

A Simple and Efficient Synthesis of *cisoid*, *transoid*, *transoid*- and all-*cisoid*-Trimers of Benzocyclobutene; a Novel Formation of *Z,Z,Z*-Tribenz[12]annulene from the Latter Trimer

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The *cisoid*, *transoid*, *transoid*- and all *cisoid*-trimers of benzocyclobutene were synthesised from 1,2-dibromo-1,2-dihydrobenzocyclobutene using nickel-catalysed cyclo-trimerisation; thermal ring-opening of the all-*cisoid*-trimer gave *Z,Z,Z*-tribenzo[*a,e,i*]cyclododecene (*Z,Z,Z*-tribenz[12]annulene) which can be converted into its silver and chromium complexes.

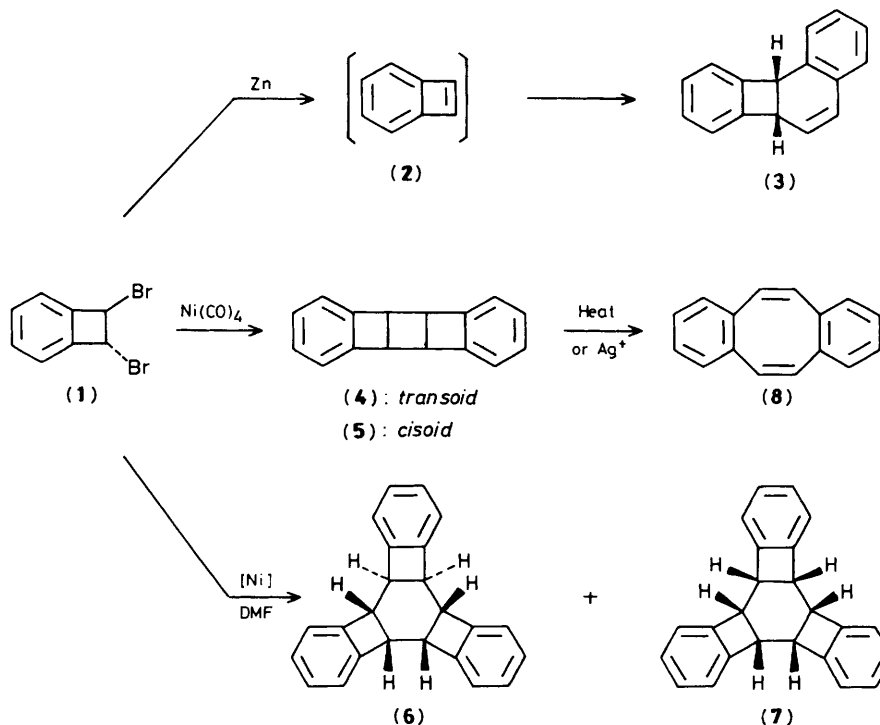
Reduction of 1,2-dibromo-1,2-dihydrobenzocyclobutene (1) with zinc is known to give the 'angular' dimer (3) through a Diels-Alder reaction of two molecules of benzocyclobutene (2),¹ whereas the reaction of (1) with Ni(CO)₄ was reported to afford the 'linear' dimer (4) or (5).² We have recently found a simple and efficient method for the nickel-catalysed coupling of alkenyl, aryl, benzyl, and phenacyl halides³ and cyclo-

oligomerisation of 2,3-dihalogenobuta-1,3-dienes.⁴ In the last case, the reaction of 2,3-dihalogenobuta-1,3-dienes in *N,N*-dimethylformamide (DMF) afforded mainly the cyclic trimer, a [6]radialene derivative. We report here a simple method for the synthesis of *cisoid*, *transoid*, *transoid*- and all-*cisoid*-trimers (6) and (7) of benzocyclobutene (2) by nickel-catalysed cyclo-trimerization.

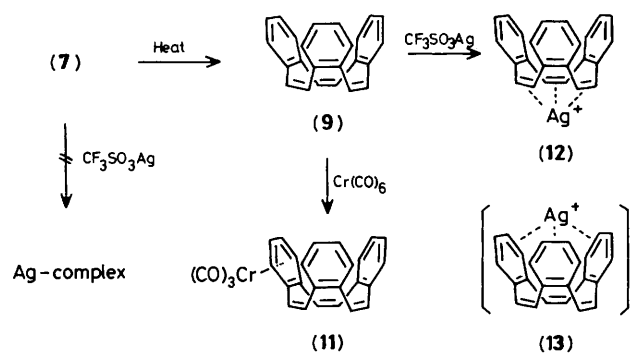
Table 1. Reaction of 1,2-dibromo-1,2-dihydrobenzocyclobutene (1) with low valent nickel complexes.

