

Facile Formation of Dihydroacepentalenediide from *centro*-Substituted Tribenzotriquinacenes with C–C Bond Cleavage

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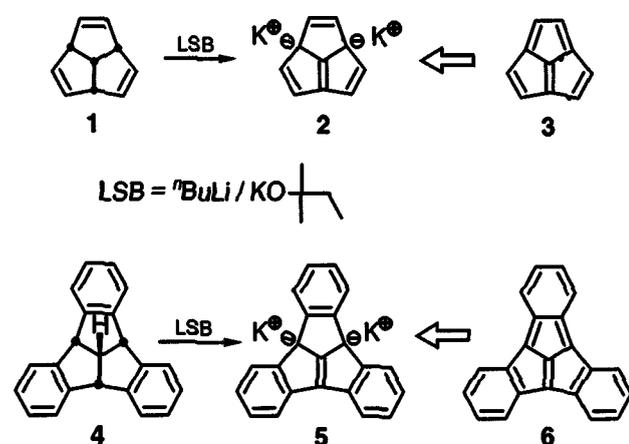
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Abstract: Tribenzodihydroacepentalenediide **5**, a potential precursor for tribenzoacepentalene **6**, can be prepared in good yields from the easily accessible *centro*-substituted tribenzotriquinacenes **7a–c** by treatment with an excess of *n*-butyl lithium/potassium *t*-pentoxide in the presence of tetramethylethylene diamine (TMEDA). The dimer **16** of tribenzodihydroacepentalene **15**, thus obtained after hydrolysis of **5** in up to 85% yield from readily accessible **7a**, undergoes [2+2]-cyclo-reversion at 220 °C, and **15** is efficiently trapped in [2+4]-cycloadditions with non-volatile dienes like tetracyclone and anthracene to give structurally interesting polycycles **17** and **18**, respectively.

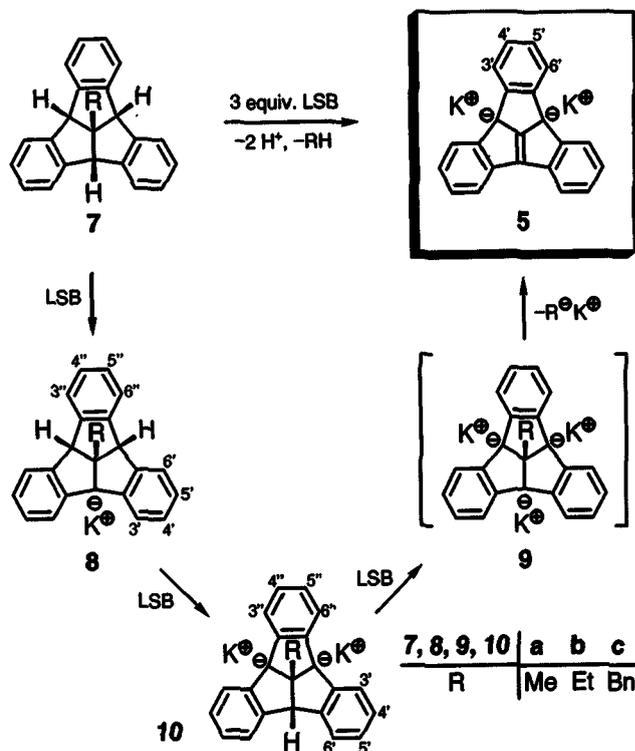
As was previously shown,¹ dihydroacepentalenediide **2** and its tribenzo analogue **5** are readily formed upon treatment of triquinacene **1** and tribenzotriquinacene **4**,² respectively, with an equimolar mixture of *n*-butyllithium and potassium *t*-pentoxide (so called Lochmann-Schlosser base³). These "dianions" are potential precursors of the fully unsaturated hydrocarbons, acepentalene **3** and tribenzoacepentalene **6**, respectively, comprising a π -electron system of longstanding theoretical interest⁴ (Scheme 1).



Scheme 1

The strongly basic Lochmann-Schlosser base (LSB)³ is known to deprotonate allylic C–H bonds.⁵ Subsequent elimination of a metal hydride⁶ from the trianionic intermediates thus formed from **1** and **4** is catalysed by alkoxides,⁷ giving rise to the central double bond in **2** and **5**, respectively. We have now turned our interest to the more easily accessible *centro*-substituted tribenzotriquinacenes **7a–c**,² from which the tribenzoacepentalene "dianion" **5** with its central double bond can only be formed by elimination of the corresponding metal alkides, hence by cleavage of the central C–alkyl¹ bond (Scheme 2).

