

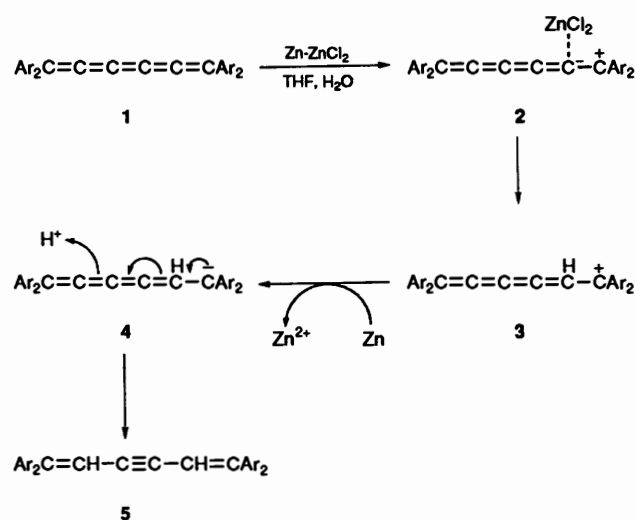
A New Synthetic Route to 1,1,6,6-Tetraalkylhexa-1,2,4,5-tetraenes by Selective Reduction of Tetraalkylhexapentaenes with Zn–ZnCl₂–H₂O

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Tetraalkylhexapentaenes were efficiently and selectively reduced to 1,1,6,6-tetraalkylhexa-1,2,4,5-tetraenes when heated with Zn–ZnCl₂ in aqueous THF.

The reagent Zn–ZnCl₂–ROH or H₂O, found to be useful in the reduction of activated olefins and various carbonyl compounds,^{1,2} coupling of aromatic aldehydes and ketones to α -glycols,³ for Reformatsky and Luche reactions⁴ and for the selective reduction of tetraarylhexapentaene **1** to 1,1,6,6-

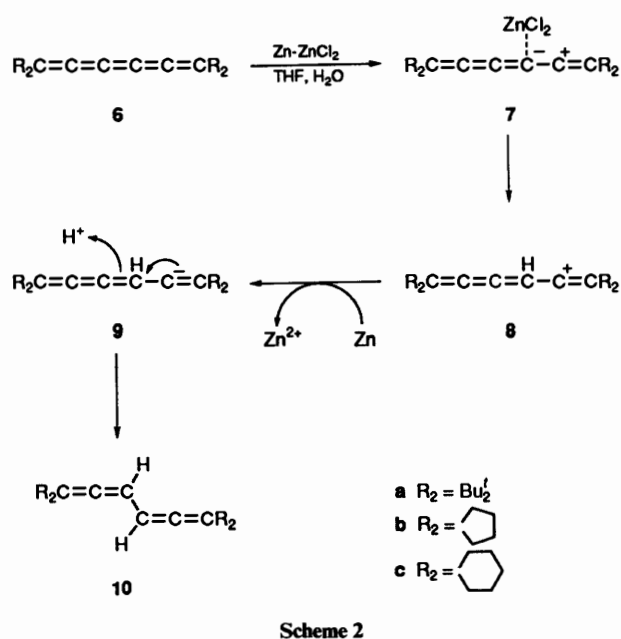


tetraarylhexa-1,5-dien-3-yne **5**,⁵ has now been found to induce selective reduction of tetraalkylhexapentaenes **6** to the diallenes, 1,1,6,6-tetraalkylhexa-1,2,4,5-tetraenes **10**. Thus, a mixture of tetra-*tert*-butylhexapentaene **6**, zinc powder, zinc chloride and aqueous tetrahydrofuran (THF) when heated under reflux gave, upon work-up, 1,1,6,6-tetra-*tert*-butylhexatetraene **10a** (97%). The structural assignment was based on spectroscopic evidence and by an X-ray crystal structure determination.⁶

By the same procedure the hexapentaenes **6b, c** were reduced selectively to the corresponding diallenes **10b, c** in the yields shown in Table 1. Structures of **10b, c** were also established on the basis of evidence and that of **10b** was finally determined by X-ray crystal structure analysis.⁶

Since the preparation of diallene derivatives is not easy,⁷ the preparation of **10** by the selective reduction of **9** is valuable. Furthermore, diallene derivatives are thermally labile and give cyclisation products, dimethylenecyclobutenes. For example, diallene itself, hexa-1,2,4,5-tetraene, which can be prepared by a [3.3] sigmatropic rearrangement of 1,5-hexadiyne, cyclises immediately to dimethylenecyclobutene,⁸ other diallene derivatives show similar behaviour.⁷ However, **10a–c** are all thermally stable, probably because the sterically bulky alkyl groups prevent cyclisation.

