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 Ni^0-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 Ni^0-complexes for the reductive coupling of aryl and vinyl halides,[4] it was expected that 2,3-dihalogenobutadienes could be co-oligomerized to radialenes *via* butatrienes using Ni^0-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(PPh$_3$)$_4$

Table 1. Reaction of the dihalogenohexadienes (**1**) and (**5**) with $Ni(PPh_3)_4$.

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 crystals sublimed at 210 °C. [d] Colourless crystals sublimed at 155 °C. [e] Vigorous stirring favours the production of (**2**).

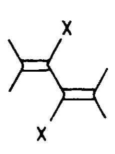
which was generated *in situ* by reduction of $NiBr_2(PPh_3)_2$ (1 equiv.) with zinc dust (10 equiv.) in the presence of triphenylphosphine (2 equiv.) in benzene, tetrahydrofuran (THF), or *N,N*-dimethylformamide (DMF), as solvent. The products (**2**) and/or (**3**) were purified by column chromatography on silica gel. The reaction of 3,4-dibromo-2,5-dimethylhexa-2,4-diene (**5**)[7] (1.5 equiv.) with $NiBr_2(PPh_3)_2$ (1.0 equiv.) was carried out as above (see Table 1).

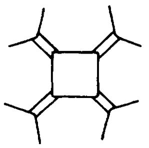
It is noteworthy that the reaction of (**1**) or (**5**) with $Ni(PPh_3)_4$ is susceptible to solvent and somewhat to halogen. In benzene, (**1**) cyclized predominantly to the [4]radialene (**2**). However, similar treatment of (**5**) yielded primarily the isomer of the [6]radialene (**4**) and small 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.

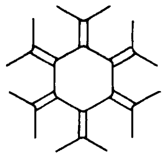
In the presence of excess of zinc the reaction is catalytic for (**1**) or (**5**). Although the reactivity in benzene decreased with larger proportions of (**1**) or (**5**), treatment of (**1**) (4 equiv.) with $NiBr_2(PPh_3)_2$ (1 equiv.) in DMF in a similar manner afforded the same result [(**2**) *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**).

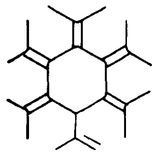
We assume that the products are formed through the intermediacy of 2,5-dimethylhexa-2,3,4-triene (**6**) which is generated by the reaction of (**1**) or (**5**) *via* the vinylnickel halide (**7**), because the reduction of (**1**) and (**5**) with zinc under the reaction conditions proceeds only very 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 $Ni(CO)_2(PPh_3)_2$ in refluxing benzene yielded the [4]radialene (**2**) (11%), the [6]radialene (**3**) (3%), and its isomer (**4**) (35%).

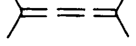
The [4]- and [6]-radialenes exhibited characteristic electronic and n.m.r. spectra,[1,2] the latter reflecting the highly symmetrical structures. The spectral data for (**2**), (**3**), and (**4**) are illustrative: (**2**), ^1H n.m.r. ($CDCl_3$) δ 1.80 (s); ^{13}C n.m.r. ($CDCl_3$) δ 138.3, 115.6, and 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); ^{13}C 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); ^{13}C 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%).

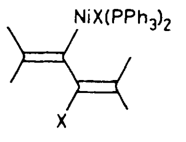

(**1**) X = I
(**5**) X = Br


(**2**)

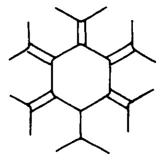

(**3**)

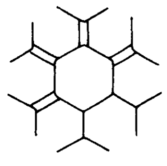

(**4**)


(**6**)



(**7**)


(**8**)


(**9**)

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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