

1,4-Epoxyarenes for the Generation of Molecular Ribbons

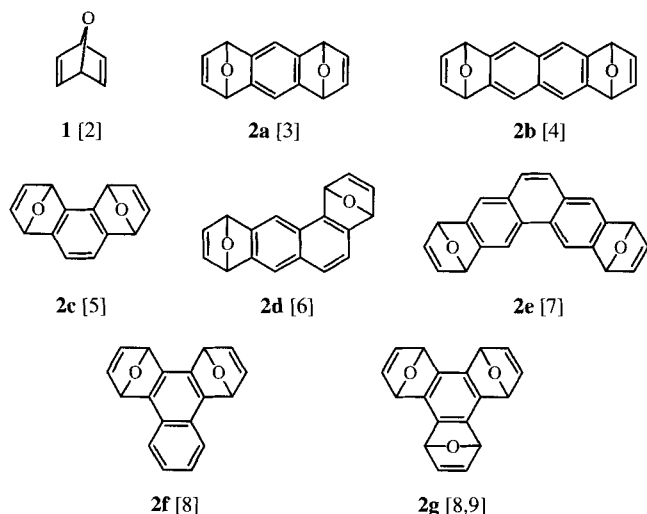
Axel Mayer and Herbert Meier

Mainz, Institut für Organische Chemie der Universität

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Repetitive [4+2] cycloaddition reactions represent a commonly applied convenient method for the generation of molecular ribbons with interesting mechanical, electrical, optical or optoelectronic properties [1]. However, the number of highly reactive *twofold* 4π and/or 2π components is rather small.

Areno-condensed derivatives **2** of 7-oxabicyclo[2.2.1]hepta-2,5-diene (1,4-dihydro-1,4-epoxybenzene) **1** provide very useful reagents as 2π components as well as precursor for 4π components. Scheme 1 summarizes the parent compounds.

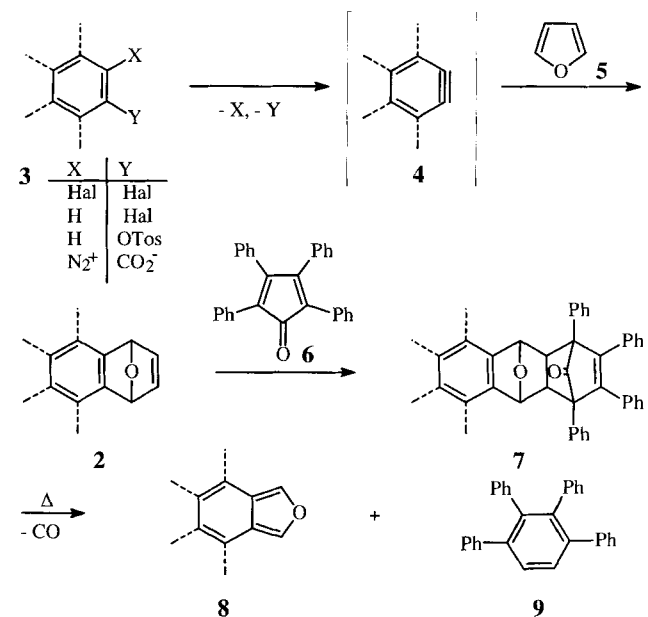


Scheme 1

The synthetic entry to **2a–g** is shown in Scheme 2. Thermal or alkaline 1,2-elimination reactions are used for the *in situ* generation of arynes (**3** → **4**). In the presence of furan (**5**) the corresponding epoxyarenes are obtained in good yields. The twofold or threefold dienophiles **2a–g** are formed in two and three such steps, respectively [4–9] (Scheme 2).

The cycloaddition of **2** and tetraphenylcyclopentadienone (**6**) yields the adducts **7** which can be thermally cleaved to the corresponding areno[*c*]furans **8**, 1,2,3,4-tetraphenylbenzene (**9**)

and CO [10–12]. Benzo[*c*]furan and naphtho[2,3-*c*]furan have to be handled in solution, whereas naphtho[1,2-*c*]furan and phenanthro[9,10-*c*]furan[8] can be isolated in a pure state.



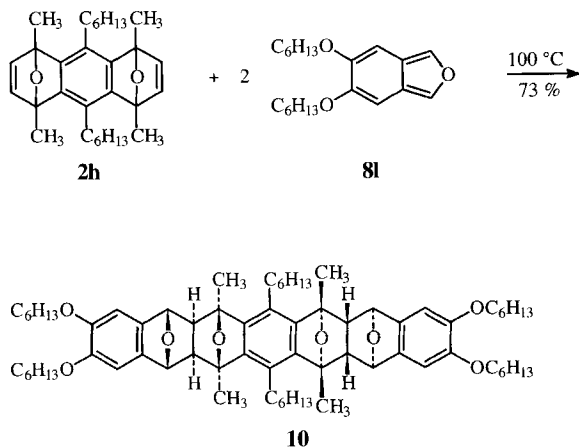
Scheme 2

Of course, mono- and bisdiene components can be generated by this procedure. Thus, repetitive cycloaddition reactions of the AB type as well as of the AABB type can be performed.

AB → ABABAB...

AA + BB → AABBAABB...

Monodienes and monodienophiles serve for the termination of the cycloaddition sequence. A first example is shown in Scheme 3 [13].