Treatment of **7a**, **7b**, and **7c** each with three equivalents of the LSB under strictly identical conditions (hexane, 24 h at 22 °C, 48 h at 69 °C) gave mixtures of "anions" in each case, which were analysed by NMR spectroscopy. Varying amounts of the "monoanions" **8a–c** and the "dianions" **10a–c**, as products of single or double deprotonation of the precursor tribenzotriquinacene, were observed.⁸ Most interesting, however, was the presence of the unsaturated "dianion" **5** in each mixture (Table 1).



Scheme 2

Table 1. Relative abundances of "anions" formed from tribenzotriquinacenes **4^a**, **7a–c** with 3 equiv. of the Lochmann-Schlosser base, as determined by ¹H NMR spectroscopy.⁸

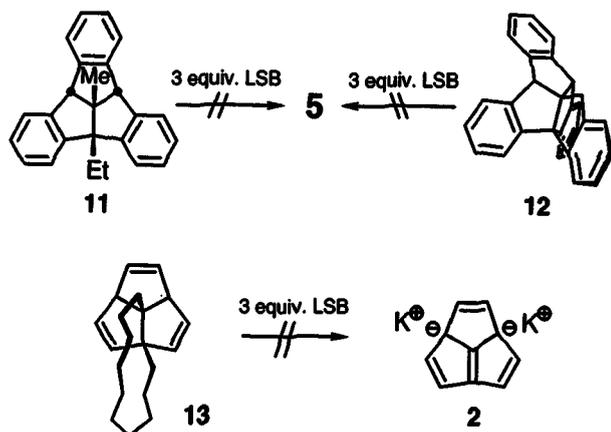
Substrate	Substituent	"Monoanion"	"Dianion"	"Dianion" 5		
4^a	H	8^a	1.0	–	2.3	
7a	CH ₃	8a	2.7	10a	2.3	1.0
7b	C ₂ H ₅	8b	9.3	10b	7.2	1.0
7c	CH ₂ C ₆ H ₅	8c	1.0	10c	1.1	1.0

^a This compound was used as a reference (R = H).^{1b,2}

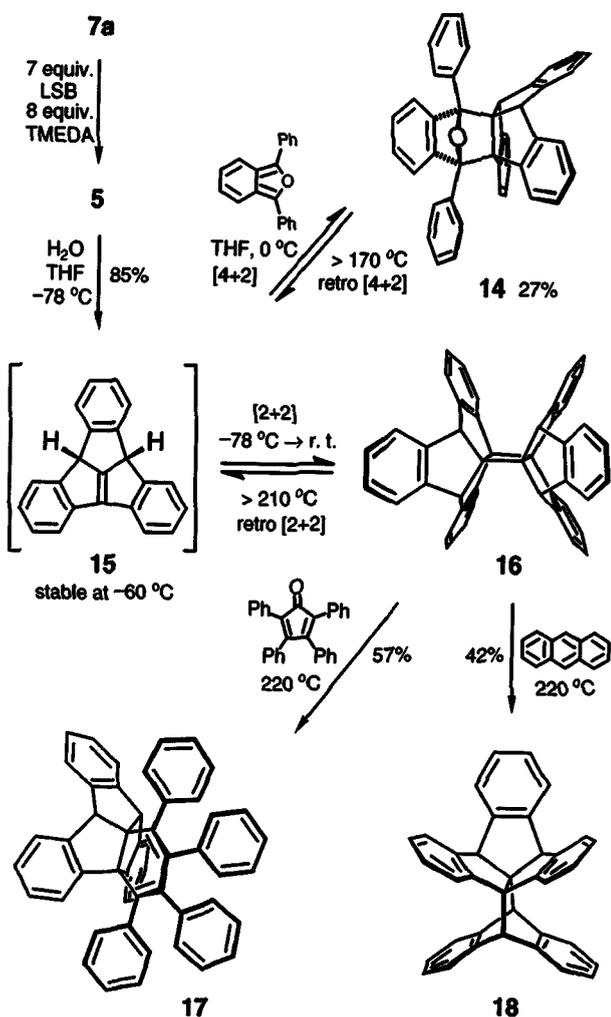
The elimination of the central substituent and subsequent formation of **5** is highly remarkable. Only very few cases of 1,2-eliminations occurring by cleavage of aliphatic C–C bonds have been reported in the literature.⁹ Obviously, the high stability of the unsaturated "dianion" **5** provides the driving force for this process. In addition, the relative stability of the expelled anion (e. g. benzylpotassium from **7c**) governs the amount of **5** in the mixture of anions (Table 1), since the relative abundances of **5** versus **8** plus **10** correlate with the relative stabilities of the expelled anions,⁷ i. e.: H[–] >> Bn[–] > Me[–] > Et[–].

