

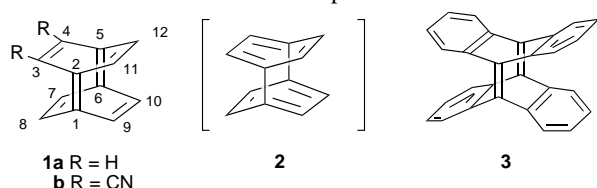
Tricyclo[4.2.2.2^{2,5}]dodeca-1,3,5,7,9,11-hexaene: generation and chemical trapping of the 3,4-dicyano derivative

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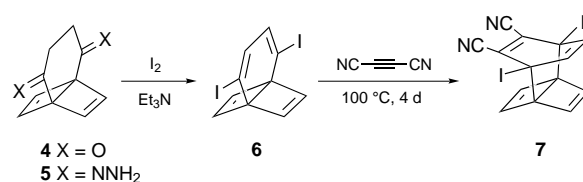
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The 3,4-dicyano derivative of hitherto unknown tricyclo[4.2.2.2^{2,5}]dodeca-1,3,5,7,9,11-hexaene, in which six double bonds are uniquely arranged, is generated and chemically trapped with 1,2-dimethylenecyclopentane and *tert*-butyllithium.

The title compound **1a** is a highly strained and symmetrical, fully unsaturated hydrocarbon¹ in which four double bonds are arranged longicyclically² and the residual two doubly bridge-head unsaturated bonds are disposed face-to-face in close

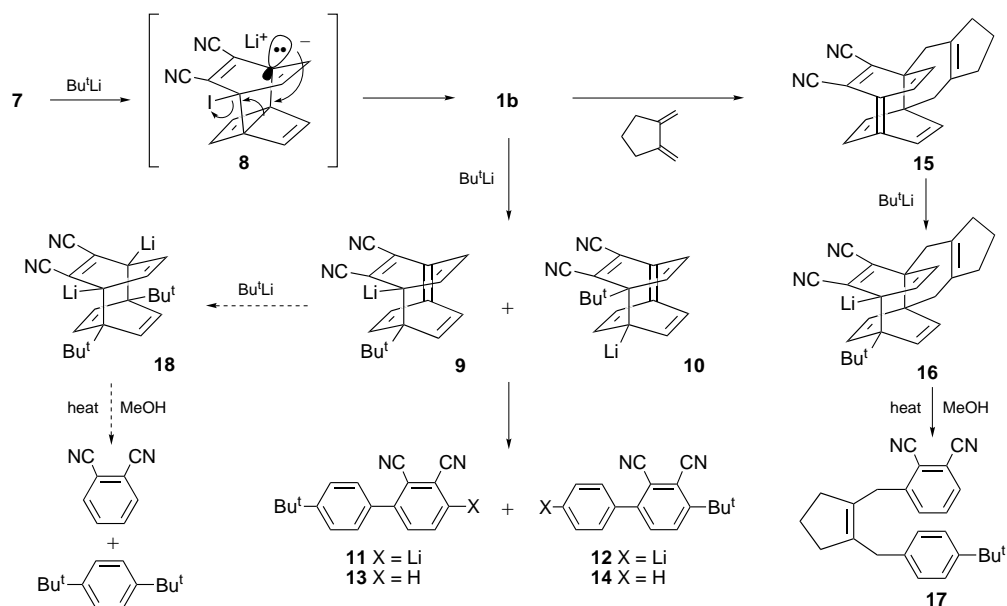


proximity. It is also of interest that the species may be regarded as a π -bond-shift isomer of [0.0]paracyclophane **2** although, according to theoretical calculations, the latter appears neither to represent a local energy minimum on the potential energy surface nor to appreciably contribute to the molecule as a canonical form.[†] To the best of our knowledge, the tetrabenzo derivative **3**³ is the only known compound closely related to **1a**. We envisaged that the title hexaene structure might be accessible *via* 1,4-elimination in **7** in which the cleaving bonds are ideally disposed antiperiplanar to each other.⁴ Moreover, strain release by the concomitant cleavage of the highly strained central σ -bond is expected to facilitate the reaction. Here the generation of the 3,4-dicyano derivative **1b** from **7** and its chemical trapping is reported.



