1,3-Bis(trimethylsilyl)propyne and Alkyltrimethylsilylalkynes as Efficient Co-oligomerisation Partners in Cobalt-catalysed Alkyne Cyclisations

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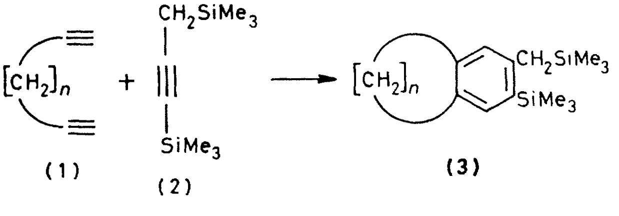
Summary αω-Diynes may be efficiently cocyclised with 1,3-bis(trimethylsilyl)propyne and several substituted trimethylsilylalkynes in the presence of $CpCo(CO)_2$ catalyst to give annelated benzenes amenable to further functionalization.

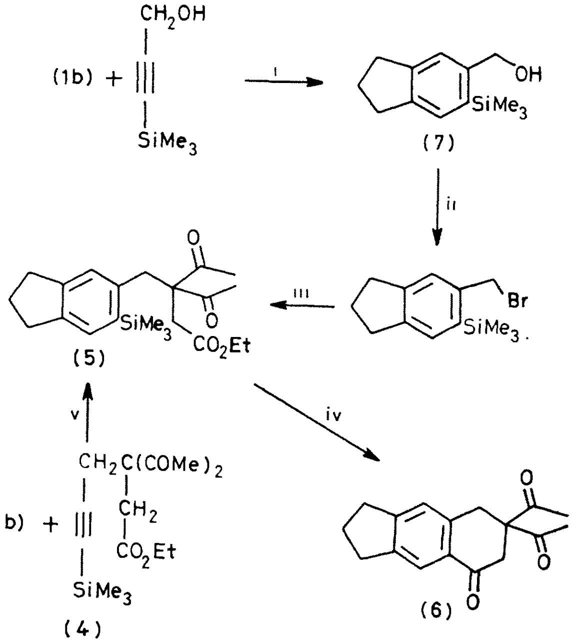
We have recently developed methodology *en route* to molecules of synthetic and theoretical interest relying on cobalt-catalysed chemicoselective cyclisations of αω-diynes with bis(trimethylsilyl)ethyne.[1] The latter appeared to be unique in its capability to cocyclise but not autocyclise, presumably owing to steric constraints.[2] We now report the application of several new cocyclisation partners effective in these reactions, significantly expanding the scope of the method.

Addition of a solution of octa-1,7-diyne (**1c**) in neat 1,3-bis(trimethylsilyl)propyne (**2**) to neat (**2**) containing $CpCo(CO)_2$ (Cp = cyclopentadienyl) [5 mol% based on (**1c**)] under N_2 using syringe pump techniques[1] over a period of 72 h at 140 °C gave 92% of the annelated benzene (**3c**).† The diynes (**1a**) and (**1b**) similarly furnished (**3a**, 64%) and (**3b**, 89%), respectively. The excess of (**2**) is readily recovered by vacuum transfer. Displacement of the aromatic silyl group in the products occurs quantitatively with electrophiles such as CF_3CO_2H and Br_2. On the other hand, selective and quantitative benzylic desilylation occurs with fluoride (tetra-n-butylammonium fluoride; tetrahydrofuran; 25%) to give *o*-methyl(trimethylsilyl)benzene derivatives. This provides an efficient route to otherwise inaccessible methylated aromatics. An alternative using the same methodology, the cobalt-catalysed cyclisation of 1-trimethylsilylpropyne, is less effective, owing to the decreased steric requirements of the monoyne leading to autocyclisation products. Thus, this monoyne (neat) reacts with (**1c**) to give a moderate yield (54%) of 2-trimethylsilyl-3-methyltetralin. The catalyst in this reaction is regioselectively converted into catalytically inert 1,2-bis(trimethylsilyl)-3,4-dimethylcyclobutadiene(cyclopentadienyl) cobalt (5%). On the other hand, increasing the length of the alkyl chain on the monoyne provides improved efficiency. For example, (**1c**) and 1-trimethylsilylhexyne furnished 2-trimethylsilyl-3-n-butyltetralin (78%) and 1,2-bis(trimethylsilyl)-3,4-di-n-butylcyclobutadiene(cyclopentadienyl) cobalt (4%). However, 4-trimethylsilylbut-3-yn-2-one[3] functioned poorly as a direct precursor of 2-trimethylsilyl-3-acetyltetralin (7%), possibly a consequence of increasingly rapid catalyst depletion to (in this case) both possible cyclobutadiene isomers (4%).



a; *n* = 2
b; *n* = 3
c; *n* = 4

Scheme 1. Co-oligomerisations of αω-diynes with the alkyne (**2**).



Scheme 2. An approach to linear tricyclic annelation; i, $CpCo(CO)_2$, 10 mol%, *o*-xylene, 144 °C, 150 h, 3 equiv. of monoyne; ii, PBr_3, C_6H_6, 80 °C, 2 h; iii, $Ac_2CH(CH_2CO_2Et)$, NaH, $HCONMe_2$, 0 °C, 2 h; iv, $BF_3\cdot Et_3O$, 80 °C, 0·5 h; v, $CpCo(CO)_2$, 5 mol%, *o*-xylene, 144 °C, 72 h, 3 equiv. of monoyne.

A novel approach to linear tricyclic annelation is outlined in Scheme 2. The silylated alkyne (**4**), prepared by treatment of 1-trimethylsilyl-3-bromopropyne[4] with ethyl 3-acetyl-4-oxopentanoate[5] (NaH; *NN*-dimethylformamide; 0 °C; 2 h; 93·4%) may be cocyclised (70%) to yield (**5**), which then undergoes a silicon-controlled regioselective intramolecular Friedel–Crafts reaction to (**6**) in good yield. An alternative, less convergent, and lower-yielding route proceeds through 2-trimethylsilyl-3-hydroxymethylindane (**7**) as shown in Scheme 2. Application of this methodology to the construction of natural products is under investigation.

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† All new compounds have been fully characterised and microanalysed.

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