Aryl-substituted methylidenecyclopropa[*b*]naphthalenes: synthesis and attempted silver(I)-mediated dimerization

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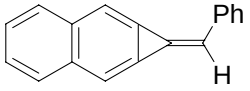
Abstract
The arylmethylidenecyclopropa[*b*]naphthalene family has been extended to include the 1- and 2-naphthyl and 9-anthryl derivatives (**5-7**). When subjected to Ag(I) in aprotic media, conditions typically employed for the linear dimerization of the parent cycloproparenes, diarylalkynes and/or ketones are obtained; in alcoholic media enol ethers are formed. Dimerization to 9,10-anthraquinodimethanes does not take place.

Keywords: Strained aromatics, small ring compounds, Ag(I) catalysis, Peterson olefination, ring opening

Introduction

As novel aromatic hydrocarbons, the alkylidenecycloproparenes, *e.g.* **1** and **2**,[1-3] have continued to provide a source of fascination[4] since their discovery in 1984,[5] not least because the various derivatives have unexpected polarities,[6-8] fluorescence characteristics,[9] and unusual properties.[4,10,11] Recently, we described five protocols that allow for the synthesis of an extensive series of 1-aryl- and 1-diaryl-methylidene-1*H*-cyclopropa[*b*]naphthalenes, their polarities, and the linear dependence of their cycloproparenyl ^{13}C NMR chemical shifts upon the Hammett σ_p^+ constant of the remote aryl substituent.[3] We also addressed conjugated and cross-conjugated cycloproparene derivatives containing cyclopentadiene and dithiole sub-units,[12] and others with simple π bonds that enhance polarity through extended conjugation.[13] Despite these advances there is no recorded attempt to utilize these exocyclic alkenes in what would be a simple and straightforward synthesis of quinodimethanes from ring opening and dimerization as occurs for the parent cycloproparenes.



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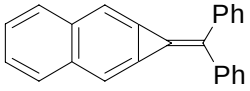

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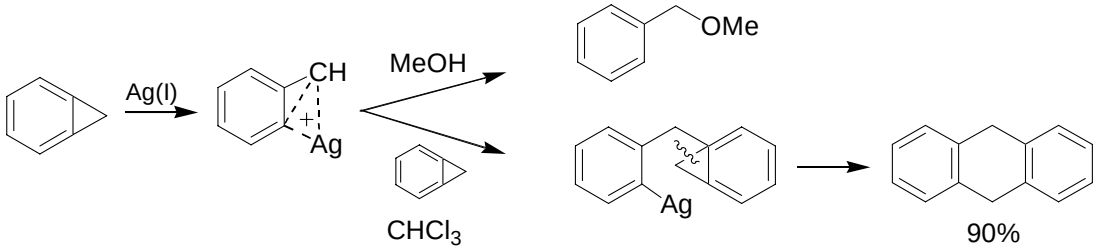
Sterically unencumbered cyclopropa[*b*]naphthalenes are ring-opened by simple acids (and halogens) in what is now regarded as a highly efficient benzylation reaction that is also promoted by Ag(I).[4] The Ag(I)-mediated opening is particularly efficacious, as illustrated by its use in the characterization of 1*H*-cyclopropa[*b*]naphthalene-3,6-dione,[14] but it is its application to the dimerization of the cyclopropa[*b*]naphthalenes that has commanded much recent attention.[15-18] For the simple cyclopropa[*b*]naphthalenes, the dimerization reaction entails the dropwise addition of an anhydrous chloroform solution of the cyclopropa[*b*]naphthalene to a suspension of $AgBF_4$ (ca. 1 mol %) in the same solvent at 0°C.[15] Such reactions are usually complete within a few minutes and, as the anhydrous non-nucleophilic solvent cannot intercept the σ complex, a second equivalent of cyclopropa[*b*]naphthalene binds with the ring-opened cation ultimately to yield cyclopropa[*b*]naphthalene dimer (Scheme 1). Of the two possible products of dimerization the linear isomer dominates, as dictated by addition of the Ag(I)-complexed cyclopropa[*b*]naphthalene to the second molecule of reactant, and it is usually present in excellent yield as illustrated by the 90% conversion of cyclopropabenzene into 9,10-dihydroanthracene (Scheme 1). We report herein the synthesis of the new arylmethylidene-1*H*-cyclopropa[*b*]naphthalenes **5-7** and the outcome of attempted dimerizations.