Scheme 1

The preparation of **7** started with tricyclic diketone **4**,⁵ from which diiodo[4.2.2]propellatetraene **6** was obtained *via* the bis(hydrazone) **5** using Barton's procedure (Scheme 1).⁶ The [2 + 4] cycloaddition of dicyanoacetylene to **5** furnished **7** in 45% yield after 4 d at 100 °C.[‡] Treatment of **7** with 3.3 equiv. of *tert*-butyllithium in the presence of 1,2-dimethylenecyclopentane (0.33 mol dm⁻³) in THF at -78 °C followed by the addition of MeOH after 1 h provided **13** (40%), **14** (5%) and **17** (10%), along with several minor unidentified products. The formation of these products seems to be best explained by postulating the generation of **1b** *via* **8** as a short lived intermediate (Scheme 2), which undergoes [2 + 4] cycloaddition with 1,2-dimethylenecyclopentane⁷ to give **15**, in competition with the regioselective addition of *tert*-butyllithium to give **9** and **10**. The addition of alkyl lithium to strained carbon-carbon double bonds is well documented¹ and the observed regioselectivity is in accord with the expected electronic polarization of the double bond and/or the steric effect exerted by the cyano substituents. The resulting adducts **9** and **10** would suffer rapid ring-cleavage to give **11** and **12**, respectively, being facilitated by an enormous gain in energy, and end up as **13** and **14** after protonation by MeOH. According to semiempirical



Scheme 2

calculations (PM3),⁸ the isomerization of the 1,2-dihydro derivative of **1a** to biphenyl is exothermic by 93 kcal mol⁻¹.[§]

Conspicuously absent in the product mixture were the substituted benzenes expected from the addition of another molecule of *tert*-butyllithium to **9** and **10** followed by ring fission, e.g. 1,4-di-*tert*-butylbenzene and phthalonitrile. Thus, the further addition of *tert*-butyllithium to **9** and **10** must be unimportant. The cycloadduct **15**, which is still highly strained but restrained from isomerizing to a biphenyl derivative by the side chain, would eventually be converted to **17** via the addition of *tert*-butyllithium,[¶] followed by the fission in the benzene *p,p*-dimer moiety of the resultant adduct and protonation by MeOH under the reaction conditions or during the isolation.⁹ When 1.1 equiv. of *tert*-butyllithium was used in an attempt to suppress its addition to **1b**, only one third of **7** was consumed and the residual two thirds were recovered intact. Apparently, the lithiation of **7** is rate-determining and the subsequent elimination of LiI from **8** and the addition of *tert*-butyllithium to the resulting **1b** must be much faster.^{||} The reported isolation of highly strained alkenes whose alkenic carbons are more highly pyramidalized than the central carbons of **1a**,^{10–12} however, suggests that the title hexaene may well become isolable if a generation method not requiring the use of strongly nucleophilic or electrophilic reagents is devised, or the skeleton is kinetically stabilized by the introduction of suitable substituents.

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Footnotes and References

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† The structure of **1a** optimized at the B3LYP/6-31G* level of theory is *D*_{2h} symmetric; the interatomic distances C(1)–C(2), C(2)–C(3), C(3)–C(4) and C(1)–C(6) are 1.369, 1.515, 1.345 and 2.399 Å, respectively, and the angle between the bond C(1)–C(2) and the plane C(1)–C(8)–C(9) is 37.0°.

‡ Selected data for **6**: δ_H(CDCl₃) 5.86 (2 H, s), 6.38 (4 H, s); δ_C(CDCl₃) 65.20, 98.04, 129.88, 143.25; Calc. for C₁₀H₆I₂: 379.8559. Found: 379.8535. For **7**: δ_H(CDCl₃) 6.26 (2 H, s), 6.29 (2 H, s), 6.42 (2 H, s); δ_C(CDCl₃) 32.08, 66.00, 113.53, 136.08, 140.14, 140.64, 141.70; Calc. for C₁₄H₆N₂I₂: 455.8620. Found: 455.8616.

§ The formation of 10-methylbiphenyl upon treatment of **3** with methylolithium has recently been reported. The addition of methylolithium in a transannular fashion, however, predominates in the reaction: R. Herges,

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¶ According to semiempirical calculations (AM1 and PM3) (ref. 8), the degree of pyramidalization around the central alkenic carbons of the 1,2-dihydro derivative of **1a** is slightly more pronounced than around those of **1a**.

|| It seems that *tert*-butyllithium also rapidly reacts with *tert*-butyl iodide arising from the lithiation of **7**. Thus, 3 equiv. of *tert*-butyllithium at least are consumed in the reaction with **7**.

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