Hexabromotricyclobutabenzene and Hexabromohexaradialene: Their Nickel-Mediated One-Pot Syntheses and Crystal Structures

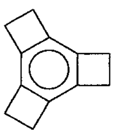
Amnon Stanger,* Nissan Ashkenazi, Roland Boese,* Dieter Bläser, and Peter Stellberg

Abstract: The reaction of hexakis(dibromomethyl)benzene with $[(Bu_3P)_2\text{-}Ni(COD)]$ (COD = 1,5-cyclooctadiene) in DMF at 65–70 °C yielded a mixture of the title compounds. The mixture was separated by column chromatography to yield hexabromotricyclobutabenzene (**3a**) and hexabromohexaradialene (**4**) in 24 and 16% yields, respectively. ^1H and ^{13}C NMR spectroscopy suggest that **3** is obtained as the *syn*-all-*trans* isomer **3a**, and the symmetric *anti*-all-*trans* isomer **3b** is not obtained at all. The X-ray structures of **3a** and **4** are reported. The hexaradialene **4** has a chair conformation, and deviates from planarity by 43.6°. Heat or radical impurities cause the clean transformation of **3a** to **4**.

Keywords
crystal structure · cyclobutenes · nickel · radialenes · radical reactions

Introduction

Tricyclobutabenzene (**1**) has been considered as one of the key compounds for the study of the long-debated Mills–Nixon effect.[1, 2] Although a strained compound, it does not show bond alternation. This was theoretically predicted (from ab initio calculations), and explained by the theoretical ability of the sp^3 carbon atoms to rehybridize and form curved ("banana") bonds.[3] Later, this was proven by X-ray and X–X electron-density deformation.[1] It was also predicted that some of the organometallic complexes of **1** will show bond alternation.[3]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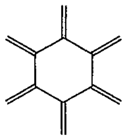
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Synthetically, there are two multistep and low-yielding methods for the preparation of **1**;[4] no derivative of the tricyclobutabenzene skeleton is known. Thus, it was desirable to find a more efficient method for the preparation of tricyclobutabenzene, preferably a functionalized system, so that it could be used for the preparation of organometallic complexes and for organic and organometallic chemical transformations of this interesting skeleton.

The elusive hexaradialene (**2**) is a nonaromatic, ring-opened isomer of **1**. This system is of particular interest among the radialenes.[5] The parent system is unstable and polymerizes immediately.[6] Only two substituted hexaradialenes have been structurally characterized, the hexamethyl[7a] and dodecamethyl[7b] derivatives. These molecules are chair-shaped, possibly owing to the steric bulkiness of the substituents causing deviation from planarity. The question of whether **1** is more stable than **2** is still open. The interconversion between cyclobutabenzene and *o*-xylylene was investigated thoroughly,[8] and it was found that the ring-opened form is less stable (by about 8 $kcal\,mol^{-1}$) than its aromatic isomer. However, none of the reports of the synthesis of [6]-radialene (or its stable derivatives) mention conversion to the respective tricyclobutabenzene.[5, 7, 9] It may thus be that **2** is more stable than **1** (only more labile) in contrast to the cyclobutabenzene case. This can be investigated only if a synthesis of authentic tricyclobutabenzene derivatives is developed.

Our interest in the Mills–Nixon effect,[1, 3, 10] the need for functionalized cyclobutabenzenes for its study, and the general interest in compounds like **1** and **2** led us to search for an efficient method to prepare such functionalized systems. We report here the "one-pot" synthesis and the X-ray structures of the title compounds hexabromotricyclobutabenzene (**3a**) and hexabromohexaradialene (**4**),[11] and some observations regarding the interconversion of these two isomers.