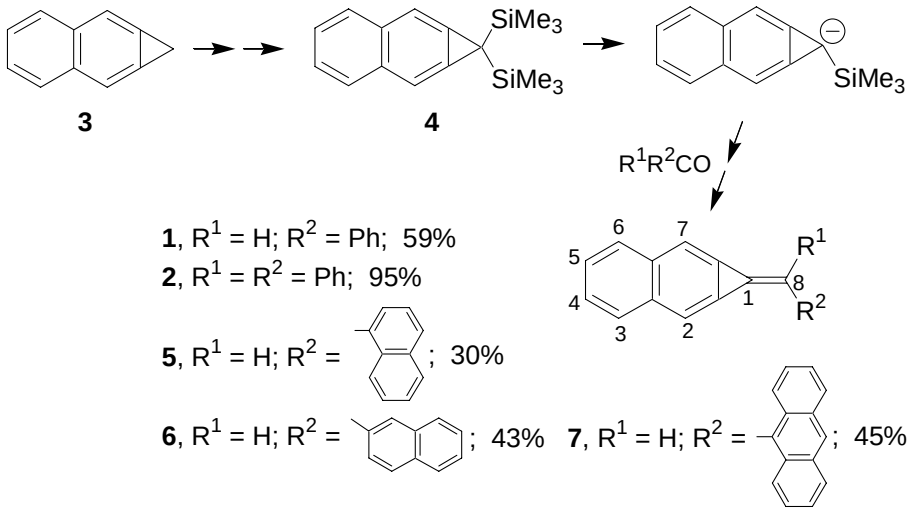


Scheme 1

Results and Discussion

The synthesis of an alkylidenecyclopropa[*b*]naphthalene is conveniently performed by subjecting the parent annulated aromatic hydrocarbon to lithiation/silylation sequences that (ultimately) provide the C1 α-silylcyclopropa[*b*]naphthalenyl anion for *in situ* reaction with an aldehyde or ketone. The derived exocyclic alkene is obtained directly from such Peterson olefination in a 'one pot' procedure from cyclopropabenzene, but only from isolation and subsequent desilylation of 1,1-bis-(trimethylsilyl)cyclopropanaphthalene **4** from **3**.[19] The precise conditions needed for a given carbonyl compound and **4**[1,2] have been the subject of detailed scrutiny, and fall into five distinct procedures that allow for the convenient synthesis of new derivatives.[3] While these procedures do not justify further discussion here, use of *'Method 1'* has provided easy access to the previously known 1-phenyl- **1**,[1] 1-diphenyl- **2**,[1] and the hitherto unrecorded 1-(1'-naphthyl)- **5**, 1-(2'-naphthyl)- **6** and 1-(9'-anthrylmethylidene)-1*H*-cyclopropa[*b*]naphthalene **7** (Scheme 2).[20] Compounds **5-7** are characterized by their C8 vinylic proton resonance (δ_H 7.35, 6.75 and 7.59,

