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Synthesis, structural characterization, and skeletal rearrangement of dibenzo tricyclo[3.3.0.0^{2,6}]-1,2,5,6-tetrasubstituted octanes

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Abstract—Dibenzo tricyclo[3.3.0.0^{2,6}]-1,2,5,6-tetrasubstituted octanes, the 'twisted' highly strained valence isomers of substituted dibenzo[*a*,*e*]cyclooctatetraenes, were synthesized and their structure characterized by single-crystal X-ray analysis. Their skeletal rearrangement was experimentally observed.

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The structural diversity of the valence isomers of strained ring systems and the intramolecular skeletal rearrangements between these valence isomers have long been of great interest from the point of view of synthetic applications and mechanistic studies.[1] Among strained ring systems, tricyclo[3.3.0.0^{2,6}]octane (**I**),[2–4] tricyclo[3.3.0.0^{2,6}]-octa-3,7-diene (**II**), and tricyclo[3.3.0.0^{2,6}]-octa-3-ene (**III**),[5–8] have attracted much attention and have been characterized by spectroscopic measurements and predicted by theoretical calculations (Fig. 1). However, their structures have not been determined by single-crystal X-ray structural analysis.[9]

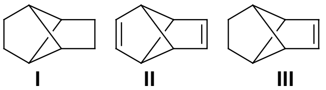
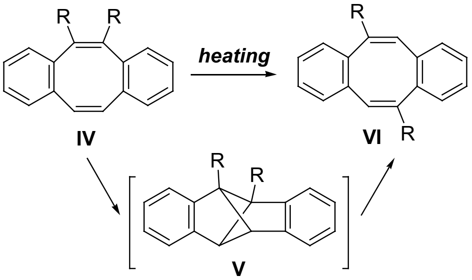


Figure 1.

In 1964, Stiles and Burckhardt reported a novel skeletal rearrangement of 5,6-disubstituted dibenzo[*a*,*e*]cyclooctatetraenes **IV** to 5,11-disubstituted dibenzo[*a*,*e*]cyclooctatetraenes **VI** either thermally or photochemically (Scheme 1).[10a] The authors proposed a 'twisted' intermediate (**V**, Scheme 1),[3a] which possesses the carbon skeleton central to **I**–**III**. Although structurally and mechanistically interesting, however, the proposed intermediate **V** has never been prepared. In this letter, we would like to report the first preparation and structural characterization of this type of highly strained compounds (Scheme 2). Complete transformation of the isolated 'twisted' intermediates **2** to the cyclooctatetraene derivatives **3** was experimentally observed.

Lithiation of diiodo compounds **4** (**4a**: R = Et, **4b**: R = Pr) in diethyl ether with *t*-BuLi generated their corresponding dilithio intermediates **1** (**1a**: R = Et, **1b**:



Scheme 1.

Keywords: Dibenzo[*a*,*e*]cyclooctatetraenes; Dibenzo tricyclo[3.3.0.0^{2,6}]-1,2,5,6-tetrasubstituted octanes; Dicopper compounds; Dilithium compounds; Skeletal rearrangement.

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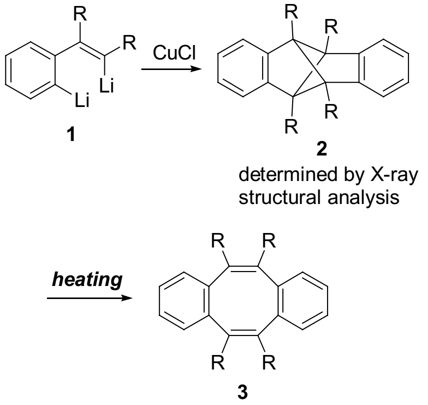


Scheme 2.

