

Thermally-induced Reorganization of [*n*]-Ladderanes

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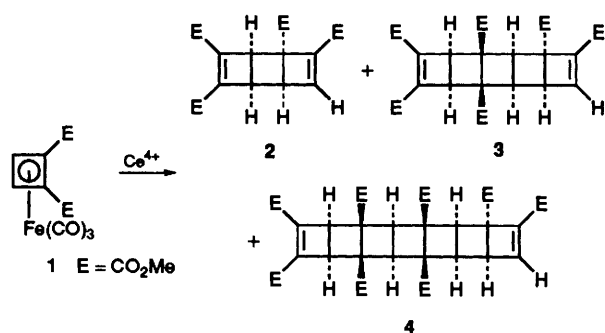
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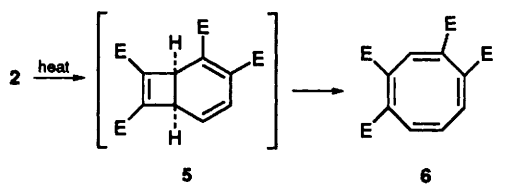
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Thermolysis of [3]-, [5]- and [7]-ladderane derivatives has unravelled some novel, deep-seated rearrangements of these fascinating molecular arrays.

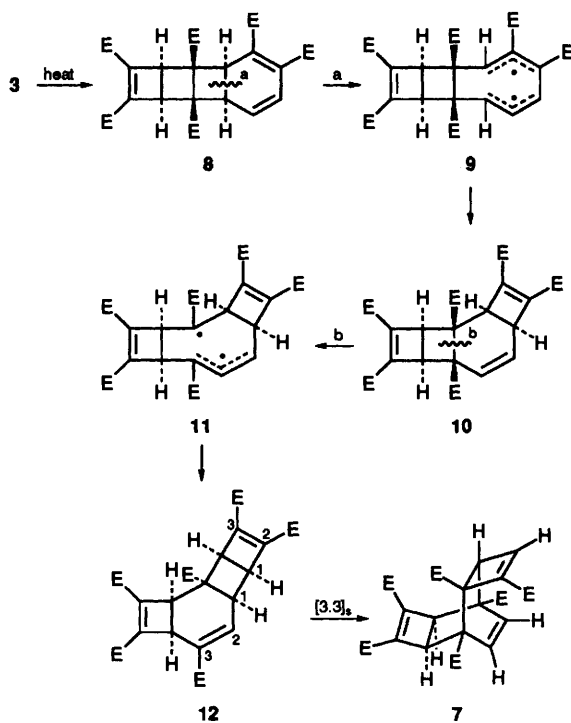
In a recent communication, we disclosed that 1,2-bismethoxycarbonylcyclobutadiene, disengaged from its iron tricarbonyl complex 1, undergoes oligomerization through serial, FMO controlled cycloadditions to furnish [3]-2, [5]-3 and [7]-ladderane 4 derivatives (Scheme 1).¹ The availability of such



Scheme 1



Scheme 2

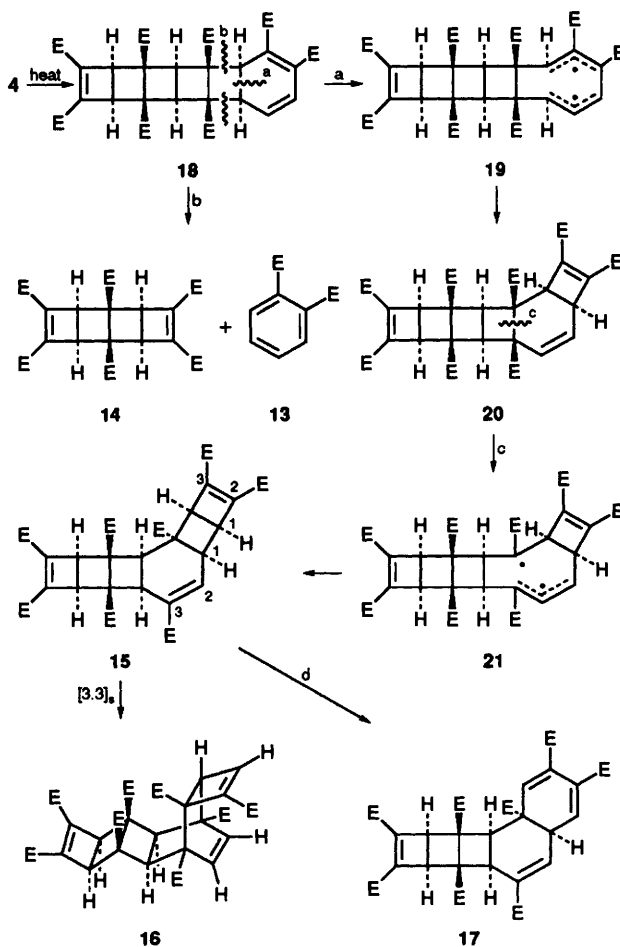


Scheme 3

multifused cyclobutanoid arrays for the first time,² prompted us to explore the potentially rich but as yet unexplored chemistry of these unusual structures. Herein, we report on the reactivity pattern displayed by ladderanes under thermal activation, which eventuates in novel, deep-seated structural reorganization.

