

A Norbornadiene–Cyclobutadiene Cycloaddition Cascade: Novel Intramolecular $\sigma^2 + \pi^2$ Trapping of a Cyclobutane Ring

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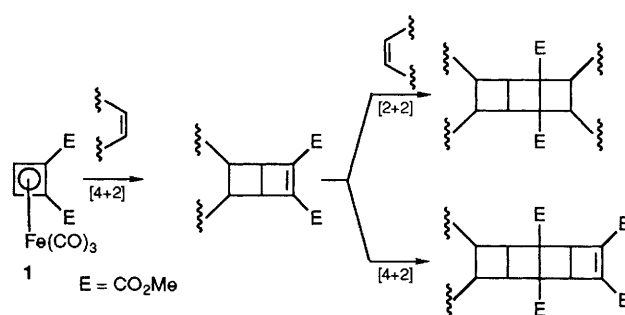
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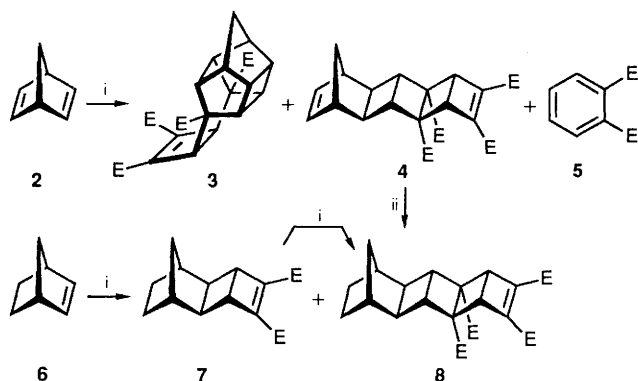
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Norbornadiene and 1,2-bismethoxycarbonylcyclobutadiene furnish a novel heptacyclic system **3** (whose X-ray crystal structure has been determined) and an annulated pterodactylane derivative **4** in a single step.

There is considerable current interest in the design of rigid spacer molecules with interspersed chromophoric or functional groups for diverse applications. In the assembly of such molecular arrays, multiple, fused cyclobutane rings as spacers offer considerable latitude in terms of rigidity, steric disposition, distal variation and an accommodating σ framework.¹ For gaining access to such fused polycyclobutanoid systems, 1,2-bismethoxycarbonylcyclobutadiene, disengaged from its tricarbonyliron complex **1**,² appeared quite promising *via* tandem cycloaddition protocols as indicated in Scheme 1. In this context, we have studied the reaction of **1** with norbornadiene **2** and our results, besides validating the principle behind Scheme 1, have also led to the observation of an unpreceden-



Scheme 1



Scheme 2 Reagents and conditions: i, **1**, CAN, acetone, 0–5 °C; ii, Pd/C–H₂, EtOAc.

ted intramolecular $\sigma^2 + \pi^2$ addition involving a norbornene π -bond and a cyclobutane σ -bond.

Reaction of **1** with an excess of norbornadiene **2** in the presence of cerium(IV) ammonium nitrate (CAN) and careful chromatographic (SiO₂ gel) separation furnished two 2 : 1 addition products **3**† (18%) and **4**‡ (21%) along with dimethyl phthalate **5** (30%). While the ¹H and ¹³C NMR spectral data of **3** established the presence of seven rings and C_s symmetry, its unique formulation was unambiguously arrived at through an X-ray crystal structure determination (Fig. 1).‡ Structure **4** for the second 2 : 1 adduct was derived through analysis of the ¹H and ¹³C NMR data and the following correlation. Reaction of norbornene **6** with **1** in the presence of CAN led to the formation of a 1 : 1 [4 + 2] adduct **7**† (34%) and a 2 : 1 adduct **8**‡ (63%). The adduct **7** on further exposure to **1** was transformed into **8**, which was shown to be identical with the product of partial hydrogenation of **4**. Thus, a caged heptacyclic system **3** and a norborneno pterodactylane derivative **4**³ were realised from **1** and **2** in a single step (Scheme 2).