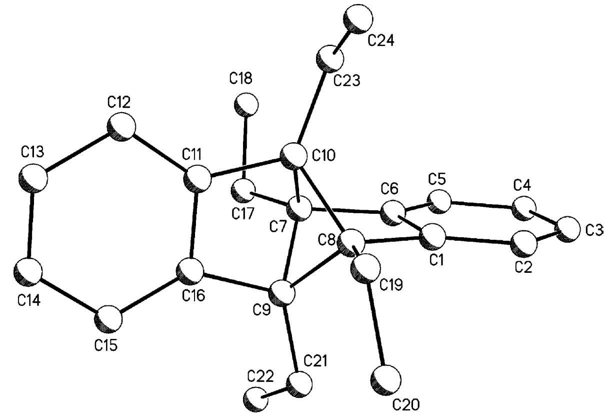


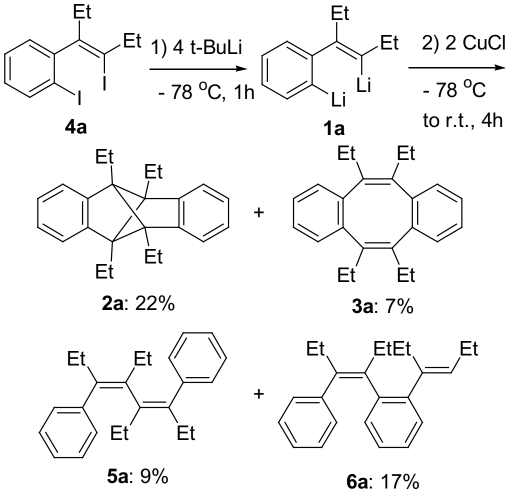
Figure 2.

R = Pr) in quantitative yields (Scheme 3).[11] Addition of 2 equiv of CuCl to the diethyl ether solution of **1a** (R = Et) afforded two cyclic products **2a** and **3a**, along with two linear products **5a** and **6a**, after the reaction mixture was stirred from −78 °C to room temperature for 4 h and was quenched with 3 N HCl (Scheme 3). Products **2a**, **3a**, **5a**, and **6a** were obtained in 22%, 7%, 9%, and 17% isolated yields, respectively. When the dilithium reagent **1b** (R = Pr) was used, its corresponding products were obtained in similar yields. It is noteworthy that formation of copper mirror is observed on the wall of the reaction vessel.

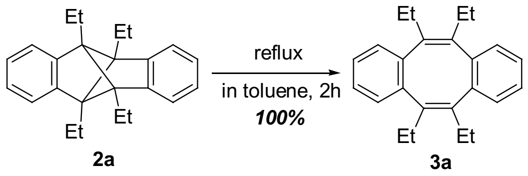
Compound **2a** was stable at room temperature,[12] its structure was determined by X-ray analysis and shown in Figure 2.[13] As determined by electron diffraction,[3c] the highly puckered four-member ring in **I** has an average C–C bond length 1.556 Å with a puckering angle of 53.3°, while the average C–C bond length was calculated to be 1.548 Å with a puckering angle of 55.8° by using MM3 and 1.552 Å with a puckering angle of 49.5° by using MM4, respectively.[3i] For **II**, ab initio MO calculation gave the C–C bond length in the puckered four-member ring as 1.570 Å, the length of the C–C single bond outside of the puckered four-member ring as 1.526 Å, and the C–C double bond length as 1.321 Å.[8a] For **2a**, the determined lengths of the C–C bonds in the puckered four-member ring were 1.597(3), 1.588(3), 1.595(3), 1.590(3) Å, respectively, for C7–C9, C7–C10, C8–C9, and C8–C10, with an average length of 1.593 Å, which is much longer than those reported numbers. The puckering angle of **2a** is determined to be 58.48° (or 58.70°), which is bigger than those reported numbers.

In order to obtain experimental evidence for the proposed transformation from **2** to **3**, the isolated compound **2a** was dissolved in toluene and the solution was heated to reflux (Scheme 4). Within 2 h, **2a** disappeared completely and transformed to **3a** in a quantitative yield.[14] This is the first experimental evidence for such skeletal rearrangement.

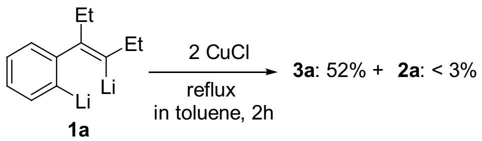
Furthermore, the CuCl-mediated reaction was carried out in reflux toluene (Scheme 5). This experiment resulted in the formation of the substituted dibenzo[*a*,*e*]cyclooctatetraene **3a** in 52% isolated yield as the major product. The intermediate **2a** was obtained in less than 3% yield. No linear products **5a** and **6a** were



