

Nickel-catalysed Butatriene Cyclizations: a Simple and Efficient Synthesis of Radialenes (Polymethylenecycloalkanes)

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Treatment of 3,4-dihalogeno-2,5-dimethylhexa-2,4-dienes (**1**) and (**5**) with tetrakis(triphenylphosphine)-nickel(0) in benzene, tetrahydrofuran, or *N,N*-dimethylformamide at 50 °C yields octamethyl[4]radialene (**2**) and/or dodecamethyl[6]radialene (**3**), in fairly good yields, *via* co-oligomerisation of 2,5-dimethylhexa-2,3,4-triene (**6**).

Radialenes (polymethylenecycloalkanes) have received considerable attention from both theorists and experimentalists.^{1,2} Although the dimerization of butatrienes with Ni⁰-complexes has been reported,³ the method has been used for the synthesis of particular [4]radialenes with cross-conjugated double bonds as terminal groups and the general instability of butatrienes has limited its general application. In view of the potent catalytic ability of Ni⁰-complexes for the reductive coupling

of aryl and vinyl halides,⁴ it was expected that 2,3-dihalo-genobutadienes could be co-oligomerized to radialenes *via* butatrienes using Ni⁰-species prepared *in situ* from Ni^{II}-species by reduction with zinc.⁵ We here report a one-pot synthesis of the stable octamethyl[4]radialene (**2**) and/or dodecamethyl[6]radialene (**3**) based on this idea.

A typical procedure involved treatment of 3,4-di-iodo-2,5-dimethylhexa-2,4-diene (**1**)⁶ (2 equiv.) at 50 °C with Ni(PPh₃)₄

Table 1. Reaction of the dihalogenohexadienes (1) and (5) with $\text{Ni}(\text{PPh}_3)_4$.

Starting material	Solvent	Yields (%) of products ^a		
		(2) ^b	(3) ^c	(4) ^d
(1)	Benzene ^e	48	—	trace
	THF	47	20	—
	DMF	1.3	50	—
(5)	Benzene	11	—	56
	THF	21	31	—
	DMF	5	63	—

^a All new compounds gave satisfactory elemental analyses.^b Colourless crystals sublimed at 155 °C. ^c Colourless crystalssublimed at 210 °C. ^d Colourless crystals sublimed at 155 °C.^e Vigorous stirring favours the production of (2).

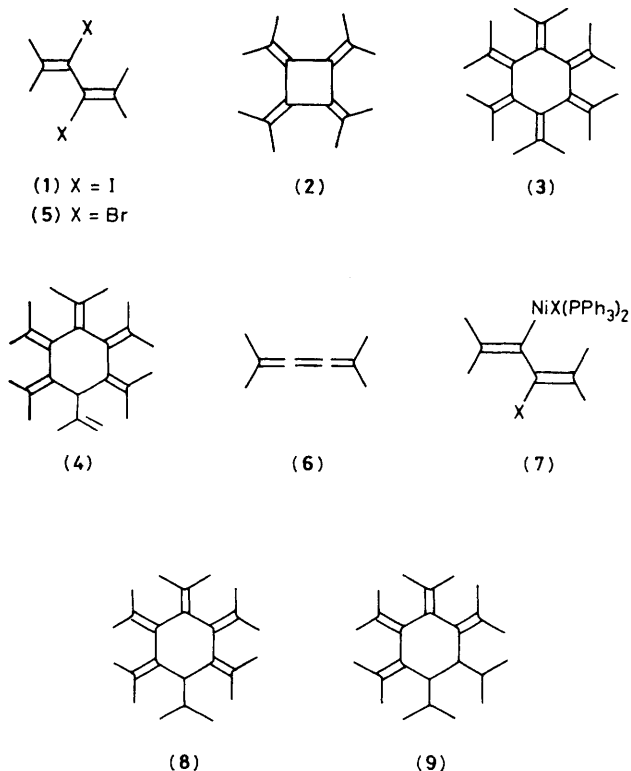
which was generated *in situ* by reduction of $\text{NiBr}_2(\text{PPh}_3)_2$ (1 equiv.) with zinc dust (10 equiv.) in the presence of triphenylphosphine (2 equiv.) in benzene, tetrahydrofuran (THF), or *N,N*-dimethylformamide (DMF), as solvent. The products (2) and/or (3) were purified by column chromatography on silica gel. The reaction of 3,4-dibromo-2,5-dimethylhexa-2,4-diene (5)⁷ (1.5 equiv.) with $\text{NiBr}_2(\text{PPh}_3)_2$ (1.0 equiv.) was carried out as above (see Table 1).

It is noteworthy that the reaction of (1) or (5) with $\text{Ni}(\text{PPh}_3)_4$ is susceptible to solvent and somewhat to halogen. In benzene, (1) cyclized predominantly to the [4]radialene (2). However, similar treatment of (5) yielded primarily the isomer of the [6]radialene (4) and small amounts of (2). In contrast to the results in benzene, the reaction of (1) or (5) in DMF gave mainly the [6]radialene (3) with small amounts of (2). The reaction of (1) or (5) in THF afforded both (2) and (3) in moderate yields.

