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Diarylmethylenecyclopropabenzenes in Cycloaddition

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Abstract: Diarylmethylenecyclopropabenzenes react in [2+4] cycloaddition at the 'cyclopropene' bridge bond rather than at the exocyclic olefin. The results are in accord with computational data.

The alkylidenecycloproparenes, e.g. **1** and **2**, have attracted considerable attention in recent times as unusual, highly strained synthetic molecules[1] whose physicochemical properties have been assessed[2] and whose chemical behaviour with a variety of reagents has been thoroughly investigated.[3] Although the reactivity of the methylenecyclopropa[*b*]naphthalenes **2** towards cycloaddition has been addressed,[4] analogous behaviour of the cyclopropabenzene analogues **1** has not been reported.

When diarylmethylenecyclopropa[*b*]naphthalenes **2** react in cycloadditions a high regioselectivity is recorded for the exocyclic double bond and the product of reaction, e.g. **5**, follows from the formation of a spirocycle, e.g. **4**, that is able to provide strain relief by ring-expansion (Scheme 1).[4] No cycloaddition to the internal, strained 'cyclopropene' bridge bond is observed despite the fact that parent cyclopropabenzene (**3**), with its HOMO located at the bridge,[5] provides many such examples.[6,7] This observation is not too surprising when it is remembered that any addition to the bridge bond of **2** leads to a high energy *o*-quinodimethane, e.g. **6**, compared with the propelladiene that ensues from **3**.

We find that the diarylmethylenecyclopropabenzenes **1** are more reluctant to undergo cycloaddition than their naphthalene homologues and, under the same conditions, resist reaction with α-pyrone.[8] However, with diphenylisobenzofuran (dpibf) **1a** and **1b** each give a single crystalline 1:1 cycloadduct in good yield.[9,10] That these compounds are propelladienes is immediately obvious from the ^{1}H NMR spectra as they each exhibit an

AB-pattern in the olefinic region[10] and, unlike **5** (that is derived from **2**), the compounds do not exhibit a carbonyl stretching frequency. The orientation of these adducts as *endo* or *exo* with respect to the fused benzenoid ring of **1** (Scheme 2) is not at all obvious as there are no in-built structural features to allow for easy differentiation. Cyclopropabenzene (**3**) adds dpibf across the bridge bond to give both *endo*- and *exo*-products,[6a] as well as the unsymmetrical adduct derived from formal addition to the strained σ-bond;[6] thus it provides no precedent. The structure of the product from **1a** has been determined as the *endo*-adduct **7a** by crystallographic methods (Figure 1)[11] and that from **1b** is assigned as **7b** in direct analogy. One must ask why the regioselectivity exhibited by **1** and **2** is so different. Unfortunately FMO analysis[12] cannot rationalize the experimental findings as the HOMO and LUMO of both **1c** and **2c** are concentrated at the exocyclic bond.

To gain some insight into the different regioselectivity, the interaction of dpibf with the (unknown) parent methylene compounds **1c** and **2c** has been examined using the semiempirical PM3 method.[13] The calculations show that addition to the exocyclic bond of **2c** is significantly more exothermic (-21.0 kcal mol^{-1}) than addition to the bridge bond (-8.9 kcal mol^{-1}). This contrasts with **1c** where addition to the bridge bond is preferred slightly over addition to the exocyclic bond (-20.6 and -19.1 kcal mol^{-1}, respectively). Provided that these differences in the thermochemistry of the products are reflected to some degree in the corresponding transition states, the results can be used to rationalize the experimentally observed regioselectivities in the reactions of dpibf with **1** and **2**.

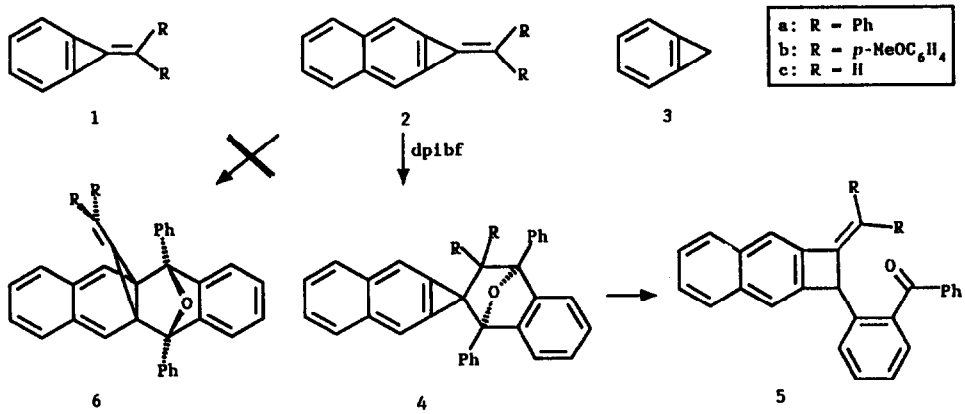
Further insight is gained by realizing that the addition of dpibf to the exocyclic bonds of **1c** and **2c** is exothermic to a similar extent, but that addition to the bridge bond is far more exothermic for **1c** than for **2c** ($\Delta\Delta E$ = -11.5 kcal mol^{-1}). These different exothermicities result from a greater loss of aromaticity in the naphthalene rings to give **6** than in the benzene ring to give **7**. Similar differences are calculated with the PM3 method for the hydrogenation of the bridge bond of cyclopropabenzene (**3**) (-32.2 kcal mol^{-1}) and of cyclopropa[*b*]naphthalene (-19.9 kcal mol^{-1}).