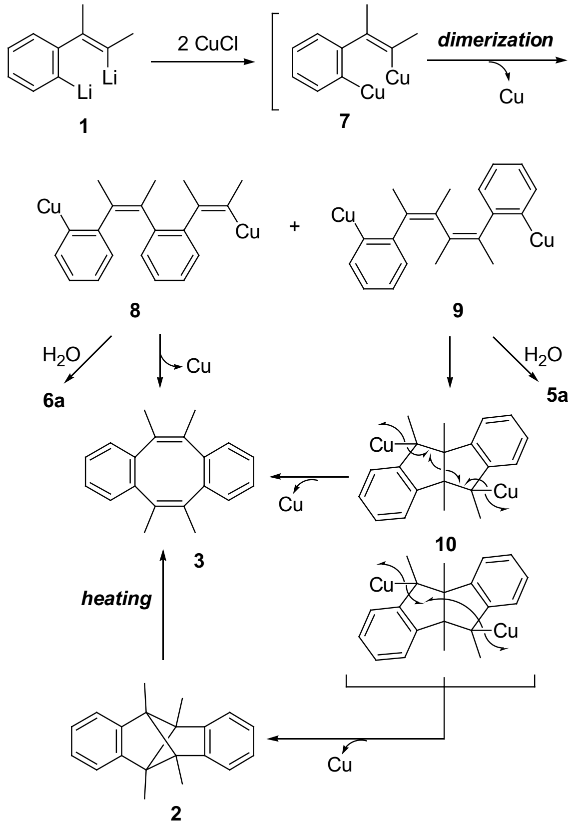
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

obtained. These results are informative for understanding the reaction mechanisms.

A proposed reaction mechanism is given in Scheme 6. A dicopper reagent **7** is assumed to be the first intermediate. Dimerization of aryl lithium and vinyl lithium compounds in the presence of CuX has been one of the frequently used methods to achieve synthesis of biaryl and dienyl compounds.[15,16] Therefore, dimerization of two molecules of **7** would afford two new dicopper reagents **8** (via cross-coupling of one vinyl copper with one aryl copper) and **9** (via coupling of two vinyl copper). Substituted dibenzo[*a*,*e*]cyclooctatetraenes **3** can be directly formed from **8** via intramolecular coupling. The diarylcopper intermediate **9** undergoes intramolecular radical attack leading to the formation of **10**, which can generate either **3** or **2** via different radical processes.

In conclusion, we report here the preparation, structural characterization, and skeletal rearrangement of the 'twisted' highly strained valence isomer of cyclooctatetraene derivatives. Further investigation into the reaction mechanisms and the reaction scope are under progress.

Acknowledgements

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12. Selected data for **2a**: ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.80 (t, $J = 7.5$ Hz, 12H), 1.64 (q, $J = 7.5$ Hz, 8H), 7.01–7.12 (m, 8H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 10.9 (4C), 19.3 (4C), 91.6 (4C), 119.5 (4C), 125.6 (4C), 145.1 (4C). HRMS calcd for $C_{24}H_{28}$ 316.2191, found 316.2194.

13. Crystal structure data for compound **2a**: molecular formula $C_{24}H_{28}$, $M_w = 316.46$, crystal dimensions $0.45 \times 0.25 \times 0.25$ mm, monoclinic, space group $P2(1)/c$, $a = 16.160(3)$ Å, $b = 15.269(3)$ Å, $c = 16.389(3)$ Å, $\alpha = 90°$, $\beta = 108.54(3)°$, $\gamma = 90°$, $V = 3834.0(13)$ Å^3, $Z = 8$, final R indices $[I > 2\sigma(I)]$, reflections collected/unique 32,233/8352 [R(int) = 0.0493], number of observations $[I > 2\sigma(I)]$ 3250, parameters 471. Absorption correction: numeric (min./max.-transmission 0.985/0.654), $R_1 = 0.0696$, $wR_2 = 0.1836$. Rigaku RAXIS RAPID IP diffractometer (MoKα radiation, $\lambda = 0.71073$ Å), $T = 293(2)$ K. The structure was solved by direct methods and refined against F^2 for all observed reflections. Programs used: Sheldrick, G. M. (1997) SHELXS97. CCDC 223354 contains the supplemental crystallographic data for this paper. These data can be obtained from the Cambridge Crystallographic Data Centre (Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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