† All new compounds were fully characterised on the basis of their spectral and analytical data. Selected spectral data: **3**: ¹H NMR (100 MHz, CDCl₃): δ 3.76 (6H, s), 3.66 (6H, s), 3.24 (2H, s), 2.92 (2H, br s), 2.58 (6H, br s), 1.61 (1H, ½ ABq, *J* 12 Hz) and 1.18 (1H, ½ ABq, *J* 12 Hz); ¹³C NMR (25.0 MHz, CDCl₃): δ 175.5, 161.7, 145.9, 54.2, 51.8, 45.1, 44.2, 42.5, 42.3, 42.1, 40.7 and 34.2. **4**: ¹H NMR (400 MHz, CDCl₃): δ 5.98 (2H, br s), 3.78 (6H, s), 3.60 (6H, s), 3.50 (2H, s), 2.78 (2H, br s), 2.34 (2H, br s), 2.14 (2H, br s), 1.59 (1H, ½ ABq, *J* 9.8 Hz) and 1.24 (1H, ½ ABq, *J* 9.8 Hz); ¹³C NMR (25.0 MHz, CDCl₃): δ 169.5, 161.1, 143.4, 135.5, 57.9, 52.0, 51.3, 46.2, 44.8, 43.9, 40.2 and 39.2. **7**: ¹H NMR (100 MHz, CDCl₃): δ 3.78 (6H, s), 2.92 (2H, dd, *J*₁ = *J*₂ = 1 Hz), 2.24 (2H, br s), 2.10 (2H, br s) and 1.83–0.90 (6H, m); ¹³C NMR (25.0 MHz, CDCl₃): δ 162.0, 143.8, 51.8, 45.1, 44.9, 39.7, 32.5 and 27.7. **8**: ¹H NMR (400 MHz, CDCl₃): δ 3.77 (6H, s), 3.63 (6H, s), 3.44 (2H, s), 2.38 (2H, br s), 2.36 (2H, br s), 2.12 (2H, br s), 1.80 (1H, ½ ABq, *J* 10.36 Hz), 1.44 (2H, d, *J* 6.9 Hz), 1.26 (1H, ½ ABq, *J* 10.36 Hz) and 1.10 (2H, dd, *J*₁ 1.8, *J*₂ 2.1 Hz); ¹³C NMR (25.0 MHz, CDCl₃): δ 169.7, 161.2, 143.2, 57.6, 52.0, 51.4, 46.1, 45.4, 43.8, 39.5, 32.8 and 27.5.

‡ *Crystal data* for **3**: C₂₃H₂₄O₈; *M*_r = 428.43; Triclinic, space group *P*1̄, *a* = 9.513(2), *b* = 11.189(1), *c* = 11.481(1) Å, α = 114.53(1), β = 92.22(1), γ = 112.33(2)°, *V* = 1000.0(3) Å³; *Z* = 2; *D*_c = 1.423 g cm^{−3}, *F*(000) = 452, *T* = 295 K, Cu-K α radiation, λ = 1.5418 Å. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using a thin transparent crystal of dimension 0.4 × 0.3 × 0.3 mm in the ω -2 θ mode. A total of 4225 reflections were recorded of which 3067 were 'observed' with $|F_o| \geq 5.0\sigma(|F_o|)$. The structure was solved by direct methods⁵ and full matrix least-squares refinement⁶ with the non-H atoms anisotropic and H atoms isotropic converged at *R* = 0.057. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1. Enquiries regarding the crystal structure should be addressed to the Bangalore group.