On the basis of these results we suggest a mechanism for the formation of **5** comprising, three consecutive deprotonations of **7** via **8** and **10** to the corresponding "trianions" **9**, followed by a fast elimination of the central substituent as a carbanion from the latter intermediates (Scheme 2). It appears reasonable to assume that the trianionic intermediates **9** are too short-lived and therefore present in concentrations too small to be observed by NMR spectroscopy.¹⁰

The postulated mechanism is corroborated by the fact that 1,10-disubstituted tribenzotriquinacenes **11**¹¹ and **12**,¹² when treated with 3 equiv. LSB under the same conditions as used for **7**, gave only singly and doubly deprotonated species, as observed by NMR spectroscopy, and none of the tribenzoacetalene "dianion" **5** (Scheme 3). Also, an attempted trapping of the anion mixtures with water did not show the possible trapping product tribenzodihydroacetalene **15** or its dimer **16**.¹³ Obviously, the formation of the postulated "trianion" **9** is blocked by the substituent on the third bridgehead position, at least under the conditions employed.



Scheme 3



Scheme 4

Finally, the 1,10-disubstituted triquinacene, **13**, so-called ellacene¹⁴ was treated with LSB (Scheme 3). In analogy to the behavior of **11** and **12**, no deprotonation-elimination product **2** was observed. This indicates that the formation of dihydroacetalenediide **2**^{1a} from the parent triquinacene **1** proceeds by a mechanism analogous to that proposed for **5** (Scheme 2).

Under preparative aspects, the conditions for the formation of tribenzodihydroacetalenediide **5** from *centro*-substituted tribenzotriquinacenes **7a-c** could be greatly improved.¹⁵ When treated with 7 equiv. of LSB and 8 equiv. of TMEDA (N,N,N',N'-tetramethylethylenediamine) as a cosolvent in hexane⁵ (addition of LSB at -30 °C, mixture then stirred for 48h at 22 °C, 72h at 69 °C),¹⁵ the methyl **7a** and the benzyl derivative **7c**, respectively, gave tribenzodihydroacetalenediide **5** as the predominant product, since the dimer **16**¹³ of tribenzodihydroacetalene **15** was isolated in 85 and 78% yield, respectively, after hydrolysis of the mixtures. Under the same conditions, the ethyl derivative **7b** gave only 26% of **16**. This new procedure offers a far better access to **5** and its substitution products, since *centro*-substituted derivatives **7a-c**, especially the methyl derivative **7a**, are more easily prepared – in only three steps from indanedione – than the parent hydrocarbon **4**.²

Cycloadditions across the highly pyramidalized double bond in **15**¹³ lead to structurally interesting polycyclic systems. The tribenzodihydroacetalene **15** can directly be trapped at 0 °C with an excess of diphenylisobenzofuran in THF to form the [4+2]-cycloadduct **14**¹⁶ (Scheme 4). This cycloaddition is reversible above 170 °C, and so is the [2+2]-dimerization of **15** to **16**.¹⁷ Thus, when **16** was heated to 220 °C in the presence of tetraphenylcyclopentadienone or anthracene, the [4+2]-cycloadducts **17** and **18** – in the case of **17** after loss of carbon monoxide – were obtained in 57 and 42% yield, respectively.¹⁶

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- (8) The relative amounts of "monoanion" **8** and "dianions" **10** and **5** in the respective anion mixtures were determined by integration of the respective line intensities in their ¹H NMR spectra. As a representative example: **8a**: ¹H NMR (250 MHz, [D₁₀]-DME/C₆D₆ 3:1): δ = 1.10 (s, 3H, CH₃), 3.80 (s, 2H, 4(7)-H), 5.82 (dt, J = 7.0, 1.0 Hz, 2H, 5'-H), 6.16 (dd, J = 7.5, 1.0 Hz, 2H, 3'-H), 6.65 (dt, J = 7.5, 1.0 Hz, 2H, 4'-H),

