

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

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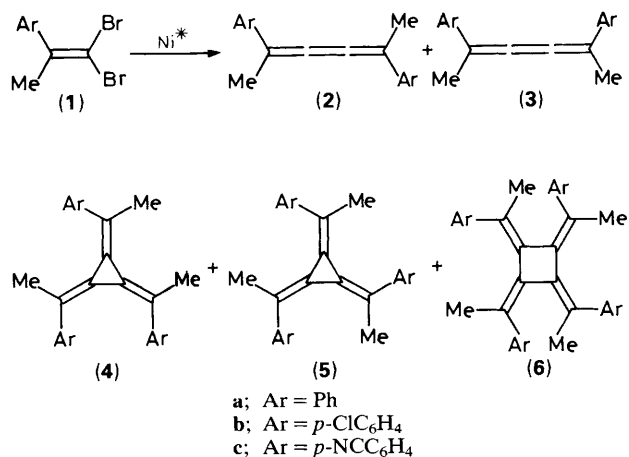
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Novel cyclo-oligomerization of nickel methylenecarbenoids generated from 1,1-dihalogenoethenes with chemically activated nickel gives [3]-, [4]-, and [5]-radialenes directly under mild conditions.

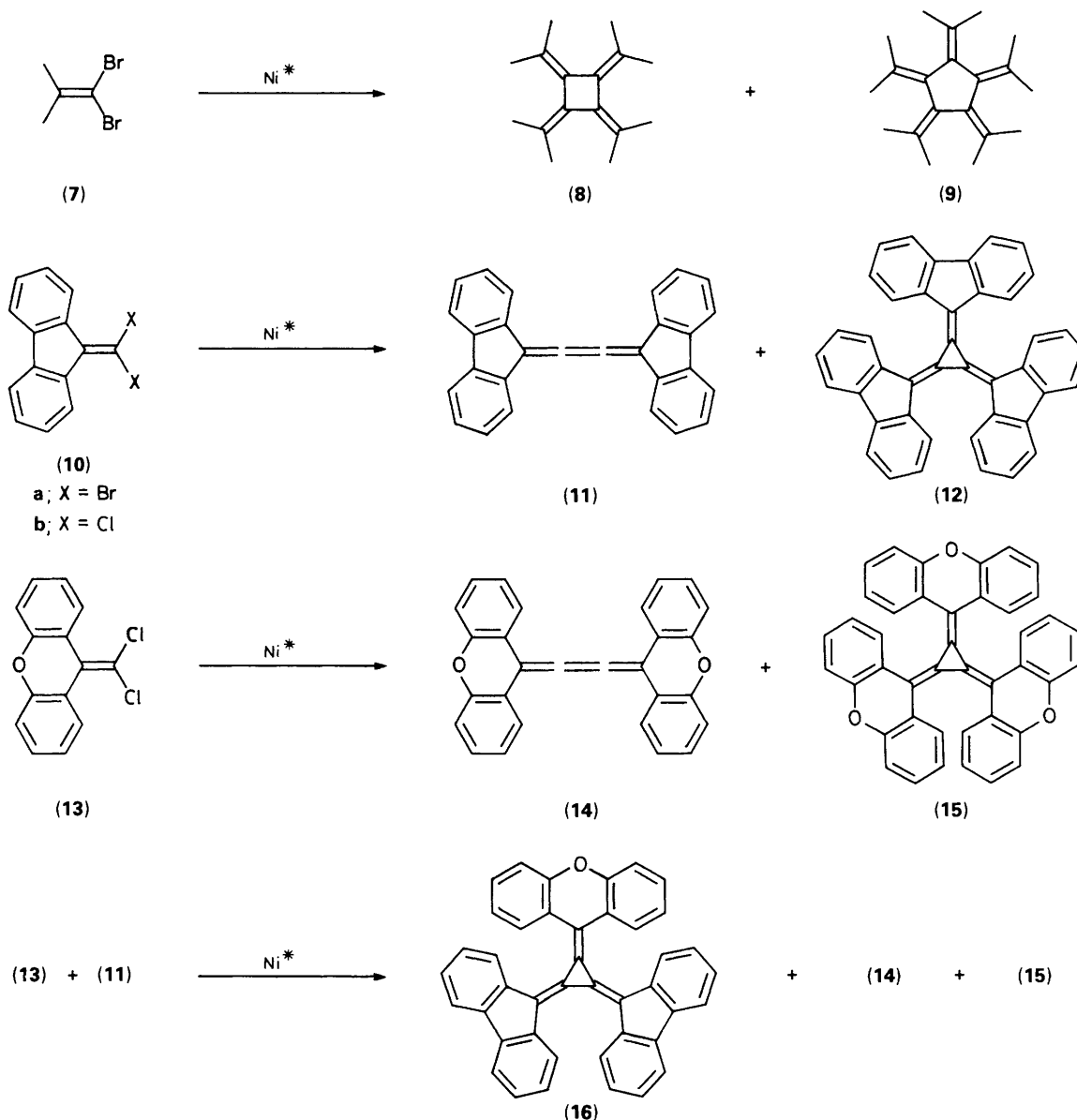
Radialenes (polymethylenecycloalkanes) have attracted considerable interest from the scientific community because they can serve as electron donors and acceptors for organic metals and ferromagnets,¹ and have particular arrangements of π -electrons.² In conjunction with our program to develop methods 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–Buttenberg–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 nickel⁷ was prepared by reduction of NiI₂ 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.



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

† All new compounds reported here exhibited spectra (u.v., i.r., ¹H and ¹³C 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 NiI₂ 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 cumulenenic 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.

Financial support for this study was provided by CIBA-GEIGY Foundation (Japan) for the Promotion of Science and by Grant-in-Aid for Scientific Research No. 63540396 from the Ministry of Education, Science and Culture.

Received, 22nd June 1989; Com. 9/02640A

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