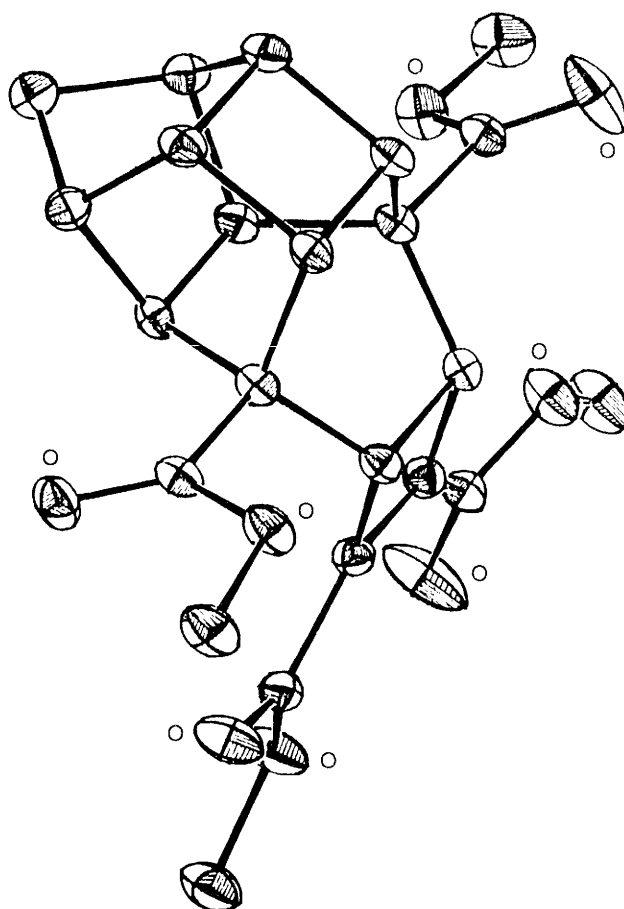
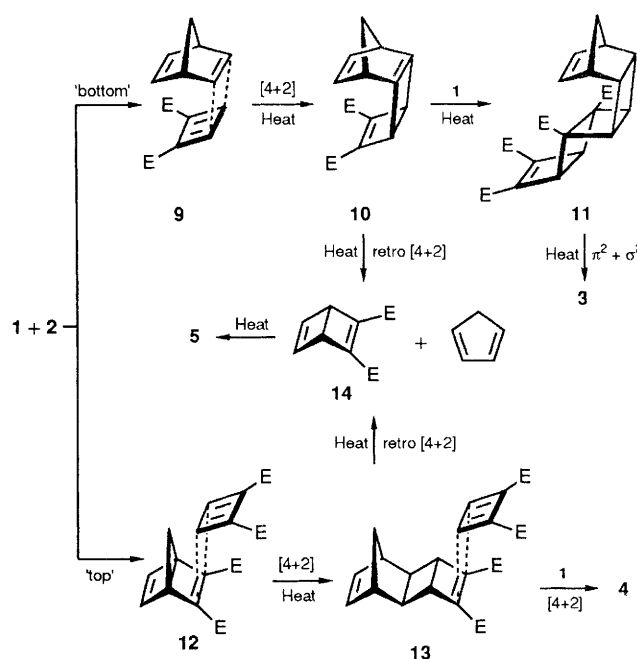


Fig. 1 Crystal structure of compound **3**



Scheme 3

It is noteworthy that norbornadiene engages **1** from both the 'bottom' side **9** as well as the 'top' side **12**, to furnish intermediate [4 + 2] adducts **10** and **13**, respectively (Scheme 3). The sterically demanding mode of addition **9** is presumably compensated through the stabilising secondary orbital interac-

tion with the distal double bond of **2**. The initially formed 1 : 1 adducts **10** and **13** further react readily with **1** as envisaged in Scheme 1 to furnish **11** and **4**, respectively. We envisage the formation of the heptacyclic product **3** from the intermediate **11** via an intramolecular $\sigma^2 + \pi^2$ addition involving the spatially proximal cyclobutane σ -bond of the pterodactylane moiety and the norbornene π -bond, (Scheme 3). Since thermal cycloaddition **11** $\rightarrow$ **3** is symmetry-forbidden, it most likely proceeds through the intervention of a 1,4-diradical species. The participation of the strained central σ -bond of bicyclo[1.1.0]butanes and bicyclo[2.1.0]pentanes in cycloadditions has been observed previously⁴ but this is possibly the first example of the involvement of a cyclobutane σ -bond, in this case the central σ -bond of a bicyclo[2.2.0]hexane moiety. Lastly, the substantial formation of dimethyl phthalate **5** can be attributed to the competitive [4 + 2]cycloreversion in either **10** or **13** or to the Dewar benzene **14** and aromatisation.

Further efforts to exploit the efficacy of **1** in rapidly assembling linearly fused polycyclobutanoid arrays are currently underway.

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