Novel Cyclo-oligomerization of Nickel Carbenoids: a Simple and Efficient Synthesis of Radialenes

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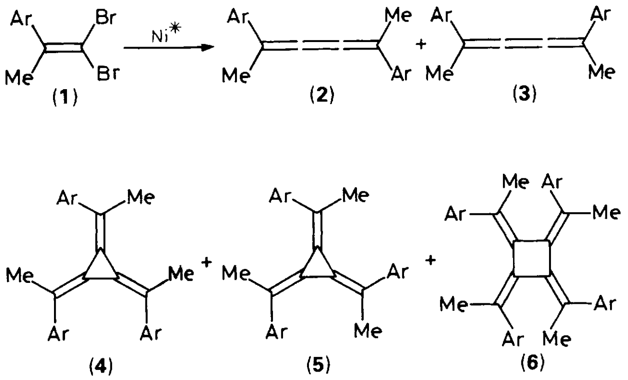
Novel cyclo-oligomerization of nickel methylenecarbenoids generated from 1,1-dihalogenoethenes with chemically activated nickel gives [3]-, [4]-, and [5]-radialenes directly under mild conditions.

Radialenes (polymethylenecycloalkanes) have attracted considerable interest from the scientific community because they can serve as electron donors and acceptors for organic metals and ferromagnets,[1] and have particular arrangements of π-electrons.[2] In conjunction with our program to develop methods for transition-metal-catalysed synthesis of new π-electron systems,[3] we previously reported a novel method for preparing radialenes by cyclo-oligomerization of the ate-type complexes derived from lithium carbenoids with an appropriate copper(I) complex.[4]

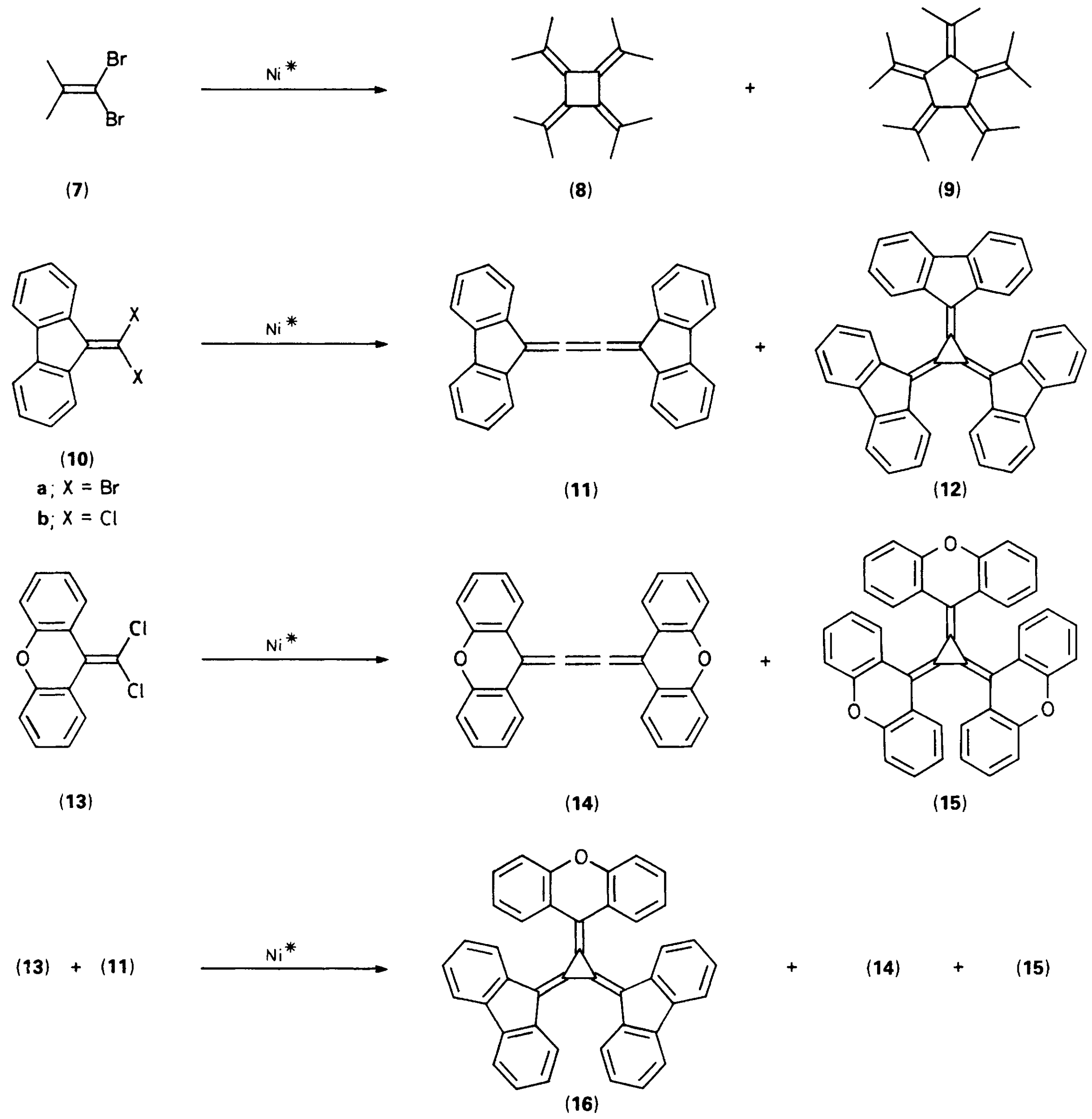
Metal methylenecarbenoids are known to give acetylenes *via* methylenecarbenes (Fritsch–Buttenbery–Wiechell rearrangement)[5] or to afford dimerized [3]cumulenes (butatrienes).[6] We report here a novel cyclo-oligomerization of nickel methylenecarbenoids to produce radialenes.