NiBr ₂ L ₂	Additive	Solvent	(4) ^b	Yields (%) of products ^a			
				(5) ^c	(6) ^d	(7) ^e	(8)
NiBr ₂ (PPh ₃) ₂	PPh ₃	THF	18	trace	7	1	4
NiBr ₂ (PPh ₃) ₂	Et ₄ Ni	THF	31	13	21	0	0
NiBr ₂ (PBu ₃) ₂	PBu ₃	THF	7	2	5	0	8
NiBr ₂ (PPh ₃) ₂	PPh ₃	DMF	6	trace	38	4	1
NiBr ₂ (PBu ₃) ₂	PBu ₃	DMF	2	1	38	1	2
NiBr ₂ (PPh ₃) ₂	Et ₄ Ni	DMF	6	trace	38	trace	2
NiBr ₂ (PPh ₃) ₂	NaI	DMF	5	trace	40	1	2

^a All new compounds gave satisfactory elemental analysis. ^b Colourless crystals, m.p. 132.5–133.5 °C (decomp.) (lit. 133 °C). ^c Colourless crystals, m.p. 122.5–123.5 °C (decomp.). ^d Colourless prisms, m.p. 161.5–163.5 °C (decomp.). ^e Colourless needles, m.p. 191.5–192.5 °C (decomp.).



Scheme 1



Scheme 2

A typical procedure involved treatment of the dibromide (1) (1 equiv.) at room temperature with a low valent nickel complex which was generated *in situ* by reduction of NiBr₂L₂ (L = PPh₃ or PBu₃) (0.2 equiv.) with zinc dust (4 equiv.) in the presence of a ligand (PPh₃ or PBu₃) or an iodide (Et₄NI or NaI, 2 equiv.). The products were purified by column chromatography on silica gel (see Table 1).

The nickel-catalysed cyclo-oligomerisation of (1) in tetrahydrofuran (THF) yielded mainly the *transoid*- and *cisoid*-dimers (4) and (5), with smaller amounts of the trimers (6) and (7).[†] In contrast to the results in THF, the reaction of (1) with Ni(PPh₃)₄ in DMF gave predominantly the trimers (6) and (7) in 42% yield, with small amounts of the dimers (4) and (5). Treatment of (1) with Ni(PBu₃)₄ in DMF afforded similar results. In addition, the reaction of (1) with NiBr₂(PPh₃)₂-Zn-Et₄NI or NaI in DMF also resulted in the predominant formation of the trimers (6) and (7). Palladium compounds often cause dimerisation or oligomerisation of alkenes⁵ but treatment of (1) with PdCl₂(PPh₃)₂ (0.2 equiv.), Zn (4 equiv.), and PPh₃ (0.4 equiv.) in DMF at room temperature afforded the *transoid*-dimer (4) and dibenzo[*a,e*]cyclo-octene (8) only in very low yields [(4) 1.3% and (8) 1.6%]. CoCl(PPh₃)₃ effected the cyclo-dimerisation of (1). Thus, the reaction of (1) with CoCl(PPh₃)₃ (2.4 equiv.) in benzene at room temperature gave the dimers (4) and (5) in 11 and 1% yields, respectively.