Results and Discussion

As the known routes for the preparation of tricyclobutabenzene yield the unfunctionalized system (in low yields),[4] they did not fit our needs. We therefore tried our recently developed nickel-mediated cyclization method (Scheme 1),[12] in the hope that the efficiency of the reaction in closing one four-membered ring would permit the cyclization of three rings within the same

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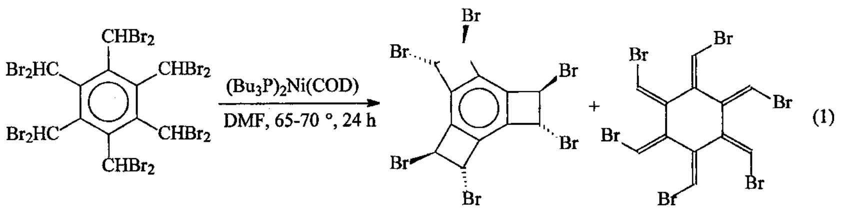
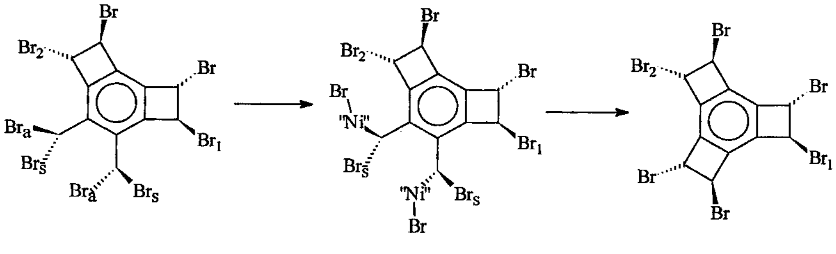


5 **3a** **4** (1)

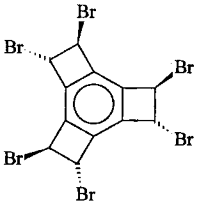
Scheme 1. The attempted nickel-mediated cyclization of **5** yielded two isomers, **3a** and **4**.



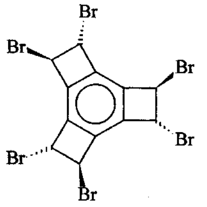
3a

Scheme 2. The formation of the third four-membered ring in **3a**. "Ni" = $(Bu_3P)_2Ni$.

molecule. The results proved to be better than expected. Three equivalents of $[(Bu_3P)_2Ni(COD)]$ (COD = 1,5-cyclooctadiene) were dissolved in dry deoxygenated DMF, hexakis(dibromomethyl)benzene (**5**)[9] was added, and the suspension stirred at 65–70 °C for 24 h. In an NMR experiment it was observed that after a few minutes at RT, before the cyclization started, the nickel complex decomposed and only free COD was present. We therefore assume that the reactive mediator is $[(Bu_3P)_2Ni(DMF)_n]$, where the complexing DMF molecules equilibrate rapidly with the solvent. The reaction takes more time than the single ring closure (24 h instead of ≈3 h[12]), probably because **5** is almost insoluble in DMF (or any other common organic solvent). The **3a**:**4** ratio in the product mixture ranges between 3:2 and 1:1, depending on exact reaction time and temperature. According to the ^1H and ^{13}C NMR spectra,[13] **3** is obtained only as the *syn*-all-*trans* isomer (**3a**). The symmetric *anti*-all-*trans* isomer (**3b**) or any of the other seven isomers that have at least one four-membered ring with a *cis* arrangement between the bromine atoms are not observed at all. The formation of the four-membered rings with only *trans* arrangement of the bromine atoms is understood on the basis of a single ring closure.[12] The sole formation of **3a** without even a trace of **3b** is probably a result of steric congestion around the *syn* bromine atom of a $CHBr_2$ unit adjacent to an already formed four-membered ring (i.e., Br_s to Br_1 and Br_2, see Scheme 2). This forces the $(Bu_3P)_2Ni$ moiety to insert into the $C-Br_a$ bond (Scheme 2), which results in a *syn* arrangement between the adjacent bromine atom on the newly formed four-membered ring and the other two. Thus, even if the first two rings were formed with an *anti* arrangement between the adjacent bromine atoms on the two rings, the third one must be formed with a *syn* relation of its bromine atoms to those in the adjacent rings.