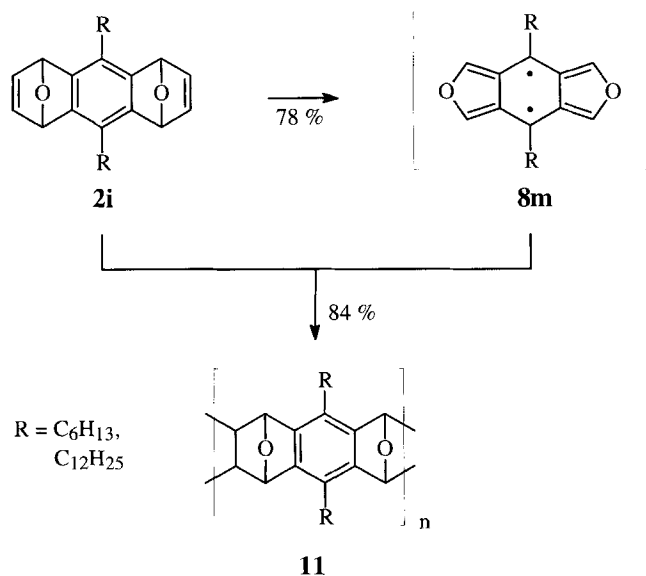


Scheme 3

In principle, a total of 6 stereoisomeric heptacene derivatives **10** could result; however, there is a strong preference of endoxides to add dienes on the *exo* side. The drawn *syn/anti/syn* configuration with a C_{2h} symmetry represents the major product.

In the absence of solubilizing side chains the repetitive cycloaddition processes would come very early to an end because of the precipitation of the adducts. Virtually alkyl or alkoxy substituted derivatives of **2a–g** or the corresponding dienes **8** are employed.

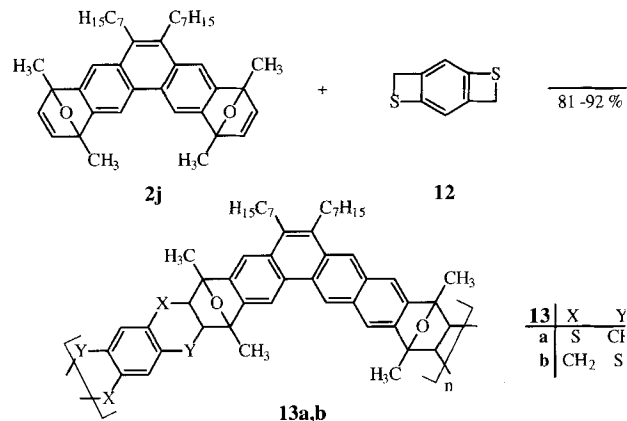
Scheme 4 shows the formation of a linear molecular ribbon (ladder polymer) [14, 15].



Scheme 4

The bisdiene **2i** yields a bisadduct with tetracyclone [13, 16], whose stepwise cleavage leads to two diene systems, which react with **2i**. Formally **8m** can be regarded as a building block of the product **11**.

The generation of bent molecular ribbons (angular annellated ladder polymers) requires bent dienophiles **2** or/and bent dienes **8**. Scheme 5 presents a heterocyclic example [

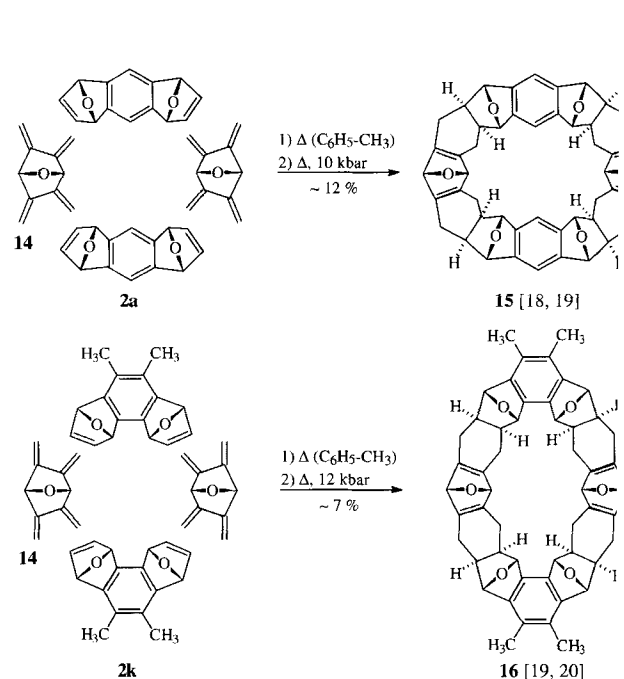


Scheme 5

Benzo [1,2-*b*:4,5-*b'*]bisthiete (**12**) represents a highly reactive bisdiene [17]. The consecutive opening of the two 4-membered rings can be achieved by heating or by irradiation.

Cyclic polyadducts – collar or belt structures – are shown in Scheme 6 [18–20]. Even when a perfect stereocontrol is realized the yields are relatively low – due to high geometrical demands or a lacking regiocontrol.

The threefold dienophile **2g** is likewise capable of formation of cage structures [19].



Scheme 6

Although there are many well-known dehydration, deoxygenation and dehydrogenation processes, it is often difficult to completely aromatize the molecular ribbons. Nevertheless, a full conjugation seems to be a precondition for highly interesting optical and electrical properties. Thus, the present synthetic efforts are not only directed towards the discovery of new, reactive twofold or threefold diene and dienophile components but are also focused on the aromatization of the ribbons, belts etc.

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Address for correspondence
Prof. Dr. H. Meier
Universität Mainz
Institut für Organische Chemie
J.-J.-Becherweg 18–22
D-55099 Mainz