The activated metallic nickel[7] was prepared by reduction of NiI_2 with 0.7—0.8 equiv. of lithium powder and 0.1 equiv. of 4,4′-di-t-butylbiphenyl as an electron carrier in tetrahydrofuran (THF) under sonication (30—40 °C) and used directly.



a; Ar = Ph
b; Ar = p-ClC_6H_4
c; Ar = p-NCC_6H_4

Scheme 1



Scheme 2

Treatment of 2-aryl-1,1-dibromopropene (**1**) with 5—10 equiv. of this activated nickel in THF under sonication at 30—40 °C for 2 h and then at room temperature for 20 h gave a mixture of (*E*)- and (*Z*)-butatrienes (**2**) and (**3**) (3—14%), two isomeric [3]radialenes (**4**) and (**5**) (29—58%) and a stereoisomeric mixture of [4]radialenes.† Results are summarized in Table 1.

The main products of the reaction of (**1**) with the activated nickel are two [3]radialenes, in which the unsymmetrical form (**4**) is always dominant. Although the products contained small amounts of a mixture of [4]radialenes, the only characterizable [4]radialene was the symmetrical (**6**). The stereoselectivity of the reaction may lead to the predominant formation of the unsymmetrical [3]radialene (**4**), whereas the [3]cumulenes are a 1 : 1 mixture of (*E*)- and (*Z*)-isomers (**2**) and (**3**), presumably owing to the nickel-catalysed isomerization of (**2**) in the reaction media. In the case of 2-phenyl-1,1-dibromopropene (**1a**), the [3]radialenes (**4a**) (bright yellow prisms, m.p. 85—86.5 °C) and (**5a**) (yellow prisms, m.p. 146—147 °C) were unstable to atmospheric oxygen and decomposed rapidly on standing at room temperature. Therefore, the yields of (**4a**) and (**5a**) are low, but the reaction of 2-*p*-chlorophenyl- and 2-*p*-cyanophenyl-1,1-dibromopropenes (**1b**) and (**1c**), which have electron-withdrawing aromatic substituents, gave the rather stable [3]radialenes (**4b**) (yellow crystals, m.p. 135—136.5 °C), (**4c**) (orange crystals, m.p. 218.5—219.5 °C), (**5b**) (yellow crystals, m.p. 185—186 °C), and (**5c**) (orange crystals, m.p. 186.5—188.5 °C) in moderate yields.

In contrast to the reaction of (**1**), treatment of 2-methyl-1,1-dibromopropene (**7**) with the activated nickel in THF at room temperature resulted in the formation of the corresponding [4]- and [5]-radialenes (**8**) and (**9**) in 14 and 7% yields, respectively. As we reported previously,[4a] cyclo-oligomerization of the ate-type complex generated from lithium carbenoid

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† All new compounds reported here exhibited spectra (u.v., i.r., ^{1}H and ^{13}C n.m.r.) in full accord with assigned structures and gave satisfactory elemental analyses and/or high-resolution mass spectra.

Table 1. Reaction of (**1**) with chemically activated nickel.

Starting material	Yields[a] of products/%			
	(**2**) and (**3**)	(**4**)	(**5**)	(**6**)
(**1a**)	5	22	7	trace
(**1b**)[b]	3	43	12	0
(**1c**)	14	53	5	trace

[a] Isolated yields of products purified by column chromatography on silica gel. [b] The activated nickel used for the reaction was prepared from NiI_2 and lithium in the presence of naphthalene.

with copper(I) gives the same [4]- and [5]-radialenes (**8**) and (**9**). Therefore, the reaction pathway of nickel carbenoids derived from dibromoethenes with the activated nickel may be analogous to that of ate-type copper carbenoids.

A steric factor plays an important part in the cyclodimerization and oligomerization of copper carbenoids to [3]cumulenes and radialenes.[4b] In agreement with this steric effect, treatment of 9-(dibromomethylene)fluorene (**10a**) with the activated nickel in THF at 50 °C afforded the [3]cumulene (**11**) (39%), together with the corresponding [3]radialene (**12**) (1%).[4b] Similar treatment of the dichloroethene derivative (**10b**) also gave (**11**) and (**12**) in 13 and 1% yields, respectively.

Furthermore, the reaction of (**13**) with the activated nickel in THF at 50 °C produced the novel [3]radialene (**15**) (black–violet needles, m.p. 295—296 °C, 2%), together with 17% of (**14**). Interestingly, a similar reaction of (**13**) with the activated nickel in the presence of 0.05 equiv. of the butatriene (**11**) resulted in the formation of the adduct (**16**) (dark blue fine crystals, m.p. 299—300 °C) in 10% yield as the main product, together with (**14**) (6%) and (**15**) (trace). The formation of (**16**) suggests the addition of the methylenecarbene derived from (**13**) to the cumulenic double bond of (**14**). However, a mechanism involving the addition of carbenes to [3]cumulenes can be ruled out as a general mechanism for radialene formation, because the stereoselectivity of the reaction of (**1**) with the activated nickel resulted in the formation of the asymmetrical (**4**) as the major product, and because [4]- and [5]-radialenes are formed in the reaction of (**7**).

In conclusion, we have shown a novel reaction of nickel carbenoids; the results 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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