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A Convenient Synthesis of Ethano-Bridged Cyclic Diynes – Preparation of 1,1,2,2-Tetramethyl-1,2-disilacycloocta-3,7-diyne.

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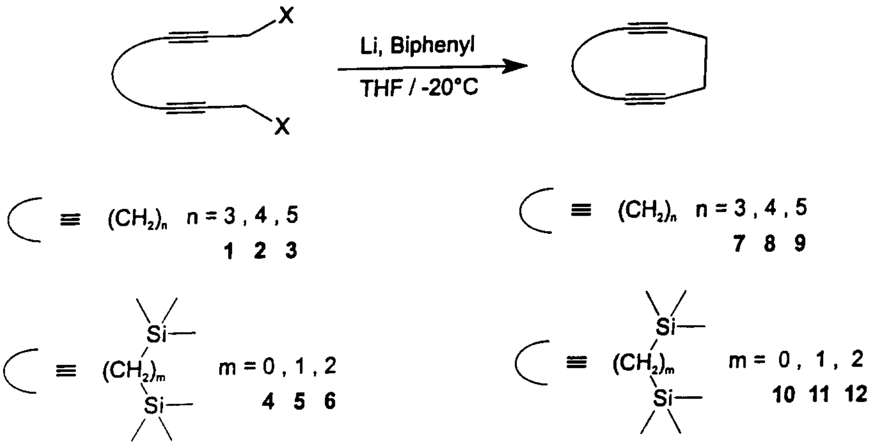
Abstract: Cyclic diynes bridged by an ethano moiety on one side are formed in the reaction of α,ω-dihalogen precursors with lithium in presence of biphenyl.

Cyclic diynes of medium ring size (C_8-C_{12}) show a number of features which are of considerable interest[1]. The two linear C-C≡C-C moieties induce a sizeable ring-strain into the ring system, there is a substantial interaction between the triple bonds and the triple bonds in close proximity are promising ligands for transition metals. To study these properties efficient procedures for the syntheses of medium sized rings are desirable. The usual methods for their syntheses were condensation methods and – especially for the more strained systems – elimination procedures[1].

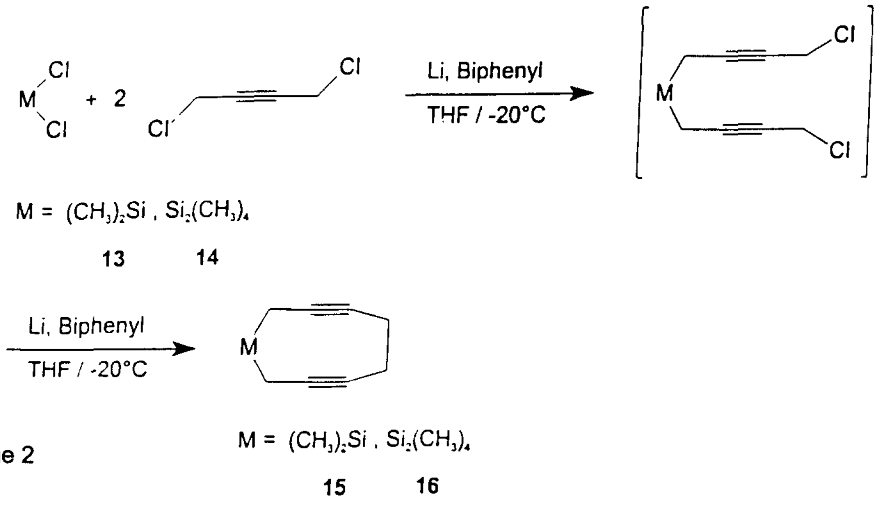
In connection with our interest in the thermolysis of cyclic diynes[2] we needed an efficient way for preparing rings with an ethano bridge between the triple bonds. Species of interest were cyclonona-1,5-diyne (**7**)[3], cyclodeca-1,5-diyne (**8**)[3], cycloundeca-1,5-diyne (**9**)[3], 1,1,2,2-tetramethyl-1,2-disilacycloocta-3,7-diyne (**10**), 1,1,3,3-tetramethyl-1,3-disilacyclonona-4,8-diyne (**11**), 1,1,4,4-tetramethyl-1,4-disilacyclodeca-5,9-diyne (**12**), 1,1-dimethyl-1-silacyclonona-3,7-diyne (**15**) and 1,1,2,2-tetramethyl-1,2-disilacyclodeca-4,8-diyne (**16**). In this paper we report a convenient procedure for the synthesis of these ethano–bridged cyclic diynes.



