

# Synthesis and reaction of 1,4-acetal-bridged 2,3,5,6-tetramethylidenebicyclo[2.2.0]hexane: the first Diels–Alder route to Dewar benzenes

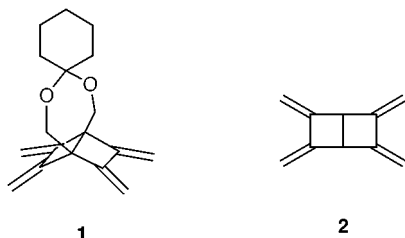
Masakazu Ohkita, Takanori Suzuki and Takashi Tsuji\*

Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan.  
E-mail: tsuji@sci.hokudai.ac.jp

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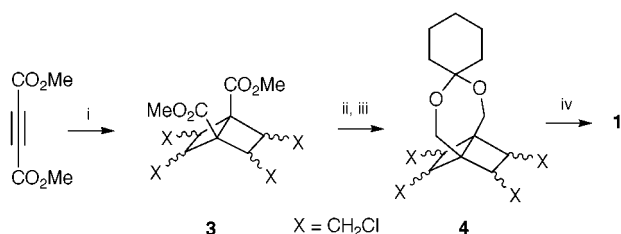
The 1,4-acetal-bridged derivative of hitherto unknown 2,3,5,6-tetramethylidenebicyclo[2.2.0]hexane, which produces the Dewar benzene skeleton through two successive Diels–Alder reactions with dienophiles, has been synthesized in four steps from dimethyl acetylenedicarboxylate and 1,4-dichlorobut-2-ene.

In the course of our studies on the chemistry of highly strained cyclophanes generated from the corresponding Dewar derivatives,<sup>1</sup> we were interested in developing a new general method for the preparation of Dewar benzenes,<sup>2</sup> especially a versatile one that is applicable to the synthesis of Dewar isomers of polyacenes.<sup>3</sup> An intriguing possibility is the application of hitherto unknown 2,3,5,6-tetramethylidenebicyclo[2.2.0]hex-



ane skeleton **2**<sup>4</sup> because its two successive Diels–Alder reactions with dienophiles formally produce a Dewar benzene structure and subsequent dehydrogenation of the two six-membered rings thus formed would give the corresponding 9,10-Dewar anthracene skeleton. We designed a 1,4-acetal-bridged derivative **1** to prevent an undesired aromatization of the Dewar benzene product under the thermal cycloaddition conditions. Here we report an efficient synthesis of **1** and its Diels–Alder reaction with dienophiles, which represents the first preparation of a Dewar benzene structure by a Diels–Alder reaction.

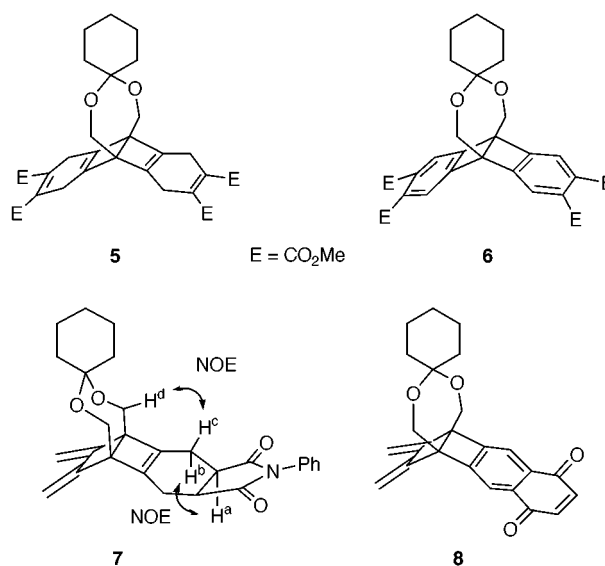
The synthesis of **1** is simple and straightforward (Scheme 1).<sup>†</sup> Thus, irradiation of dimethyl acetylenedicarboxylate (DMAD) in 1,4-dichlorobut-2-ene with a high-pressure mercury lamp at 12 °C afforded a mixture of bicyclo[2.2.0]hexane derivatives **3** in 32% yield. LiAlH<sub>4</sub> reduction of the esters **3** followed by treatment of the resultant diols with 1,1-dimethoxycyclohexane under the influence of a catalytic amount of TsOH provided cyclohexylidene acetal **4** in 48% yield. Quadruple dehydrochlorination of **4** with *t*-BuOK in the presence of 18-crown-6 at