A plausible mechanism for the selective reduction is shown in Scheme 2. By coordination of ZnCl₂ to **6**, the vinyl cation **7** is produced, which is protonated to give the free vinyl cation **8**.



Two-electron reduction of the cation **8** by Zn gives the anion **9**, which is protonated to give the diallene **10**.

In the case of tetraarylhexapentaene **1**, however, the divinylacetylene derivative **5** is produced by the same treatment with Zn–ZnCl₂–H₂O.⁵ In this case, coordination of ZnCl₂ to **1** may produce the diarylcarbocation **2** first, which then gives the free cation **3** by protonation. Two-electron reduction of **3** by Zn followed by protonation finally gives **5** (Scheme 1).

It was interesting to know whether the substituted alkyl and aryl hexapentaene would give a vinyl or a benzyl cation in the reduction process. Reduction of a 1:1 mixture of *cis*-**11** and *trans*-1,6-di-*tert*-butyl-1,6-diphenylhexapentaene **13** with Zn–ZnCl₂ in 20% aqueous THF gave a 1:1 mixture of *syn*-**12** and *anti*-1,6-di-*tert*-butyl-1,6-diphenylhexa-1,2,4,5-tetraene **14** (91%). This result shows that, at least, *tert*-butyl and phenyl

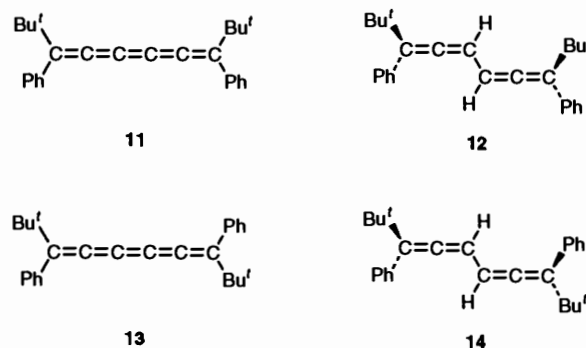


Table 1 Yield and m.p. of **10** produced by the reduction of **6** with Zn-ZnCl₂-H₂O^a

6	Reaction time (h)	Product		
		10	Yield (%)	M.p. (°C)
6a	8	10a	97	62-64
6b	13	10b	88	179-180
6c	8	10c	97	53-54

^a Reactions were carried out by heating **6**, Zn and ZnCl₂ in 20% aqueous THF under reflux.

substituted hexapentaene give a vinyl cation during the reduction. Both compounds **12** and **14** are also thermally stable.

Experimental

Typical example. A mixture of tetra-*tert*-butylhexapentaene **6a** (1g), Zn-powder (20 g), ZnCl₂ (8 g) and 20% aqueous THF (60 cm³) was heated under reflux for 8 h. After filtration, the THF solution was evaporated and extracted with toluene. The toluene solution was washed with dil. aq. HCl and water, dried (Na₂SO₄) and evaporated to give 1,1,6,6-tetra-*tert*-butylhexa-1,2,4,5-tetraene **10a**, after recrystallisation from EtOH, as colourless prisms (1.7 g, 97%, m.p. 62-64 °C); the diallene structure was supported by spectroscopic evidence:

ν_{\max} (Nujol)/cm⁻¹ 1930 (C=C=C); δ_{H} (CDCl₃) 5.43 (s, 2 H, C=C=CH) and 1.18 (s, 36 H, Me); and δ_{C} (CDCl₃) 32.4 (Me), 35.2 (Me₃C), 91.7 (C=C=CH), 122.9 (Bu^tC=C=C), and 199.7 (C=C=C). The structure was finally determined by an X-ray structure analysis.⁶

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