Terminal phenyl substituents strongly disfavour the products of addition to the exocyclic bond due to steric interactions. Thus addition of dpibf to the bridge bond of **1a** is calculated to be exothermic by 12.4 kcal mol^{-1}, but addition to the exocyclic bond is endothermic by 2.7 kcal mol^{-1}. This steric effect is not large enough to overide the large inherent preference for exocyclic addition of **2c**, and the naphthalene derivatives **2a,b** exhibit exocyclic reactivity.

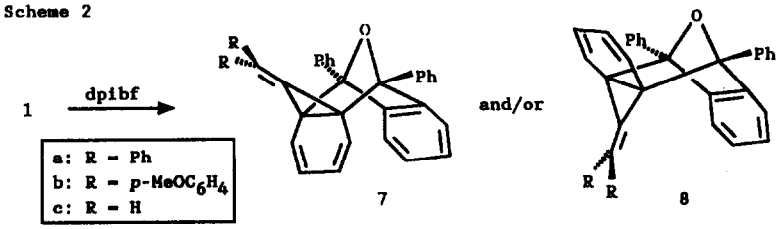
The PM3 calculations also reproduce the observed *endo*-stereochemistry in the addition of dpibf to the bridge bonds of **1a,b**. Thus the product **7a** resulting from *endo*-addition to the bridge bond of **1a** is calculated to be more stable by 0.4 kcal mol^{-1} than **8a**, the product of *exo*-addition (this difference is 3.1 kcal mol^{-1} for **1c**). The same *endo* preference is calculated for **2c**, but here addition to the exocyclic bond is preferred.

Further theoretical studies, in which the transition states for the various addition processes will be calculated, are in progress and will be reported in the full paper.

Scheme 1



Scheme 2



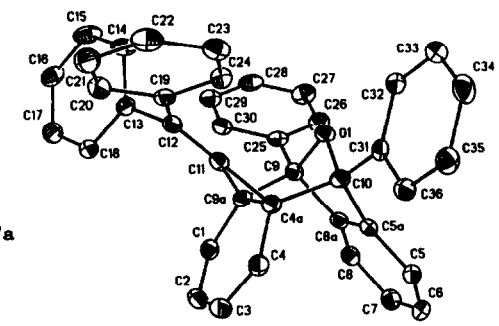


Figure 1. ORTEP diagram of 7a

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8. With ethylene glycol as solvent **1a** provides an amorphous mass from two molecules interacting with one of solvent (*m/z* 570); compound **1b** gives a 1:1 adduct (*m/z* 376) under the same conditions. The structures remain unknown.
9. All new compounds were fully characterized by elemental analysis, MS, IR and multinuclear NMR spectroscopy.
10. **7a**: 48% (93% based on dpibf consumed) as colourless crystals, mp 242-244°C; ^{1}H NMR δ 5.66, d of d, *J* 7.5, 2.3 Hz, 2H; 6.11, d of d, *J* 7.5, 2.3 Hz, 2H; 7.05-7.60, m, 24H. Mass spectrum *m/z* 524 (23, M^{+}), 419 (16, M-PhCO^{+}), 341 (17), 339 (17), 270 (100%, dpibf^{+}). **7b**: 27% (68% based on dpibf consumed) as colourless crystals, mp 223.5-225°C; ^{1}H NMR δ 3.80, s, 2 x OMe; 5.65, d of d, *J* 7.5, 2.2 Hz, 2H; 6.11, d of d, *J* 7.5, 2.2 Hz, 2H; 6.68, d, *J* 8.6 Hz, 4H; 7.05-7.12, m, 8H; 7.29-7.60. m, 10H. Mass spectrum *m/z* 584 (13, M^{+}), 479 (10, M-PhCO^{+}), 314 (100, M-dpibf^{+}), 270 (68%, dpibf^{+}).
11. **7a**: [4aα,9α,9aα,10α]-9,10-Diphenyl-11-diphenylmethylene-4a,9,9a,10-tetrahydro-9,10-epoxy-4a,9a-methanoanthracene: crystal size approx. 0.25x0.35x0.30 mm; cell data, a=9.557(2), b=10.111(3), c=14.752(4) Å, α=84.73 (2), β=82.55(2), γ=88.08(2)°, *V*=1407.2(6) Å^3, no. reflns for unit cell refinement=50 (2Θ range(°) $15 \leq 2\Theta \leq 25$) 120 K, triclinic, space group $P\bar{1}$, Z=2, ρ_{calc}=1.238 gcm^{-3}, $Mo_{K\alpha}$ radiation, μ=0.07 mm^{-1}, $2\Theta_{max}$=50°, 4944 unique reflections, 3499 observed [$F_o \geq 4\sigma(F)$], structure refinement by Direct Methods with SHELXTL-PLUS, 398 parameters, R=0.0518, R_w=0.0516, maximum residual electron density 0.243 eÅ^{-3}. Further details of the crystal structure analysis are available from the Cambridge Crystallographic Data Centre. The numbering scheme is shown in the ORTEP representation of the molecule (Figure 1). Selected bond lengths C1-C2 1.344(4), C4a-C9a 1.584(3), C4a-C11 1.475(4), C11-C12 1.330(4) Å; bond angles C1a-C9a-C4a 120.6(2), C4a-C9a-C11 57.5, C4a-C11-C9a 64.9(2), C4a-C11-C12 148.2(2)°; interplanar angle C10-O1-C9:C4a-C11-C9a 122.8°.
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