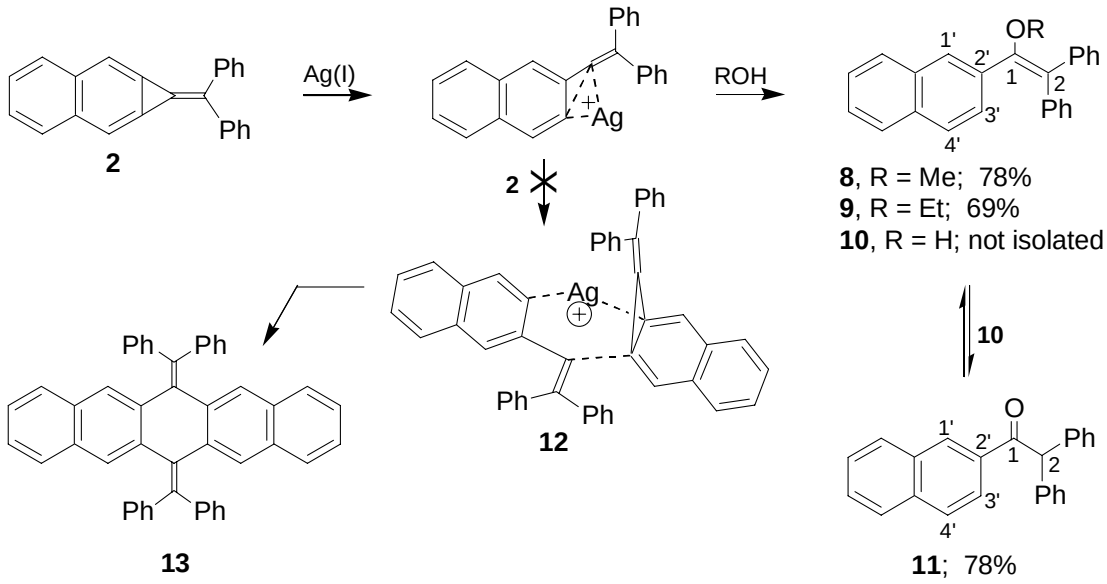
respectively) and the appearance of H2/H7 as narrowly coupled doublets (J ~1.4 Hz) between 7.3 and 7.6 ppm. The ^{13}C NMR resonances for C2/C7 fall in the typical range[3,4] and at 108.2-108.6 ppm, and while C8 for **5** and **7** is at δ 102.9 it is at δ 107.3 for **6**. The increased shielding of H8 (6.75 ppm) and deshielding of C8 in **6** are fully consistent with the same resonances of **1** (δ_H 6.53; δ_C 107.1). These reflect the angular (C2') attachment of the naphthalene ring that allows the substituent to lie closer to planarity in **6** than in **5** or **7** in analogy to the phenyl group of **1** that is twisted by about 5° out of the cycloproparenyl plane.[2,4]



Scheme 2

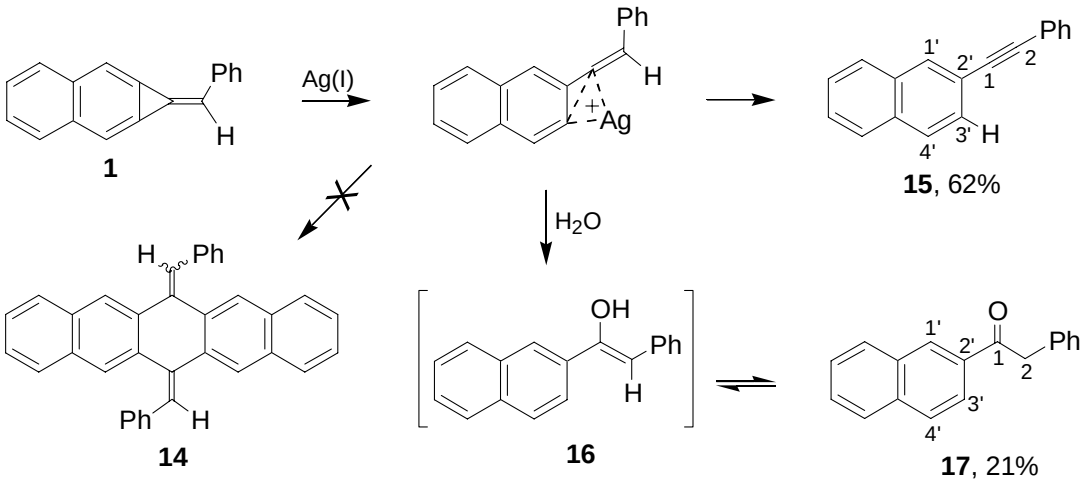
While the interactions of the simple cycloproparenes with silver ion have been determined in a largely systematic manner,[21,22] there has been no analogous study of the alkylidenecycloproparenes. Rather, the first derivatives were subjected to silver(I) in methanol in a study[23] that predates the dimerization work of Billups.[15-18] To date this gap has not been bridged. Thus complexation of, *e.g.* **2**, with Ag(I) opens the strained three-membered ring σ bond in direct analogy with the parent hydrocarbon of Scheme 1, and the methoxystyrene **8** is obtained in 78% yield from capture of the complex by the nucleophilic solvent (Scheme 3).[23] When the analogous reaction was attempted in chloroform it was far from spontaneous. Only after a 2 h reflux period did the yellow fluorescence characteristic of unchanged **2** fade. Conventional work-up gave colorless crystals of product that is identified as ethoxystyrene **9** from its analytical and spectroscopic data (Experimental section) and it arises from capture of the silver complex by the ca. 2% ethanol used to stabilize chloroform! Colorless crystals of product were again obtained from **2** and Ag(I) in freshly distilled chloroform from which ethanol had been carefully removed. However, infrared stretching at 1658 cm^{-1} indicates the presence of a conjugated (aryl) carbonyl function and the product, formed in 85% yield, is characterized as 1-(2-naphthyl)-2,2-diphenylethanone (**11**).[23] The formation of **11** is again rationalized by Ag(I)-mediated opening of the lateral three-membered ring bond to give the σ complex but, with no nucleophile present, intercep-