When [3]-ladderane 2 was heated (CHCl₃, reflux, 20 h), 1,2,4,5-tetrakis(methoxycarbonyl)cyclooctatetraene 6† was isolated as the only product in 85% yield. The presence of 16 lines (8 olefinic Cs) in the ¹³C NMR and 4-methyl ester resonances in the ¹H NMR spectra indicated that only the static structure 6, arising through 5, was present and no evidence of bond-shifting³ was observed under ambient conditions (Scheme 2).

[5]-Ladderane 3 in refluxing benzene (48 h) also furnished a single crystalline product in 60% yield. Its ¹H and ¹³C NMR spectral data (presence of three isolated double bonds and three olefinic protons) clearly indicated a major structural change and further incisive analyses (NOE) led to the formulation 7.† This structure was further secured through X-ray crystal structure determination.‡ We envisage the formation of 7 from 3 through a series of radical-mediated bond



Scheme 4

reorganizations in which as many as 14 (σ and π) bond-making and -breaking events take place in a single pot reaction (Scheme 3). Particularly noteworthy is the sequential 'slipping' of the two cyclobutane rings in **8** to the 'angular' position in **12** via **10**. Also, the stabilized diradicals **9** and **11** undergo stereoselective ring closure to eventuate in an all *cis* stereochemistry in **12** required for the terminal [3.3] sigmatropic process leading to **7**.

The [7]-ladderane **4** on thermolysis (C_6H_6 , reflux, 15 h) furnished a complex mixture from which dimethyl phthalate **13** (8%), **14**[†] (8%), **15**[†] (14%), **16**[†] (7%) and **17**[†] (28%) could be isolated through extensive column chromatography (silica gel) (Scheme 4).[§] The *sym*-[4]-ladderane **14** was recognized readily on the basis of its three line 1H and seven line ^{13}C NMR spectra. The structure of **15** could not be gleaned readily from the spectral data alone and was secured through X-ray crystal structure determination, Fig. 1.[¶] The structure of **16** is similar to the product **7** obtained from [5]-ladderane **3** (*vide supra*) and is in consonance with the detailed analysis of its 1H NMR (NOE and NOESY) data. Finally, the structure of **17** was determined through incisive analysis of the 1H and ^{13}C NMR data (decoupling, NOE and COSY) and on the basis of the observation (NMR monitoring) that the angular ladderane **15** converts into **16** and **17** on heating. Formation of **13**–**17** from **4** is depicted in Scheme 4. While the formation of **13** and **14** is straightforward through the intermediate **18**, the novel cyclobutane 'slipping' process is once again operative here and leads stereoselectively to the angular polycyclobutanoids **20** and **15** via **19** and **21**, respectively. The cyclobutane 'slipping' is most likely a thermodynamically-driven strain relaxation process, which breaks and partitions the linearly-fused cyclobutane arrays in **4** to **15** and in **3** to **12**. The middle cyclohexene ring in **15** has an all *cis* arrangement and undergoes either a [3.3]-shift or a cyclobutene ring opening to terminate in **16** and **17**, respectively.

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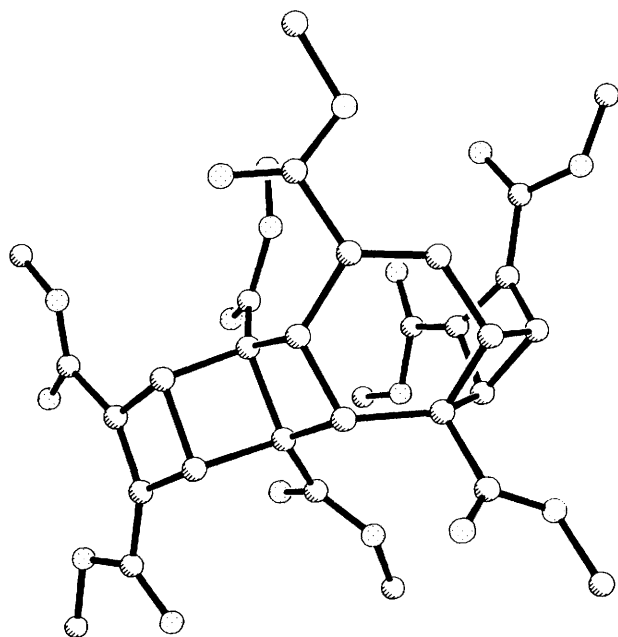