[†] Spectroscopic data: (*J* in Hz). (4): ¹H n.m.r. (CDCl₃) δ 3.76 (s, 4H), 7.20 (br. s, 8H); ¹³C n.m.r. (CDCl₃) δ 49.8, 122.8, 127.5, 147.6; *m/z* 204 (*M*⁺); u.v. (cyclohexane) λ_{max}/nm (log ε) 257sh (3.28), 265sh (3.53), 2.71 (3.82), 2.78 (3.93); (5): ¹H n.m.r. (CDCl₃) δ 4.09 (s, 4H), 6.72–6.98 (m, 8H); ¹³C n.m.r. (CDCl₃) δ 41.4, 122.6, 126.8, 145.7; *m/z* 204 (*M*⁺); λ_{max}/nm (log ε) 257sh (3.15), 263 (3.38), 269 (3.54), 276 (3.51); (6): ¹H n.m.r. (CDCl₃) δ 3.96–4.20 (m, 6H), 7.05 (m, 8H), 7.26 (m, 4H); ¹³C n.m.r. (CDCl₃) δ 40.4, 42.5, 42.9, 121.1, 121.5, 123.9, 126.7, * 127.6, 146.7, 148.3, 148.4 (an asterisk indicates two different carbon signals overlapped); *m/z* 306 (*M*⁺); λ_{max}/nm (log ε) 213sh (3.75), 262 (2.95), 268 (3.11), 274 (3.08); (7): ¹H n.m.r. (CDCl₃) δ 4.19 (s, 6H), 6.97 (br. s, 12H); ¹³C n.m.r. (CDCl₃) δ 40.6, 123.7, 126.4, 147.2; *m/z* 306 (*M*⁺); λ_{max}/nm (log ε) 218sh (4.23), 262 (3.53), 268 (3.63), 275 (3.54); (9): ¹H n.m.r. (CDCl₃) δ 6.75 (s, 6H), 6.78–7.13 (AA'BB', m, 12H); ¹³C n.m.r. (CDCl₃) δ 125.8, 129.9, 132.2, 136.2; *m/z* 306 (*M*⁺); λ_{max}/nm (log ε) 219sh (4.50), 267sh (3.23); (11): ¹H n.m.r. (CDCl₃) δ 4.92–5.02 (m, 2H), 5.14–5.26 (m, 2H), 6.62 (d, *J* 12, 2H), 6.66 (s, 2H), 6.87 (d, *J* 12, 2H), 7.07–7.26 (m, 8H); *m/z* 442 (*M*⁺); λ_{max}/nm (log ε) 254sh (3.87), 326 (3.88); (12): ¹H n.m.r. (CDCl₃) δ 7.08 (br. s, 12H), 7.46 (s, 6H); ¹³C n.m.r. (CDCl₃) δ 127.2, 130.1, 130.7, 134.0; field desorption mass spectrometry (*m/z*) 415, 413 (*M*⁺).

The cyclic trimers (6) and (7) can be expected to serve as useful precursors for structurally interesting tribenzo-(CH)₁₂-valence isomers. Treatment of the all-*cisoid*-trimer (7) in *o*-dichlorobenzene under reflux for 16 h gave *Z,Z,Z*-tribenz[12]annulene (9) (colourless plates, m.p. 185.5–186.0 °C) in 90% yield together with *E,Z,Z*-tribenz[12]annulene (10), 3% yield.⁶ The thermal ring-opening of (7) retains the configuration of the starting material, presumably owing to rigidity of the molecular framework.

Molecular models show that *Z,Z,Z*-tribenz[12]annulene (9) has a rigid, crown-like structure with C_{3v}-symmetry. Therefore, π-electrons of benzene rings and ethylene linkages are orthogonal and cannot conjugate with each other. Thus, (9) shows no delocalisation in the macrocyclic ring, but a face-to-face geometry of the three benzene rings and three ethylene units in (9) makes it possible for it to behave like 'π-prismand'.⁷ The (η⁶-arene)chromium tricarbonyl complex (11) [yellow crystals, m.p. ca. 160 °C (decomp.)] was prepared by treatment of (9) with Cr(CO)₆ in diglyme-THF (4:1) under reflux for 10 h in order to evaluate the possibility of π-electron delocalisation among its three benzene rings held face to face to each other at a relatively short distance. However, the electronic spectra of (11) and also of (9) showed no through-space or through-bond interaction of the benzene rings, in contrast to the results for deltaphane.^{7b} Secondly, we synthesised the complex of (9) with silver trifluoromethanesulphonate, since metal ion complexation might be expected to occur using the π-binding sites (*i.e.*, the three benzene rings or the three ethylene units) in the cavity of (9). Treatment of (9) with CF₃SO₃Ag (1 equiv.) in THF afforded the silver complex (12) [colourless needles, m.p. 164.5–165.5 °C (decomp.)] in 60% yield. ¹H and ¹³C N.m.r. spectra of the complex showed that complexation occurred using the ethylene units to form (12) instead of (13). This 1:1 complex of (9) with CF₃SO₃Ag showed a sharp melting point and was stable at room temperature in the dark. Although the silver ion was found to accelerate the isomerisation of (4) to dibenzo[*a,e*]cyclo-octene (8), (7) exhibits no detectable isomerisation nor complexation after standing at room temperature.

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