tion can only be by water during work-up and this leads to **11** via enol **10** as shown in Scheme 3. It is clear that the σ complex is *not* captured by an unopened molecule of **2** as no evidence was gained for the presence of dimer **13**, even in trace quantities. In all probability the steric requirements of the exocyclic substituents disfavor formation of the silver-bridged dimeric ion **12**. However, the involvement of Ag(I) with the slightly polar hydrocarbon **2** is assumed as the reaction does not appear to take place on standing at room temperature.



Scheme 3

In similar vein, use of the less sterically demanding phenylmethylidene homologue **1** did not afford dimer **14**. In this case the reaction provided a separable 3:1 mixture of 1-(2-naphthyl)-2-phenylethyne (**15**)[23] and 1-(2-naphthyl)-2-phenylethanone (**17**)[23] in 83% combined yield, along with unchanged substrate **1** (15%) (Scheme 4). Alkyne **15** has been isolated previously from **1**, but in only 31% yield, by reaction with Ag(I) in *tert*-butanol where relief of ring strain by proton transfer is facilitated by the metal ion;[23] the size and nucleophilicity of the *tert*-butyl group does not allow for capture to give enol but does provide for a more complex product mixture.[23] The formation of benzyl naphthyl ketone **17** from **16** during aqueous work-up matches that of ethanone **11** from **10** as described above. In the absence of Ag(I), but in chloroform, **1** and **2** are stable for periods longer than the reaction times involved. Because of the failure of **1** (and **2**) to provide dimer, analogous reactions with the sterically more demanding new arylmethylidene compounds **5-7** have not been performed.



Scheme 4

An alternative route to linear alkylidenecycloproparene dimers could commence with disilylcycloproparene **4**. Thus Ag(I)-mediated dimerization would lead to 6,6,13,13-tetrakis(trimethylsilyl)pentacene that could be subjected to Peterson olefination in direct analogy with the procedure depicted by Scheme 2. In the event, disilane **4** failed to dimerize and it was recovered almost quantitatively, even after reflux for two days with $AgBF_4$ in anhydrous chloroform. That the reaction conditions employed herein are appropriate for dimerization has been confirmed from successful dimerization of **3** to 6,13-dihydropentacene in 73% yield.[15,17] The steric constraints present at C1 of the exocyclic alkenes **1-5** (and disilane **4**) are too large to allow dimerization as only products of ring opening (or unchanged starting material) are recorded .

Experimental Section

General Procedures. The general procedures followed and the spectrometers used have been described previously.[3]

Compound characterization

The methylidenecyclopropa[*b*]naphthalenes **1**,[1] **2**,[1] and **5-7** were synthesized by the recently described method, *Method 1*.[3]