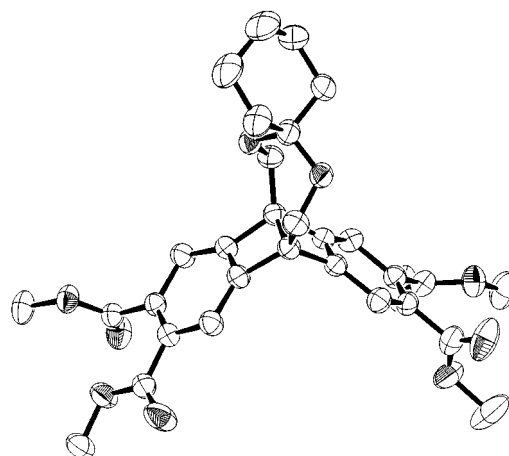
**Scheme 1** Reagents and conditions: i, *hν*, 1,4-dichlorobut-2-ene, 12 °C, 32%; ii, LiAlH<sub>4</sub>, Et<sub>2</sub>O, 90%; iii, 1,1-dimethoxycyclohexane, TsOH, benzene, 40%; iv, *t*-BuOK, 18-crown-6, THF, room temp., 78%.

room temperature afforded desired **1** in 78% yield as a colorless oil. Compound **1** is prone to polymerization, as has been observed in other bisdiene systems,<sup>5</sup> but shows adequate stability to allow its chromatographic purification and spectroscopic characterization.<sup>‡</sup>

Reaction of **1** with DMAD proceeded smoothly in benzene at 65 °C to afford 1:2 adduct **5** in 65% yield. The structure of **5** was



confirmed by X-ray structural analysis (Fig. 1), which clearly indicates a Dewar benzene structure along with nearly flat cyclohexa-1,4-diene rings and a seven-membered acetal ring adopting a twist conformation in the solid state.<sup>§</sup> Dehydrogenation of **5** to 9,10-Dewar anthracene derivative **6** was accomplished (87% yield) with activated MnO<sub>2</sub> in benzene at room temperature. Reaction of **1** with *N*-phenylmaleimide (65 °C,



**Fig. 1** Molecular structure of **5**. Hydrogen atoms are omitted for clarity.

4 h) gave **7** in 75% yield as a major product, whose stereochemistry was determined by examining the NOESY spectrum; H<sup>c</sup> which is *trans* to H<sup>a</sup> exhibits a NOE with H<sup>d</sup>. The formation of **7** may be most reasonably explained by the *exo*-orientation approach of the dienophile from the *endo*-face of **1**. Reaction of **1** with benzo-1,4-quinone (65 °C, 44 h) followed by successive treatment of the adduct with DDQ in acetonitrile and activated MnO<sub>2</sub> in benzene afforded **8**, a possible precursor for cyclic polyacenequinone derivatives, in 55% yield.

In summary, we have successfully developed a novel Diels–Alder route to Dewar benzenes as well as Dewar polyacenes by introducing **1** as a new bisdiene molecule. Further elaboration and an application of the present method to the syntheses of novel cyclophanes as well as polyacenes are the subjects of our ongoing study.

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## Notes and references

† All new compounds were characterized spectroscopically.

‡ Selected data for **1**: δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>) 1.40 (m, 2 H), 1.49 (m, 4 H), 1.69 (m, 4 H), 4.02 (s, 4 H), 4.89 (s, 4 H), 5.28 (s, 4 H); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>) 22.79, 25.71, 33.27, 60.99, 62.14, 103.62, 104.10, 150.46; ν(neat)/cm<sup>-1</sup> 2932, 2860, 1100, 882; λ<sub>max</sub>(hexane)/nm (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 231 (7800), 238 (16700), 255 (sh, 6900); m/z 270 (M<sup>+</sup>, 0.5), 172 (100).

§ Crystal data for **5**: C<sub>30</sub>H<sub>34</sub>O<sub>10</sub>, *M* = 554.59, colorless crystals (0.2 × 0.2 × 0.2 mm), monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 7.814(2), *b* = 20.404(2),

*c* = 17.643(2) Å, β = 101.77(1)°, *V* = 2753.8(6) Å<sup>3</sup>, *D*<sub>c</sub> = 1.338 g cm<sup>-3</sup>, *Z* = 4, Mo-Kα radiation (λ = 0.71069 Å), *T* = 296 K, μ = 1.00 cm<sup>-1</sup>, *F*(000) = 1176. A total of 6494 unique reflections were collected, of which 3903 observed reflections [*I* > 3σ(*I*)] were used in the structure solution (direct methods) and refinement (full-matrix least-squares) to give final *R* = 0.041 and *R*<sub>w</sub> = 0.037. CCDC 182/1399. See <http://www.rsc.org/suppdata/cc/1999/1999/> for crystallographic data in .cif format.

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