978).
- (7) See P. F. Hudrlik in "New Applications of Organometallic Reagents in Organic Synthesis, Vol I," ed. D. Seyferth, Elsevier, Amsterdam, 1976, p. 127.
- (8) This research was financially assisted by Grant CH-58 from the American Cancer Society. We wish to thank Dr. R. A. Ruden for helpful discussions about the synthesis of 3.

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