1-(1'-Naphthylmethylidene)-1*H*-cyclopropa[*b*]naphthalene (5). Disilyl **4** (157 mg, 0.55 mmol) and 1-naphthaldehyde (86 mg, 0.55 mmol) gave the *title compound* **5** (46 mg, 30%) as bright yellow needles (dichloromethane/light petroleum), mp 228-230°C (Found: C, 93.98; H, 4.68. $C_{22}H_{14}$ requires C, 94.92; H, 4.54%). IR υ_{max} 2922, 2851, 1948, 1927, 1759, 1699, 1651, 1584, 1514, 1427, 1393, 1339, 1250, 1175, 1146, 1090, 1017, 949 cm^{-1}. UV λ_{max} (cyclohexane) 222 (4.58), 240 (4.48), 276 (4.48), 304 (4.06), 314 (4.02), 400 (sh, 4.50), 422 (4.62), 450 nm (log ε 4.50); λ_{max} (acetonitrile) 220 (4.92), 268 (3.35), 300 (3.75), 318 (3.75), 398 (sh, 4.34), 416 (4.49), 446 nm (log ε 4.39). δ_H 7.35 (s, 1H, H8), 7.45-7.62(m, 2H), 7.47-7.51 (m, 2H, H4/H5), 7.61 (d, J_{para} 1.40 Hz, 1H, H2 or

H7), 7.73 (d, J_{para} 1.30 Hz, 1H, H7 or H2), 7.81-7.90 (m, 2H, H3/H6), 7.85-7.95 (m, 3H), 8.30-8.35 (m, 2H). δ_C 102.9 (C8), 108.2/108.6 (C2/C7), 113.4 (C1), 122.9, 123.4, 125.8, 125.8, 126.1, 126.3 (C1a/C7a), 126.8/126.9 (C4/C5), 127.4, 127.7, 128.8, 128.9/129.0 (C3/C6), 130.9, 134.8, 134.1, 138.5/138.7 (C2a/C6a). Mass spectrum (70 eV) *m/z* (relative intensity): 279 (24, M+1), 278 (100, M), 277 (51, M-1), 138 (77%, M-$C_{11}H_8$).

1-(2'-Naphthylmethylidene)-1*H*-cyclopropa[*b*]naphthalene (6). Disilyl **4** (160 mg, 0.56 mmol) and 2-naphthaldehyde (87 mg, 0.56 mmol) gave the *title compound* **6** (67 mg, 43%) as bright green plates (dichloromethane/light petroleum), mp 228-230°C (Found: C, 95.09; H, 4.88. $C_{22}H_{14}$ requires C, 94.92; H, 4.54%). IR υ_{max} 3048, 2920, 2851, 1786, 1744, 1586, 1507, 1348, 1250, 1144, 949, 901, 855, 824, 741 cm^{-1}. UV λ_{max} (cyclohexane) 218 (3.89), 236 (3.96), 284 (3.79), 300 (sh, 3.46), 314 (sh, 3.29), 384 (sh, 3.66), 404 (3.96), 434 nm (log ε 4.09); λ_{max} (acetonitrile) 218 (4.24), 236 (4.30), 266 (4.04), 288 (4.22), 302 (sh, 3.87), 312 (3.72), 384 (sh, 4.11), 402 (4.39), 430 nm (log ε 4.44). δ_H 6.75 (s, 1H, H8), 7.40-7.55 (m, 3H), 7.48-7.51 (m, 2H, H4/H5), 7.59 (d, J_{para} 1.50 Hz, 1H, H2 or H7), 7.77 (d, J_{para} 1.30 Hz, 1H, H7 or H2), 7.85-8.00 (m, 3H), 7.91-7.98 (m, 2H, H3/H6), 8.07-8.14 (m, 1H). δ_C 107.3 (C8), 108.2/108.4 (C2/C7), 112.2 (C1), 124.1, 125.5 (C1a/C7a), 125.8, 126.3, 126.8/126.9 (C4/C5), 127.8, 128.0, 128.4, 128.9/129.0 (C3/C6), 132.7, 133.9, 135.5, 138.5/139.1 (C2a/C6a). Mass spectrum (70 eV) *m/z* (relative intensity): 279 (24, M+1), 278 (100, M), 277 (35, M-H), 276 (66, M-2H), 138 (57%, M-$C_{11}H_8$).

