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ALTERNATIVE SYNTHESES AND DIELS-ALDER REACTIONS OF 2,3-Bis(TRIMETHYLSILYL)BUTA-1,3-DIENE

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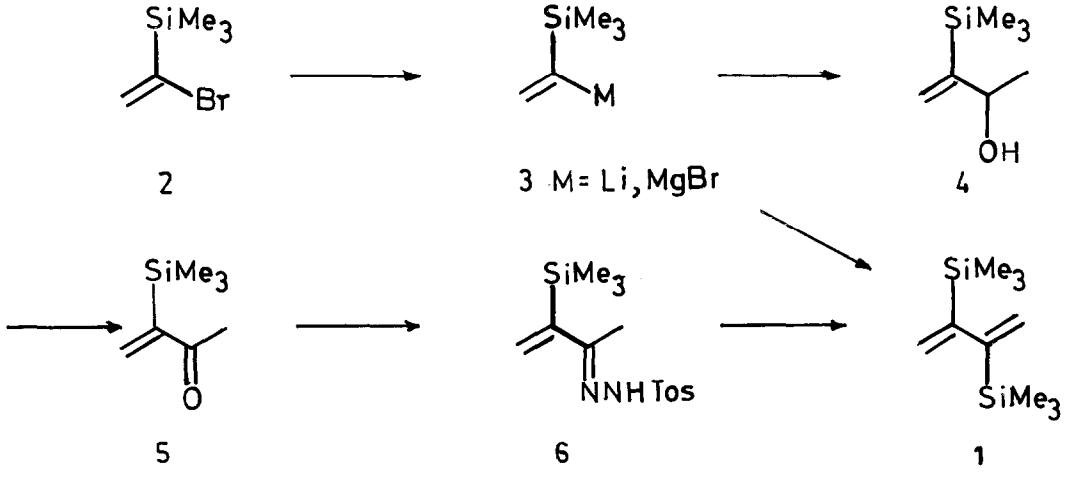
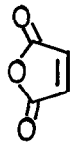
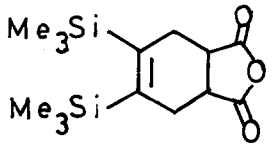
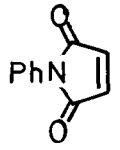
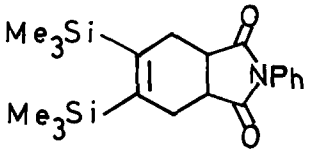
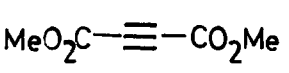
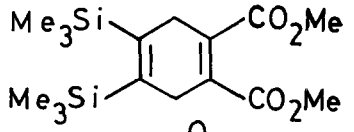
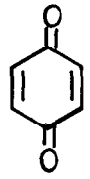
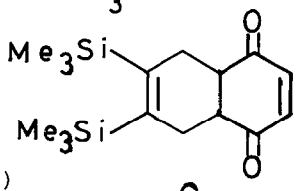
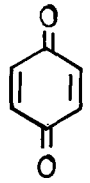
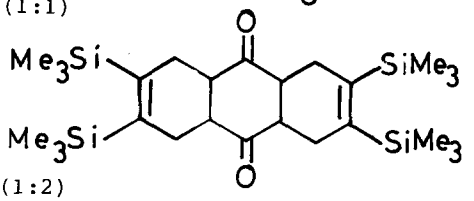
Summary: The title compound has been prepared by two routes and some Diels-Alder reactions of it investigated.

Although 2,3-bis(trimethylsilyl)buta-1,3-diene (1) has been prepared,[1] none of its chemistry has been described. We required 1 as a synthetic intermediate and now describe its preparation by two new routes and report some cycloaddition reactions of it. Treatment of α-bromovinyltrimethylsilane (2) with Mg gave the Grignard 3 [2] which on treatment with ethanal gave 4.[3,4] Oxidation with CrO_3 in H_2SO_4 gave the eneone 5 [3,4] which with tosylhydrazine in MeOH gave the tosylhydrazone 6, mp 127-129 °C.[4] Treatment of 6 in tetramethylenediamine with n-BuLi at -78 °C followed by warming to room temperature, cooling to -78 °C and addition of Me_3SiCl [5] gave 1 (32% from 2); bp 35 °C/0.5 mm Hg); ^{1}H NMR δ 0.0 (s, 18H), 5.41, 5.36 (AB q, 4H, J = 3.4 Hz); ^{13}C NMR δ -0.8, 123.7, 155.9; IR 3075, 2960, 2880, 1610, 880, 850 cm^{-1}; UV 223 (ε 13,000), 237(sh), 249(sh) nm.[1] The second route to 1 involved treatment of 2 with t-BuLi at -78 °C, warming to -23 °C, cooling to -78 °C, addition of Cu_2I_2, stirring, warming to -23 °C, and addition of $CuCl_2$.[6] A 52% yield of 1 was obtained by this method, spectrally identical with that obtained by the first route.

The diene 1 underwent Diels-Alder reactions with a number of dienophiles in benzene at 60 °C in the presence of quinol.[7] The results are shown in the Table.



Table

Dienophile	Adduct[4]	Isolated Yield %, physical properties[8]
		80, mp 116-118 °C; 1800, 1745 cm^{-1}; δ 3.3-3.0 (m, 2H), 1.7 (m, 4H).
		85, mp 140-141 °C; 1650, 1340 cm^{-1}; δ 2.4 (m, 2H), 1.8 (m, 4H).
		87, 1605 cm^{-1}; δ 3.65 (s, 6H), 2.95 (s, 4H).
	 (1:1)	75, 1670 cm^{-1}; δ 6.75 (s, 2H), 3.25-2.95 (m, 2H), 1.75 (m, 4H).
	 (1:2)	80, mp 176-177 °C; 1705 cm^{-1}; δ 2.5-2.3 (m, 2H), 1.0 (m, 4H).

References and Notes

1. Bock, H.; Seidl, H. *J. Am. Chem. Soc.* 1968, *90*, 5694; Reich, H.J.; Yelm, K.E.; Reich, I.L. *J. Org. Chem.* 1984, *49*, 3440.

2. Normant, H. *Bull. Soc. Chim. France*, 1957, 728; Ottolenghi, A.; Fridkin, M.; Zilkha, A. *Can. J. Chem.* 1963, *41*, 2977.

3. Stork, G.; Ganem, B. *J. Am. Chem. Soc.* 1973, *95*, 6152.

4. Satisfactory ms and/or analytical and consistent spectral data were obtained for this/these compound/s.

5. Chan, T.H.; Baldassarre, A.; Massuda, D. *Synthesis*, 1976, 801; Taylor, R.T.; Degenhardt, C.R.; Melega, W.P.; Paquette, L.A. *Tetrahedron Lett.* 1977, 159.

6. Trost, B.M.; Shimizu, M. *J. Am. Chem. Soc.* 1982, *104*, 4299.

7. For Diels-Alder reactions of 2-triethylsilylbuta-1,3-diene see, Batt, D.G.; Ganem, B. *Tetrahedron Lett.* 1978, 3323.

8. Me_3Si group protons are all at *ca.* δ 0.0 in ^1H NMR spectra.

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