3a



3b

Abstract in German: *Die Reaktion von Hexakis(dibrommethyl)benzol mit* $[(Bu_3P)_2Ni(COD)]$ *(COD = 1,5-Cyclooctadien) in DMF bei 65–70 °C führte zu einem Gemisch der Titelverbindungen. Nach Säulenchromatographie wurden Hexabromtricyclobutabenzol (**3a**) und Hexabromhexaradialen (**4**) in 24 bzw. 16%-iger Ausbeute erhalten.* ^1H *und* ^{13}C *NMR-spektroskopische Daten ließen darauf schließen, daß **3** als das syn-all-trans Isomer **3a** gebildet wurde, and das symmetrische anti-all-trans Isomer **3b** nicht entstand. Die Ergebnisse aus den Röntgenstrukturanalysen von **3a** und **4** werden vorgestellt. Das Hexaradialen **4** hat Sesselkonformation mit einer Abweichung von 43.6° von der planaren Anordnung. Durch Erwärmen oder durch radikalische Verunreinigungen wird **4** glatt aus **3a** gebildet.*

The workup of the reaction consists of high vacuum evaporation of the volatiles at room temperature, dissolution of the residue in chloroform, and aqueous workup. The products can be separated on an alumina column (hexane/chloroform 1:3) or by fractional crystallization (chloroform, −20 °C) to give **3** and **4** in 24 and 16% isolated yields, respectively. The mass spectrum of the mixture (CI) shows two compounds with the same molecular mass (629.4) and the same isotopic pattern (that fits $C_{12}H_6Br_6$), but with totally different fragmentation patterns. However, all the fragments are less than 8% (relative to the molecular peak).

Reacting **5** under metallic nickel cyclization conditions gave similar results; the reaction temperature needed was somewhat higher (80 °C) and the workup similar, except that the crude reaction mixture was filtered before evaporation. In this case a minor amount (3%) of a reduction product, hexakis(bromomethyl)benzene,[14] was also isolated, and the yields of **3** and **4** were 22 and 10%, respectively.

As some of the organometallic complexes that we intended to use in the Mills–Nixon effect study[3] require the parent system **1** as a precursor, we attempted the reduction of **3**. Application of the methods that were employed for the reduction of 1,2-dibromocyclobutabenzene to cyclobutabenzene ($Bu_3SnCl/LiAlH_4$[15a] or H_2 under Pd/C[15b] or Raney $Ni/NaOCH_3$ catalysis) did not yield any of the desired product **1**. Probably the presence of radicals in these reactions mediated the electrocyclic ring opening of **1** (or **3a**) to **2** that polymerized (see below).

However, "superhydride" ($LiEt_3BH$) successfully reduced **3a** to **1** in 54% isolated yield (i.e., 90% yield per bromine atom). Thus, the total yield from commercially available starting materials (hexamethylbenzene) to **1** is 13%, an order of magnitude higher than the yields obtained in the previously published methods.[4]

Crystals suitable for X-ray crystallography were obtained by slow crystallization of the clean compounds from chloroform at −20 °C. It was not easy to obtain the crystal structures of isomers **3a** and **4**. The molecular structure of **3a** (Figure 1) clearly reveals a conformation with C_1 symmetry, with a planar ring system. Owing to the dominant scattering of the bromine atoms, the esd's of the C–C bond distances are too high to allow a discussion of possible bond fixation, but (as expected) there are no large differences between exocyclic and endocyclic bonds.[1, 3a, 16] The molecular structure of **4** with crystallographic C_i symmetry shows that the all-*E* isomer (Figure 2, top) chair-shaped (Figure 2, bottom) conformer is formed, similar to the known hexamethyl[7a] and dodecamethyl[7b] derivatives of hexaradialene. The angle between the C(1)C(2)C(1A)C(2A) and C(2)C(3)C(1A) planes is 43.6°, that is, rather similar to the chair geometry of cyclohexane (49.3°).[17] The deviation from planarity of the substituted [6]-radialenes probably has steric and electronic causes.[18] All the other geometrical features are in the expected range.

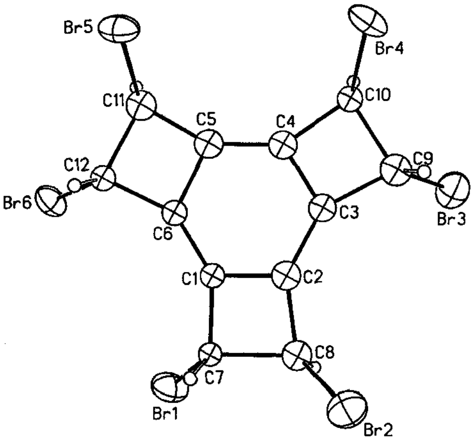


Figure 1. Ellipsoid plot of **3a**, relevant distances (Å) and angles (°): Br1–Br2 4.53, Br2–Br3 5.33, Br3–Br4 4.46, Br4–Br5 4.37, Br5–Br6 4.47, Br6–Br1 4.39; Br1-C7-C8-Br2 −126.4, Br3-C9-C10-Br4 −121.9, Br5-C11-C12-Br6 122.9.