In the presence of excess of zinc the reaction is catalytic for (1) or (5). Although the reactivity in benzene decreased with larger proportions of (1) or (5), treatment of (1) (4 equiv.) with $\text{NiBr}_2(\text{PPh}_3)_2$ (1 equiv.) in DMF in a similar manner afforded the same result [(2) *ca.* 1%, (3) *ca.* 57–63%]. The formation of (4) was not detected in THF and DMF for either substrate, whereas (4) was a major product in the reaction of (5) in benzene. In the case of (1), the reaction at room temperature in benzene resulted in an increase in the yield of (4).

We assume that the products are formed through the intermediacy of 2,5-dimethylhexa-2,3,4-triene (6) which is generated by the reaction of (1) or (5) *via* the vinylnickel halide (7), because the reduction of (1) and (5) with zinc under the reaction conditions proceeds only very slowly to give (6). This neatly accommodates the finding that the cyclo-oligomerization of (6) under the same reaction conditions gave similar products [in benzene: (2) 7%, (4) 19%; in DMF: (2) 4%, (3) 24%, (4) 21%]. The cyclo-oligomerization of (6) with catalytic amounts of $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ in refluxing benzene yielded the [4]radialene (2) (11%), the [6]radialene (3) (3%), and its isomer (4) (35%).

The [4]- and [6]-radialenes exhibited characteristic electronic and n.m.r. spectra,^{1,2} the latter reflecting the highly symmetrical structures. The spectral data for (2), (3), and (4) are illustrative: (2), ¹H n.m.r. (CDCl_3) δ 1.80 (s); ¹³C n.m.r. (CDCl_3) δ 138.3, 115.6, and 23.8 p.p.m.; *m/z* 216 (M^+); u.v. λ_{max} (log ϵ , cyclohexane) 260sh (4.176), 272 (4.279), 283sh (4.230), and 307sh nm (3.857); (3), ¹H n.m.r. (CDCl_3) δ 1.61 (s); ¹³C n.m.r. (CDCl_3) δ 136.8, 122.6, and 21.2 p.p.m.; *m/z* 324 (M^+); u.v. λ_{max} (log ϵ , cyclohexane) 240sh (4.307) and 248 nm (4.324); (4), ¹H n.m.r. (CDCl_3) δ 1.55 (s), 1.61 (s), 1.62 (s), 1.64 (m), 1.66 (s), 1.79 (s, Me), 4.48 (br. s, methine H), and



4.61–4.66 (m, olefinic H); ¹³C n.m.r. (CDCl_3) δ 147.2, 136.9, 135.1, 135.0, 125.9, 124.3, 122.7, 110.1, 50.5, 22.9, 21.9, 21.4, 21.2, and 20.1 p.p.m.; *m/z* 324 (M^+); u.v. λ_{max} (log ϵ , cyclohexane) 247.5 nm (4.207). The structure was confirmed by catalytic reduction of (4); hydrogenation with Pd in EtOH–cyclohexane– MeCO_2H at room temperature gave (8) (70%) and (9) (30%).

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

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References

- For the synthesis and properties of [4]radialene, see G. W. Griffin and L. I. Peterson, *J. Am. Chem. Soc.*, 1963, **85**, 2268; F. A. Miller, F. R. Brown, and K. H. Rhee, *Spectrochim. Acta, Part A*, 1972, **28**, 1467; T. Bally, U. Buser, and E. Hasebach, *Helv. Chim. Acta*, 1978, **61**, 38; L. Trabert and H. Hopf, *Liebigs Ann. Chem.*, 1980, 1786.
- For the synthesis and properties of [6]radialene, see A. J. Barkovich, E. S. Strauss, and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 1977, **99**, 8322; P. Schiess and M. Heitzmann, *Helv. Chim. Acta*, 1978, **61**, 844; L. G. Harruff, M. Brown, and V. Boekelheide, *J. Am. Chem. Soc.*, 1978, **100**, 2894.
- L. Hagelee, R. West, J. Calabrese, and J. Normant, *J. Am. Chem. Soc.*, 1979, **101**, 4888; B. Hagenbruch, K. Hesse, S. Hünig, and G. Klug, *Liebigs Ann. Chem.*, 1981, 256.
- M. F. Semmelhack, P. Helquist, L. D. Jones, L. Keller, L. Mendelson, L. S. Ryono, J. G. Smith, and R. D. Stauffer, *J. Am. Chem. Soc.*, 1981, **103**, 6460, and references cited therein.
- A. S. Kende, L. S. Liebeskind, and D. M. Braitsch, *Tetrahedron Lett.*, 1975, 3375; M. Zenbayashi, K. Tamao, J. Yoshida, and M. Kumada, *ibid.*, 1977, 4089; D. J. Pasto and D. K. Mitra, *J. Org. Chem.*, 1982, **47**, 1381.
- Y. S. Zalkind, B. Rubin, and A. Kruglov, *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 1044.
- W. Kretinsky, *Chem. Ber.*, 1926, **59**, 1930.