Tetrahedron Letters,Vol.29,No.15,pp 1833-1836,1988
Printed in Great Britain

0040-4039/88 $3.00 + .00
Pergamon Press plc

(Z,Z)-2,3-BIS(TRIMETHYLSILYL)-1,4-DIBROMO- AND 2,3-BIS(TRIMETHYLSILYL)-1,1,4,4-TETRABROMOBUTA-1,3-DIENES. SYNTHESIS AND DIELS-ALDER REACTIONS.

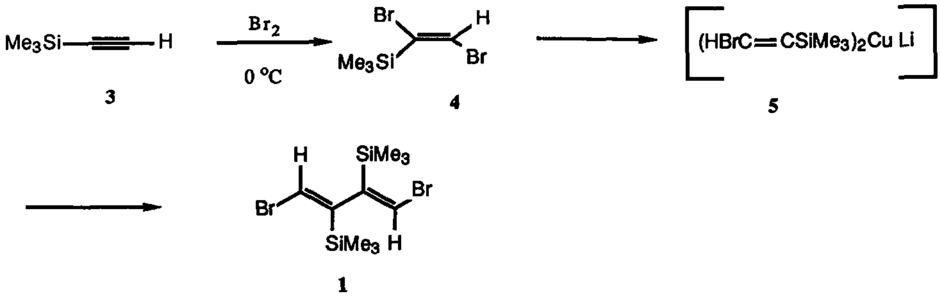
Peter J. Garratt and Andrew Tsotinis

Department of Chemistry, University College London, 20 Gordon Street,
London WC1H 0AJ.

Summary: The two title compounds (1,2) have been prepared and some Diels-Alder reactions investigated.

We have recently reported on the Diels-Alder reactions of 2,3-bis(trimethylsilyl)buta-1,3-diene[1] and this success led us to investigate the preparation of more highly substituted bis(trimethylsilyl)buta-1,3-dienes in order to explore their reactivity. We now report the synthesis of 1 and 2 and show that these highly congested dienes still readily undergo cycloaddition.

Bromine addition to 3 at 0 °C gave 4.[2,3] Coupling of 4 to give 1, presumably via 5, could be effected with CuI, t-BuLi at -112 °C, followed by $CuCl_2$ at -83 °C in 35% yield.[4] A superior method, however, was found to be a modification of that described by Whitesides *et al.*[5] t-Butyllithium (2.0 M, 30 ml, 60 mmol) was added to a stirred solution of 4 (7.74 g, 30 mmol) in Trapp solvent (30 ml)[6] at -112 °C. The mixture was stirred for 30 min and then allowed to warm to -83 °C. A solution of $(ICuPBu_3)_4$[7] (5.89 g, 3.75 mmol) in Trapp solvent (20 ml) was added dropwise at -83 °C and stirring continued for 30 min. Dioxygen was then passed as a fine stream until no more precipitate formed and the mixture was stirred for a further 15 min at -83 °C and allowed to warm to room temperature. After work-up, bulb-to-bulb distillation gave 1 (6.62 g, 18.6 mmol, 62%, bp 47-49 °C, 0.01 mm Hg).[8,9]



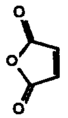
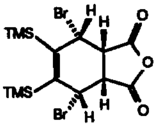
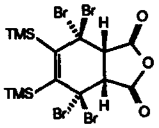
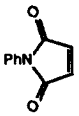
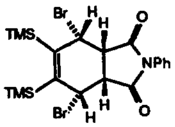
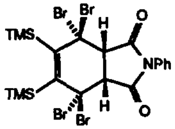
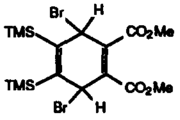
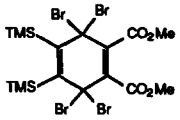
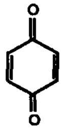
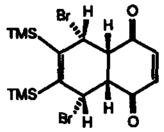
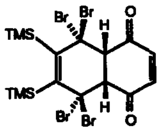
The bromoalkene 6, prepared from bis(trimethylsilyl)acetylene by a two step procedure,[2,10,11] was coupled in a similar manner to give 2 (18%, 48%),[8.9] the second method again being superior.

It is essential to control the temperature strictly in both these coupling reactions, dehalogenation occurring at higher temperatures.[12] Dienes 1 and 2 polymerise rapidly at room temperature despite their steric bulk but, by heating equimolar amounts of the diene and dienophile to reflux in toluene containing hydroquinone, Diels-Alder adducts can be obtained in good to excellent yield (Table).[13] Both the dienes were also heated in toluene with 2 equivalents of benzoquinone but no di-adducts were obtained. This is in contrast to the behaviour of 2,3-bis(trimethylsilyl)buta-1,3-diene which gave a di-adduct with excess benzoquinone.[1]

The adducts shown in the Table are potential precursors of highly substituted aromatic compounds having a variety of functional groups.

