A Cobalt-catalysed Biphenylene Synthesis

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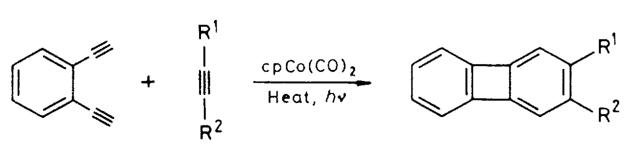
o-Diethynylbenzene is catalytically co-cyclised with alkynes in the presence of dicarbonyl(cyclopentadienyl)-cobalt to provide a versatile synthesis of the biphenylene nucleus.

Owing to its unusual electronic make-up, biphenylene is the most studied cyclobutadiene,[1,2] both theoretically and experimentally, but methods for its synthesis lack flexibility and/or practicality, particularly with respect to the preparation of unsymmetrical systems.[3] We now report a one-step approach to 2,3-disubstituted biphenylenes, in which the strained and the substituted ring are generated simultaneously.

The interaction of terminally substituted *o*-diethynylbenzenes with metal carbonyl derivatives usually results in complex mixtures,[4] primarily of organometallics. However, the parent compound (**1**)[5] catalytically co-cyclises with monoalkynes (**2**) in the presence of [cpCo(CO)$_2$] (cp = cyclopentadienyl) to furnish 2,3-disubstituted biphenylenes (**3**) in moderate to excellent yields (Table 1). Reaction conditions were as reported previously for similar catalytic cyclisations.[6] The success of this transformation is remarkable considering the thermal instability of (**1**), the finding that its structural and electronic analogue, η^4-1,2-diethynylcyclobutadienyl(η^5-cyclopentadienyl)cobalt does not lead to analogous cyclisation products,[7] and the strain-related and electronic destabilisation of the biphenylene nucleus.[1,2] Yields were not optimised except for the preparation of 2,3-bis(trimethylsilyl)biphenylene (entry 1) from the cocyclisation of (**1**) with neat bis(trimethylsilyl)ethyne,[8] where the yield is essentially quantitative.



(1) (2) (3)

The other reactions were carried out with near equimolar quantities [(**1**):(**2**) = 1:1.05] of starting materials. Compound (**3**; $R^1 = R^2 = SiMe_3$) should prove to be a useful substrate in sequential electrophilic substitutions, as observed for other *o*-bis-silylated arenes prepared by this method.[6,8,9] Protodesilylation (CF_3CO_2H, CH_2Cl_2, 25 °C, 1 h) gave biphenylene (72%). Similarly, (**3**; $R^1 = SiMe_3$, $R^2 = C_5H_{11}$) was converted into (**3**; $R^1 = H$, $R^2 = C_5H_{11}$) under the same conditions. All biphenylenes exhibited characteristic electronic and n.m.r. spectra,[1,2] the latter reflecting the paratropicity of the four-membered ring.[10] The spectral data for (**3**; $R^1 = R^2 = SiMe_3$) are illustrative: ^1H n.m.r. ($CDCl_3$) δ 6.94 (s, 2H), 6.71 (AA′m, 2H), 6.64 (BB′m, 2H), and 0.31 (s, 18H); ^{13}C n.m.r. ($CDCl_3$) δ 152.46, 150.47, 147.69, 128.09 122.67, 117.62, and 2.14 p.p.m.; u.v. λ_{max} (log ϵ, 1-methylheptane) 363 (3.838), 347 (3.738), 343 (3.703), 334 (3.418), 330 (3.418), 257 (4.971), 248 (4.751), and 205 nm (4.310).

The results reported here should lead to an expansion of the chemistry of biphenylene by providing access to novel derivatives of potential theoretical and synthetic interest.

Table 1. Biphenylenes (**3**) from (**1**) and (**2**).

Entry	R^1	R^2	% Yield of (**3**)[a]
1	$SiMe_3$	$SiMe_3$	96[g]
2	$SiMe_3$	C_5H_{11}	58[b]
3	H	C_5H_{11}	41[c]
4	Bu^n	Bu^n	44[b]
5	H	Ph	25[d]
6	Ph	Ph	35[e]
7	CO_2Me	CO_2Me	30[f]

[a] All new compounds gave satisfactory analytical and/or high resolution mass spectral data. [b] Pale yellow oil. [c] M.p. 34 °C. [d] M.p. 127—128 °C. [e] M.p. 120—121 °C. [f] M.p. 80—81 °C. [g] M.p. 64.5—65 °C.

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