Scheme 1

Starting point of our syntheses were the α,ω-dibromides **1-6** (Scheme 1) which can be prepared following literature procedures. We prepared **1-3** from the corresponding diols by treating them with PBr_3[4]. The diols were synthesized from the bislithium salts of α,ω-diynes and paraformaldehyde[5]. To obtain **4-6** we made to react the corresponding α,ω-dichlorides of the α,ω-bis(dimethylsila)alkanes with the lithium salt of propargyl chloride. The bromides **4-6** were furnished by a Finkelstein reaction.

The ring closure is effected by the reaction of **1-6** with lithium in the presence of biphenyl[6] under an argon atmosphere. Thus, 5 mmol of the starting material **1-6** in 15 ml of dry tetrahydrofuran



Scheme 2

(THF) were added at –20°C to a solution of 0.5 mmol of biphenyl and a suspension of 50 mmol of lithium in 70 ml of dry THF. After stirring for 5–20 min at -20 °C and filtering off the lithium, the solvent was removed and the residue purified by column chromatography. The yields of **7-12** vary between 10% and 20%.[9]

Similarly reaction of the dichlorides **13** and **14** with two equivalents of 1,4-dichloro-2-butyne under the same conditions as described above furnished the cyclic diynes **15** and **16** in yields of 10-15%.

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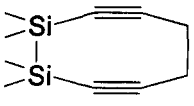

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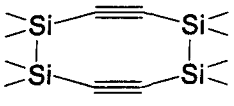

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The properties of **7-9** have been described in the literature[3]. The synthesis of **10** deserves special interest because it fills the gap between cycloocta-1,5-diyne (**17**)[7] and 1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilaocta-3,6-diyne (**18**)[8]. Furthermore the synthesis of **10** demonstrates that the new procedure is effective also for systems with a considerable strain energy.

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References and Notes

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9. Yields (%) and Selected Spectroscopic Data of **7-12**, **15** and **16**.

   Yields: **7**^{3}: 15 %; **8**^{3}: 12 % **9**^{3}: 18 %.

   10: 10 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.24 (s, 12 H), 2.58 (s, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 116.47 (s), 93.20 (s), 19.69 (t), –2.95 (q); HRMS (EI): *m/z* calcd. 192.0791, found 192.0832.

   11: 17 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.01 (s, 2 H), 0.14 (s, 12 H), 2.42 (s, 4 H; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 109.37 (s), 91.25 (s), 18.94 (t), 6.84 (t), 0.71 (q); HRMS (EI): *m/z* calcd. 206.0947, found 206.0985.

   12: 20 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.10 (s, 12 H), 0.71 (s, 4 H), 2.39 (s, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 106.00 (s), 88.06 (s), 19.48 (t), 7.98 (t), –2.67 (q); HRMS (EI): *m/z* calcd. 220.1104, found 220.1094.

   15: 15 %; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.18 (s, 6 H), 1.61 (m, 4 H), 2.30 (m, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 86.26 (s), 81.06 (s), 19.81 (t), 7.32 (t), –2.94 (q); HRMS (EI): *m/z* calcd. 162.0865, found 162.0859.

   16: 10 %; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.19 (s, 12 H), 1.51 (m 4 H), 2.29 (m, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 81.38 (s), 78.65 (s), 19.43 (t), 5.72 (t), –3.42 (q); HRMS (EI): *m/z* calcd. 220.1104, found 220.1104.

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