Acknowledgement A.T. thanks the Department of Chemistry, UCL for the award of a Franz Sondheimer Bursary.

Table

Dieneophile	Diene	Adduct[8,13]	Isolated yield %, physical properties.[15]
 (7)	1		59, mp 148-150 °C; ν_{max} 1800, 1740 cm^{-1}; δ, 4.10(d,2H,J = 9.5 Hz), 3.20(d,2H,J = 9.5 Hz).
7	2		55, mp 164-166 °C; ν_{max} 1805, 1725 cm^{-1}; δ, 3.80(s,2H).
 (8)	1		65, mp 170-172 °C; ν_{max} 1670, 1340 cm^{-1}; δ, 7.41(s,5H), 4.05(d,2H,J = 10.5 Hz), 2.55(d,2H,J = 10.5 Hz).
8	2		62, mp 185-186 °C; ν_{max} 1675, 1335 cm^{-1}; δ, 7.42(s,5H), 3.1(s,2H).
DMAD	1		82, ν_{max} 1762, 1680 cm^{-1}; δ, 4.15(s,2H), 3.95(s,6H).
DMAD	2		80, ν_{max} 1760, 1690 cm^{-1}; δ, 3.90(s,6H).
 (9)	1		80, ν_{max} 1670 cm^{-1}; δ, 6.80(s,2H), 4.10(d,2H,J = 10.0 Hz), 3.05(d,2H,J = 10.0 Hz).
9	2		78, ν_{max} 1680 cm^{-1}; δ, 6.60(s,2H), 3.20(s,2H).

References and Notes

1. Garratt, P.J.; Tsotinis, A. *Tetrahedron Letters* 1986, **27**, 2761.
2. Shostakovskii, M.F.; Komarov, N.V.; Yarosh, O.G. *Izv. Akad. Nauk. SSSR, Ser. Khim.* 1967, **3**, 693.
3. The Russian workers did not suggest a stereochemistry for **4** but we assumed that the addition was *anti* and this is substantiated by the stereochemistry of the Diels-Alder adducts.
4. Trost, B.M.; Shimizu, M. *J. Am. Chem. Soc.* 1982, **104**, 4299.
5. Whitesides, G.M.; Filippo, J.S.; Casey, C.P.; Paneck, E.J. *J. Am. Chem. Soc.* 1967, **89**, 5302.
6. Köbrich, G.; Trapp, H. *Chem. Ber.* 1966, **99**, 670.
7. Kauffman, G.B.; Teter, L.A. *Inorg. Synth.* 1963, **7**, 9.
8. Satisfactory analytical and mass spectral data were obtained for all new compounds.
9. **1**, ^{1}H NMR, δ, -0.25(s, 18H), 6.16(s, 2H); ^{13}C NMR, δ, -0.85, 124.8, 158.2; UV, λ_{max} (cyclohexane) 235 nm (log ε 4.15), 240(sh), 255(sh); IR, ν_{max} (film) 3025, 2890, 2850, 1745, 840 cm^{-1}.
   2, ^{1}H NMR, δ, -0.20(s); ^{13}C NMR, δ, -0.85, 124.95, 165.2; UV, λ_{max} (cyclohexane) 242 nm (log ε 4.23), 250(sh); IR, ν_{max} (film) 3010, 2985, 1565, 835 cm^{-1}.
10. Buchert, H.; Zeil, W. *Spectrochimica Acta,* 1962, **18**, 1043; Miller, J.A.; Zweifel, G. *Synthesis,* 1983, 128.
11. Seyferth, D.; Hanson, E.M.; Prokai, B.; Cross, R.J. *J. Organometal. Chem.* 1970, **24**, 33.
12. Köbrich, G. *Angew. Chem. Int. Ed. Engl.* 1965, **4**, 49.
13. The stereochemistry shown for the adducts is based on the ^{1}H NMR spectral coupling constants, which indicate that the bridge and cyclohexene protons have the cis configuration.[14]
14. Rao, B.D.N.; Baldeschwieler, J.D. *J. Mol. Spectr.* 1963, **11**, 440.
15. Me$_3$Si group protons are all at ca. δ 0.0 in the ^{1}H NMR spectra.

(Received in UK 20 February 1988)