Fig. 1 A perspective of structure **15**

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Footnotes

[†] All new compounds were characterized on the basis of their 1H and ^{13}C NMR ($CDCl_3$) and microanalytical data. Selected spectral data for **6**: 1H NMR (400 MHz): δ 7.29 (1H, d, J 1.0 Hz), 7.27 (1H, br d, J 3.8 Hz), 6.27 (1H, d of $\frac{1}{2}$ ABq, J_1 11.7, J_2 3.8 Hz), 6.11 (1H, t of $\frac{1}{2}$ ABq, J_1 11.7, $J_2 = J_3$ 1.0 Hz), 3.80 (3H, s), 3.80 (3H, s), 3.76 (3H, s), 3.75 (3H, s). For **7**: 1H NMR (400 MHz): δ 6.58 (1H, d, J 1.2 Hz), 6.19 (1H, $\frac{1}{2}$ ABq, J 8.0 Hz), 6.17 (1H, $\frac{1}{2}$ ABq, J 8.0 Hz), 3.82 (3H, s), 3.81 (3H, s), 3.78 (3H, s), 3.74 (3H, s), 3.70 (3H, s), 3.69 (3H, s), 3.62 (1H, br s), 3.56 (1H, $\frac{1}{2}$ ABq, J 4.9 Hz), 3.33 (1H, $\frac{1}{2}$ ABq, J 4.9 Hz). For **14**: 1H NMR (400 MHz): δ 3.82 (12H, s), 3.63 (4H, s), 3.55 (6H, s). For **16**: 1H NMR (400 MHz): δ 6.73 (1H, d, J 0.7 Hz), 6.16 (1H, $\frac{1}{2}$ ABq, J 7.9 Hz), 5.96 (1H, d of $\frac{1}{2}$ ABq, J_1 7.9, J_2 0.7 Hz), 3.83 (3H, s), 3.79 (3H, s), 3.76 (3H, s), 3.75 (3H, s), 3.71 (1H, d, J 2.4 Hz), 3.70 (3H, s), 3.64 (3H, s), 3.63 (1H, br s), 3.60 (3H, s), 3.55 (3H, s), 3.50 (1H, d, J 2.4 Hz), 3.15 (1H, $\frac{1}{2}$ ABq, J 9.7 Hz), 3.10 (1H, $\frac{1}{2}$ ABq, J 9.7 Hz). For **17**: 1H NMR (400 MHz): δ 7.38 (1H, br s), 6.75 (1H, br s), 6.33 (1H, d, J 5.3 Hz), 4.40 (1H, d, J 5.3 Hz), 3.95 (1H, br d, J 8.7 Hz), 3.84 (1H, d, J 2.4 Hz), 3.82 (3H, s), 3.80 (1H, d, J 8.7 Hz), 3.80 (6H, s), 3.74 (1H, d, J 2.4 Hz), 3.74 (3H, s), 3.72 (3H, s), 3.56 (3H, s), 3.45 (3H, s), 3.23 (3H, s).

[‡]We thank Professor T. N. Guru Row and his colleagues at I.I.Sc., Bangalore for this X-ray crystal structure determination.

[§] The yield and percentage of products obtained from **4** showed considerable variation as a function of time and the results reported here are of a typical run.

[¶] Crystal data for $C_{32}H_{32}O_{16}$, monoclinic, space group $C2/c$, $a = 32.810(4)$, $b = 10.760(2)$, $c = 18.624(3)$ Å, $\beta = 106.17(2)^\circ$, $V = 6315(2)$ Å³, $Z = 8$, $D_c = 1.415$ Mg m⁻³, $T = 293$ K, 4521 reflections measured, range ($0 \leq \theta \leq 23^\circ$) and $0 \leq h \leq 35$, $0 \leq k \leq 11$, $-20 \leq l \leq 20$; 4162 unique reflections ($R_{int} = 0.064$, averaging double measured) and 1317 (29%) observed with $I \geq 3\sigma(I)$, $\mu = 1.1$ cm⁻¹. Mo-K α Radiation ($\lambda = 0.71073$ Å), graphite crystal monochromator, SIEMENS R3m/v single crystal diffractometer, ω - 2θ scan technique. Data corrected for Lorentz and polarization but not for absorption. The structure was solved by direct methods (SHELXTL-Plus)⁴ and anisotropically refined using blocked matrix technique. H-atoms calculated to their idealized positions and refined as riding atoms with fixed isotropic temperature factors ($U = 0.08$ Å²). The final R factor was 0.090 and $R_w = 0.092$. The relatively high R value is probably the consequence of the very poor scattering power of the crystal, resulting in the poor ratio of the number of observations to parameters. Nevertheless, the stereostructure of the molecule is clear, Fig. 1. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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