Heating **3a** transformed it cleanly into **4**. Thus, if the reaction mixture (Scheme 1) was kept at the reaction temperature for a prolonged period, the yield of **3a** dropped and that of **4** increased. This happened also if a solution of **3a** in DMF or chloroform was heated. Moreover, when a solution of **3a** in $CDCl_3$[19] was placed in an open vial (in an attempt to crystallize the compound by slow evaporation of the solvent) beautiful clean crystals of **4** were found. A concerted ring opening of **3a** should be conrotatory, and therefore cannot lead to **4** (which is the all-*E* isomer). Thus, we believe that the transformation proceeds by a radical mechanism. Interestingly, although this transformation changes many properties of the molecule (for example, six carbon atoms that are sp^3 hybridized in **3a** are sp^2 hybridized in **4**), most of the geometrical changes are relatively small. Figure 3 shows an overlap presentation of **3a** and **4**, based on a fit of both six-membered rings. The positions of the six internal atoms deviate by an average distance of 0.21 Å, and the six external carbon and four bromine atoms reveal an average displacement of 1.12 and 1.30 Å, respectively. However, two of the bromine atom positions are relatively far from each other (average 3.36 Å) and suggest a rotation about the external C–C bonds during the **3a** to **4** transformation.

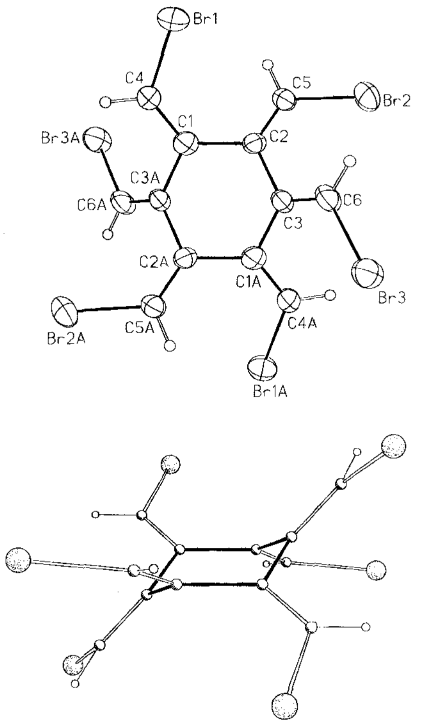


Figure 2. Ellipsoid plot of **4** (top, top view; bottom, side view); relevant distances (Å) and angles (°): C–C (ring, mean value) 1.496(7), C=C (mean value) 1.318(7), C–Br (mean value) 1.878(8); Br1–Br2 4.91, Br2–Br3 4.97, Br3–Br1A 4.80; C2-C1-C4-Br1 1.9, C1-C2-C5-Br2 −174.4, C2-C3-C6-Br3 173.5, C1-C2-C3-C1A 48.3.

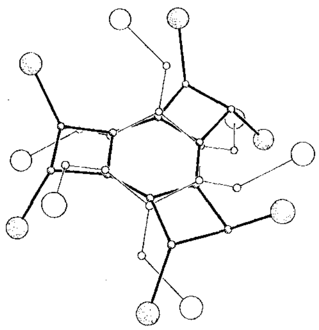


Figure 3. Overlap presentation of **3a** and **4** with best fit of the two six-membered rings.

Conclusion

The nickel-mediated cyclization of α,α,α′,α′-tetrabromo-*o*-xylene has been successfully applied to synthesize the tricyclobutabenzene skeleton. The only isomer obtained was **3a**, which can be reduced in 54% yield to the parent system **1**. The hexaradialene **4** was also obtained in this reaction, and both compounds were characterized by X-ray crystallography, which revealed no unusual structural property in these two novel systems. It was shown that **3a** cleanly transforms to **4**, probably by a radical mechanism; none of our attempts to reverse the reaction were successful. Thus, the [6]-radialene is probably thermodynamically more stable than its aromatic isomer, in contrast to what was found for the cyclobutabenzene/*o*-xylylene case. The