1-(9'-Anthrylmethylene)-1*H*-cyclopropa[*b*]naphthalene (7). Disilyl **4** (200 mg, 0.70 mmol) and 9-anthraldehyde (147 mg, 0.70 mmol) gave the *title compound* **7** (104 mg, 45%) as bright orange needles (dichloromethane/light petroleum), mp 191-192°C (Found: C, 94.86; H, 4.71. $C_{26}H_{16}$ requires C, 95.05; H, 4.90%). IR υ_{max} 3034, 2920, 2851, 1909, 1744, 1622, 1587, 1539,1520, 1441, 1343, 1246, 1140, 947, 849, 723 cm^{-1}. UV λ_{max} (cyclohexane) 238 (4.70), 268 (4.69), 354 (3.96), 442 nm (log ε 4.14); λ_{max} (acetonitrile) 212 (4.89), 240 (4.74), 260 (4.57), 354 (3.73), 332 nm (log ε 3.90). δ_H 7.05-9.95 (broad m, 8H), 7.28 (broadened d, 1H, H2 or H7), 7.47-7.51 (m, 2H, H4/H5), 7.59 (s, 1H, H8), 7.67 (broadened d, 1H, H7 or H2), 8.03-8.06 (m, 2H, H3/H6), 8.43 (s, 1H, H13). δ_C 103.0 (C8), 108.5/109.6 (C2/C7), 117.7 (C1), 125.2/125.4 (C4/C5), 126.2 (C13), 126.6, 126.8, 127.1, 127.2, 128.0, 128.9/129.1 (C3/C6), 129.8, 131.3, 131.8, 133.6, 134.1, 138.8/139.0 (C2a/C6a). Mass spectrum (70 eV) *m/z* (relative intensity): 329 (25, M+1), 328 (98, M), 327 (65, M-H), 324 (26, M-2H), 163 (100%, M-$C_{13}H_9$).

1-Ethoxy-1-(naphthyl)-2,2-diphenylethene (9). 1-(Diphenylmethylidene)-1*H*-cyclopropa[*b*]naphthalene (**2**)[1] (50 mg, 0.16 mmol) in anhydrous chloroform (30 mL) was refluxed with silver tetrafluoroborate (ca. 1 mol%) for 2 h under nitrogen. During this time the yellow color slowly faded. Following conventional work-up, concentration, and radial chromatography [light petroleum/dichloromethane (6:1) elution], colorless crystals (light petroleum) of *ethoxystyrene* **9** were obtained (39 mg, 69%), mp 142.0-143.5°C. (Found: $[M+H]^+$ 351.1740. $C_{26}H_{23}O$ requires 351.1749; Δ 2.5 ppm). IR υ_{max} 1610, 1590, 1275, 1266, 1233, 1230, 1195, 1080, 956, 864 cm^{-1}. δ_H 1.27 (t, *J* 7.1 Hz, 3H, Me), 3.76 (q, *J* 7.1 Hz, 2H, OCH_2), 7.02-7.08 (m, 5H), 7.25-7.49 (m, 8H), 7.64-7.80 (m, 4H). δ_C 15.1 (Me), 66.2 (OCH_2), 126.0 (C1'), 126.0(5) (C3'), 126.2 (C8'), 126.5 (C5'), 126.5(5) (C2), 127.3 (C7'), 127.5 (C6'), 127.7 (C4/C8 or C10/C14), 127.8 (C4'), 127.9

(C5/C7 or C11/C13), 128.1 (C6 or C12) 129.9 (C10/C14 or C4/C8), 131.5 (C11/C13 or C5/C7), 132.7 (C9' or C10'), 133.0 (C10' or C9'), 132.2 (C2'), 141.1 (C3 or C9), 141.3 (C9 or C3), 152.1 (C1).

1-(2-Naphthyl)-2,2-diphenylethanone (11). 1-(Diphenylmethylidene)-1*H*-cyclopropa[*b*]naphthalene (**2**)[1] (50 mg, 0.16 mmol) was treated as above, except the anhydrous chloroform was ethanol-free. Following work-up and radial chromatography [light petroleum/dichloromethane (3:1) elution], colorless crystals (light petroleum) of ethanone (**11**) were obtained (40 mg, 78%), mp 102.0-103.0°C (lit.[23] 103-104°C). (Found: $[M+H]^+$ 323.1429. Calc. for $C_{24}H_{18}O$: 323.1436; Δ 1.5 ppm). IR υ_{max} 3052, 3022, 1658, 1622, 1592, 1490, 1449, 1350, 1276, 1206, 1190, 1170, 1118, 906, 858, 820, 766, 754, 744, 732, 714, 698, 638, 618 cm^{-1}. δ_H 6.33 (s, 1H, H2), 7.40-7.45 (m, 10H), 7.65-8.32 (m, 6H), 8.65 (s, 1H). δ_C 59.4 (C2), 124.6 (C5'), 124.8 (C8'), 126.7 (C6'), 127.1 (C7'), 128.4 (C4/C8), 128.5 (C5/C7), 128.7 (C6), 129.2 (C4'), 129.7 (C3'), 130.7 (C1'), 132.4 (C2'), 134.1 (C9'), 135.5 (C10'), 139.2 (C3), 198.1 (C1).