- 7.01 (d, $J = 7.0$ Hz, 2 H, 6'-H), 7.02 (m, 2 H, 4''(5'')-H), 7.27 (AA'BB', 2 H, 3''(6'')-H).
- 10a: $^1\text{H NMR}$ (250 MHz, $[\text{D}_{10}]\text{-DME}/\text{C}_6\text{D}_6$ 3:1): $\delta = 1.08$ (s, 3 H, CH_3), 3.50 (s, 1 H, 7-H), 5.76 (dt, $J = 7.0, 1.0$ Hz, 2 H, 5'-H), 6.12 (dd, $J = 7.5, 1.0$ Hz, 2 H, 3'-H), 6.30 (AA'BB', 2 H, 4''(5'')-H), 6.48 (AA'BB', 2 H, 3''(6'')-H), 6.57 (dt, $J = 7.5, 1.0$ Hz, 2 H, 4'-H), 6.92 (d, $J = 7.0$ Hz, 2 H, 6'-H).
- 5: $^1\text{H NMR}$ (250 MHz, $[\text{D}_{10}]\text{-DME}/\text{C}_6\text{D}_6$ 3:1): $\delta = 6.75$ (AA'BB', 6 H, 4'(5')), 7.80 (AA'BB', 6 H, 3'(6')-H).
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- (10) The "dianions" 10a-c slowly abstract deuterons from the NMR solvent $[\text{D}_{10}]\text{-DME}$ to give the corresponding "monoanions" 8a-c ($t_{1/2} < 1$ h at 25 °C).
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- (15) **Preparation of Dipotassium Tribenzodihydroacepentalenediide (5) from 10-Methyltribenzotriquinacene (7a):**
To a stirred suspension of 10-methyltribenzotriquinacene (294 mg, 1 mmol) in 10 mL of *n*-hexane was added dropwise at -30 °C potassium *t*-pentoxide (3.5 mL, 7.0 mmol, 2.0 M), *n*-butyllithium (2.9 mL, 7.0 mmol, 2.44 M) and TMEDA (1.2 mL, 8.0 mmol). The mixture, which turned red immediately, was allowed to warm up slowly to 22 °C, then stirred for 48 h at 22 °C and 72 h at 69 °C. The reaction mixture was filtered under argon and the red-brown residue was washed with three portions of each 20 mL of dry *n*-hexane under an argon atmosphere. The product was dried in vacuo (0.01 Torr) for 1 h to yield 414 mg (117 %) 5, containing some aliphatic impurities. For $^1\text{H NMR}$ data see ref. 8.
- (16) All new products were fully characterized by spectroscopic methods (IR, $^1\text{H NMR}$, $^{13}\text{C NMR}$, MS) and their molecular formulas established by high resolution mass spectrometry.
- 14: $^1\text{H NMR}$ (250 MHz, CDCl_3): $\delta = 4.67$ (s, 1 H), 4.78 (s, 1 H), 6.32 (d, $J = 7.7$ Hz, 1 H), 6.76 (t, $J = 7.5$ Hz, 1 H), 6.91-7.23 (m, 9 H), 7.28-7.66 (m, 13 H), 7.92 (d, $J = 6.9$ Hz, 2 H). - $^{13}\text{C NMR}$ (62.9 MHz, CDCl_3): $\delta = 57.0, 78.6, 83.2, 92.7, 93.0, 120.5, 120.8, 123.4, 124.2, 124.3, 124.4, 124.8, 125.9, 126.1, 126.2, 126.3, 126.5, 127.2, 127.3, 127.4, 127.5, 127.6, 127.7, 128.1, 128.7, 137.7, 137.8, 143.1, 144.3, 144.6, 145.4, 145.7, 146.3, 147.9, 148.5$.
- 17: $^1\text{H NMR}$ (250 MHz, CDCl_3): $\delta = 5.54$ (s, 2 H), 6.53-6.75 (m, 10 H), 6.78-6.94 (m, 3 H), 6.96-7.05 (m, 8 H), 7.06-7.22 (m, 7 H), 7.25-7.33 (m, 2 H), 7.48 (d, $J = 7.5$ Hz, 2 H). - $^{13}\text{C NMR}$ (62.9 MHz, CDCl_3): $\delta = 64.6, 66.5, 68.7, 123.2, 123.7, 124.5, 124.8, 126.0, 126.2, 126.3, 126.9, 127.0, 127.3, 127.4, 128.3, 130.6, 130.9, 131.0, 133.6, 134.2, 135.0, 136.5, 138.8, 139.2, 139.5, 140.3, 140.8, 142.8, 145.0, 148.7$.
- 18: $^1\text{H NMR}$ (250 MHz, CDCl_3): $\delta = 4.43$ (s, 2 H), 4.49 (s, 1 H), 4.88 (s, 1 H), 6.85-7.06 (m, 7 H), 7.07-7.24 (m, 6 H), 7.27-7.33 (m, 2 H), 7.35-7.46 (m, 3 H), 7.48-7.58 (d, $J = 7.7$ Hz, 2 H). - $^{13}\text{C NMR}$ (75.5 MHz, CDCl_3): $\delta = 53.5, 54.8, 59.2, 71.3, 73.4, 122.7, 124.0, 124.4, 125.0, 125.1, 125.4, 125.9, 127.2, 127.3, 127.5, 140.5, 142.3, 145.1, 146.4, 147.0$.
- (17) A differential scanning calorimetry (DSC) curve disclosed a small peak at 216 °C, indicating a thermal transformation of the dimer 16 at this temperature. We are indebted to Dr. H. Butenschön, Max-Planck-Institut für Kohleforschung, Mülheim a. d. Ruhr, for the recording of the DSC curve.