[2.2.2.2.2.2]Metacyclophane-1,9,17,25,33,41-hexayne from *m*-Iodophenylacetylene by Sixfold Stephens-Castro Coupling

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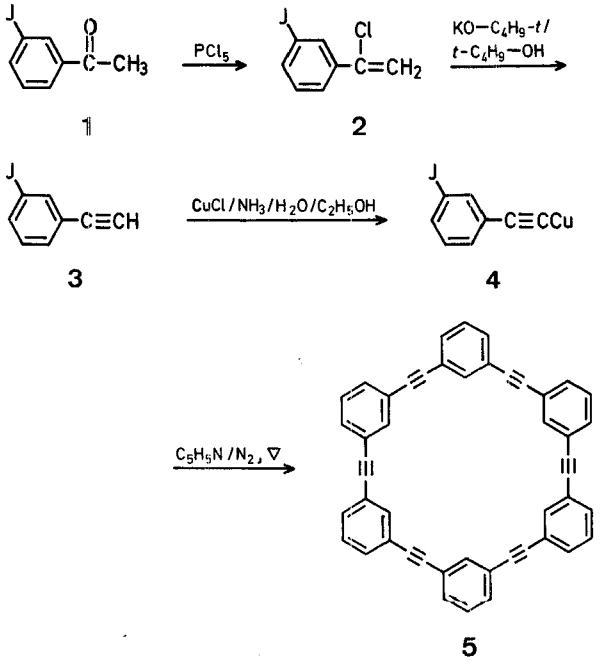
Stephens-Castro coupling of copper(I) arylacetylides with iodoarenes[1] and iodoalkenes[2] has been successfully applied to the synthesis of macrocyclic di- and triynes of the benzo[12]annulene series from bifunctional components[3]. Accordingly, Stephens-Castro coupling of copper(I) *m*-iodophenylacetylide (**4**) might be expected to result in the formation of [2.2.2.2.2.2]metacyclophane-1,9,17,25,33,41-hexayne (**5**) by six successive coupling steps.

m-Iodoacetophenone (**1**)[4] was converted with phosphorus pentachloride into α-chloro-*m*-iodostyrene (**2**) from which, by elimination with potassium *t*-butoxide in *t*-butyl alcohol, *m*-iodophenylacetylene (**3**) was obtained. Treatment of **3** with copper(I) chloride in aqueous ammonia/ethanol yielded the acetylide **4** which in boiling pyridine under nitrogen was coupled to produce **5**. The small yield of 4.6% is not surprising considering the fact that the formation of the 30-membered macrocyclic system requires six coupling steps the last one being an intramolecular cyclisation competing with intermolecular coupling to linear products.



Compound **5** forms colourless crystals which include—obviously due to the large inside holes of the molecules—solvent which is difficult to remove completely. The spectroscopic data for **5** show that macrocyclic π-conjugation does not play any important role in the structure of **5**. Catalytic hydrogenation of **5** with Pd/C in xylene at 20° resulted in the addition of 12 equivalents of hydrogen to give [2.2.2.2.2.2]metacyclophane[5].

m-Iodophenylacetylene (3):

m-Iodoacetophenone (**1**)[4] (100 g, 0.405 mol) and phosphorus pentachloride (85 g, 0.405 mol) were heated for 1 h at 70°. On distillation, α-chloro-*m*-iodostyrene (**2**) was obtained; yield: 85 g (80%); b.p. 96–110°/1 torr; it was used without further purification for the following reaction.

α-Chloro-*m*-iodostyrene (129 g, 0.487 mol) was added slowly to potassium *t*-butoxide (0.845 mol, from 33 g potassium) in boiling *t*-butyl alcohol (800 ml). After 3 h heating under reflux the solution was diluted with water and extracted with ether. By distillation, *m*-iodophenylacetylene was obtained; yield: 56 g (50%); b.p. 63 to 63.5°/1 torr.

C_8H_5J	calc.	C 42.14	H 2.21	J 55.65
(228.0)	found	42.10	2.19	55.67

[2.2.2.2.2.2]Metacyclophane-1,9,17,25,33,41-hexayne (5):

A solution of *m*-iodophenylacetylene (104 g, 0.456 mol) in ethanol (1000 ml) was added under stirring to copper(I) chloride (45.2 g, 0.456 mol) in aqueous ammonia. The precipitate of copper acetylide was separated by filtration, washed successively with water, ethanol and ether, and dried in a vacuum desiccator until constant weight was reached (51 g, 39%).

Pure nitrogen was bubbled through boiling pyridine (800 ml) with careful exclusion of oxygen. Then copper *m*-iodophenylacetylide (**4**, 50 g, 0.172 mol) was added and the reaction mixture was kept at reflux temperature for 24 h. After 500 ml pyridine were distilled off in vacuum the remaining solution was poured into water. The precipitate separated by filtration, washed and dried was extracted successively by boiling ether, benzene, and toluene. From the toluene extract product **5** was obtained; yield: 800 mg (4.6%); m.p. >350° (dec.).

$C_{48}H_{24}$	calc.	C 95.97	H 4.04
(600.7)	found	95.34	4.42

I.R. (KBr): $\nu_{C\equiv C} = 2225\ cm^{-1}$ (very weak).
Raman (Cryst.): $\nu_{C\equiv C} = 2223, 2212\ cm^{-1}$.
U.V. (THF): $\lambda_{max} = 284.5$ ($\varepsilon = 222000$), 302 nm ($\varepsilon = 160000$).
Mass spectrum (70 eV): $m/e = 600$ (M^+, 100%), 300 (M^{++}, 38%).
M^+ *exact mass* = 600.1878 (calc. 600.1881).

Hydrogenation of 5:

Compound **5** (90 mg, 0.15 mmol) in xylene (250 ml) was hydrogenated in the presence of palladium on charcoal. After addition of 12 equivalents hydrogen (40.5 ml) the solution was filtrated and evaporated. Recrystallisation from acetone gave [2.2.2.2.2.2]metacyclophane; yield: 70 mg (75%); m.p. 126° (Lit.[5] 128–129°), identical with an authentic sample[5].

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[1] R. D. Stephens, C. E. Castro, *J. Org. Chem.* **28**, 3313 (1963).
[2] Cf. J. Burdon, P. L. Coe, C. R. Marsh, J. C. Tatlow, *Chem. Commun.* **1967**, 1259.
[3] I. D. Campbell, G. Eglinton, W. Henderson, R. A. Raphael, *Chem. Commun.* **1966**, 87.
H. A. Staab, F. Graf, *Chem Ber.* **103**, 1107 (1970).
H. A. Staab, R. Bader, *Chem. Ber.* **103**, 1157 (1970).
[4] D. E. Pearson, H. W. Pope, W. W. Hargrove, W. E. Stamper, *J. Org. Chem.* **23**, 1412 (1958).
[5] K. Burri, W. Jenny, *Helv. Chim. Acta* **50**, 1978 (1967).