Reaction of 1-(phenylmethylidene)-1*H*-cyclopropa[*b*]naphthalene (1) with Ag(I). 1-(Phenylmethylidene)-1*H*-cyclopropa[*b*]naphthalene (**1**)[1] (50 mg, 0.22 mmol) in anhydrous ethanol-free chloroform (30 mL) was refluxed with silver tetrafluoroborate (ca. 1 mol%) for 2 h under nitrogen. During this period, the colour changed from yellow to a very dull yellow. Conventional work-up and radial chromatography [light petroleum/dichloromethane (6:1) elution] gave three fractions. The most mobile component yielded colorless crystals (light petroleum) of 1-(2-naphthyl)-2-phenylethyne (**15**) (31 mg, 62%) m.p. 115.0-117.0°C (lit.[24] 117°C). (Found: $[M+H]^+$ 229.1010. Calc. for $C_{18}H_{12}$: 229.1017; Δ 3.1 ppm). IR υ_{max} 1605, 1456, 1277, 1080, 987, 977, 965, 928, 910 cm^{-1}. δ_H 7.25-7.61 (m, 8H, H4/H8, H5/H7, H6/H6', H7' and H8'), 7.70-7.84 (m, 3H, H3'/H4'/H5'), 8.03 (s, 1H, H1'). δ_C 89.9 (C2), 90.0 (C1), 120.5 (C2'), 123.5 (C3), 126.5 (C7'), 126.7 (C6'), 127.4 (C8'), 127.8 (C5'), 128.0 (C6), 128.4 (C4'), 129.0 (C5/C7), 131.5 (C3'), 131.8 (C1'), 131.9 (C4/C8), 133.0 (C10'), 133.2 (C9').

The second fraction yielded colorless crystals (light petroleum) of 1-(2-naphthyl)-2-phenylethanone (**17**) (11 mg, 21%) mp 98.0-99.5°C (lit.[25] 99-99.5°C). (Found: $[M+H]^+$ 247.1115. Calc. for $C_{18}H_{14}O$: 247.1123; Δ 3.2 ppm). IR υ_{max} 1680, 1652, 1505, 1444, 1504, 1330, 1212, 1193, 1178, 1130, 1038, 839, 832, 756, 732, 708 cm^{-1}. δ_H 4.40, s, 2H, 2 x H2; 7.26-7.32, m, 5H, H4/8, H5/7 and H6; 7.48-7.63 (m, 2H, H7' and H8'), 7.79-8.02 (m, 4H, H3', H4', H5', H6'), 8.52 (s, 1H, H1'). δ_C 46.5 (C2), 124.4 (C5'), 124.7 (C8'), 126.5 (C6'), 127.0 (C7'), 128.5 (C4/C8), 128.7 (C5/C7), 128.7(5) (C6), 129.4 (C4'), 129.5 (C3'), 130.6 (C1'), 132.7 (C2'), 134.3 (C9'), 134.8 (C10'), 136.0 (C3), 197.5 (C1).

The third fraction gave unchanged alkene **1** as yellow needles (light petroleum) (7 mg, 15%).

Attempted reaction of 1,1-bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene with Ag(I). Disilane **4** (100 mg, 0.35 mmol) in ethanol-free anhydrous chloroform (30 mL) was refluxed under nitrogen for 2 days with ca. 1 mol% of silver tetrafluoroborate. Work-up afforded unchanged starting material (95 mg, 95 %) with no evidence gleaned for the sought after dimer.

Acknowledgements

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References and Footnotes

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