Aryl-substituted methylenecyclopropa[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 fascination4 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-1H-cyclopropa[b]naphthalenes, their polarities, and the linear dependence of their cycloproparenyl 13C NMR chemical shifts upon the Hammett σp 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.
Sterically unencumbered cycloproparenes 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 \(1H\)-cyclopropa\([b]\)naphthalene-3,6-dione,\(^{14}\) but it is its application to the dimerization of the cycloproparenes that has commanded much recent attention.\(^{15-18}\) For the simple cycloproparenes, the dimerization reaction entails the dropwise addition of an anhydrous chloroform solution of the cycloproparene 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 \(\sigma\) complex, a second equivalent of cycloproparene binds with the ring-opened cation ultimately to yield cycloproparene dimer (Scheme 1). Of the two possible products of dimerization the linear isomer dominates, as dictated by addition of the Ag(I)-complexed cycloproparene 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-\(1H\)-cyclopropa\([b]\)naphthalenes 5-7 and the outcome of attempted dimerizations.

![Scheme 1](image)

**Results and Discussion**

The synthesis of an alkylidenecycloproparene is conveniently performed by subjecting the parent annulated aromatic hydrocarbon to lithiumation/silylation sequences that (ultimately) provide the C1 \(\alpha\)-silylcycloproparenyl anion for \textit{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 ‘\textit{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)-\(1H\)-cyclopropa\([b]\)naphthalene 7 (Scheme 2).\(^{20}\) Compounds 5-7 are characterized by their C8 vinylic proton resonance (\(\delta_H\) 7.35, 6.75 and 7.59,
respectively) and the appearance of H2/H7 as narrowly coupled doublets ($J \sim 1.4$ 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 $\delta$ 102.9 it is at $\delta$ 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 ($\delta_H$ 6.53; $\delta_C$ 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 cyclopropenyl plane.$^{2,4}$

![Scheme 2](image)

**Scheme 2**

While the interactions of the simple cyclopropenes with silver ion have been determined in a largely systematic manner,$^{21,22}$ there has been no analogous study of the alkylidencyclopropenes. 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 $\sigma$ 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-diphenylethanedione (11).$^{23}$ The formation of 11 is again rationalized by Ag(I)-mediated opening of the lateral three-membered ring bond to give the $\sigma$ complex but, with no nucleophile present, interce-
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](image)

**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) and 1-(2-naphthyl)-2-phenylethanone (17) 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, 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. 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 alkyldienecycloproparene dimers could commence with disilylcycloproparene 4. Thus Ag(I)-mediated dimerization would lead to 6,6,13,13-tetakis(tri-methylsilyl)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 AgBF₄ 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 methyldienecyclopropa[b]naphthalenes 1,¹ 2,¹ and 5-7 were synthesized by the recently described method, Method I.³

1-(1'-Naphthylmethylidene)-1H-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. C₂₂H₁₄ requires C, 94.92; H, 4.54%). IR ν max 2922, 2851, 1948, 1927, 1759, 1699, 1651, 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). δH 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-C11H8).

**1-(2'-Naphthylmethylidene)-1H-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 (51, M-1), 138 (77%, M-C_{11}H_{8}).

**1-(9'-Anthrylmethylene)-1H-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 (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 103.0 (C8), 108.5/109.6 (C2/C7), 117.7 (C1), 125.2/125.4 (C2/C5), 126.2 (C13), 126.1, 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-Ethoxy-1-(naphthyl)-2,2-diphenylethene (9).** 1-(Diphenylmethylidene)-1H-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 (C3'), 126.2 (C8'), 126.5 (C5'), 126.5 (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)-1H-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.\(^\text{23}\) 103-104°C). (Found: \([\text{M+H}]^+\) 323.1429. Calc. for C\(_{24}\)H\(_{18}\)O: 323.1436; \(\Delta\) 1.5 ppm). IR \(\nu_{\text{max}}\) 3052, 3022, 1658, 1622, 1592, 1490, 1449, 1350, 1320, 1276, 1266, 1190, 1170, 1118, 906, 858, 820, 766, 754, 744, 732, 714, 698, 638, 618 cm\(^{-1}\). \(\delta_{\text{H}}\) 6.33 (s, 1H, H2), 7.40-7.45 (m, 10H), 7.65-8.32 (m, 6H), 8.65 (s, 1H).

\(\delta_{\text{C}}\) 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’), 198.1 (C3), 199.1 (C1).

Reaction of 1-(phenylmethylidene)-1H-cyclopropa[b]naphthalene (1) with Ag(I). 1-(Phenylmethylidene)-1H-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.\(^\text{24}\) 117°C). (Found: \([\text{M+H}]^+\) 229.1010. Calc. for C\(_{18}\)H\(_{12}\): 229.1017; \(\Delta\) 3.1 ppm). IR \(\nu_{\text{max}}\) 1605, 1456, 1277, 1080, 987, 977, 965, 928, 910 cm\(^{-1}\). \(\delta_{\text{H}}\) 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’). \(\delta_{\text{C}}\) 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%) m.p. 98.0-99.5°C (lit.\(^\text{25}\) 99-99.5°C). (Found: \([\text{M+H}]^+\) 247.1115. Calc. for C\(_{18}\)H\(_{14}\)O: 247.1123; \(\Delta\) 3.2 ppm). IR \(\nu_{\text{max}}\) 1680, 1652, 1505, 1444, 1504, 1330, 1212, 1193, 1178, 1130, 1038, 839, 832, 756, 732, 708 cm\(^{-1}\). \(\delta_{\text{H}}\) 4.40, s, 2H, 2 x H2; 7.26-7.32, m, 5H, H4/H8, H5/7/6; 7.48-7.63 (m, 2H, H7’ and H8’), 7.79-8.02 (m, 4H, H3’, H4’, H5’, H6’), 8.52 (s, 1H, H1’). \(\delta_{\text{C}}\) 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 (S) (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 I as yellow needles (light petroleum) (7 mg, 15%).

Attempted reaction of 1,1-bis(trimethylsilyl)-1H-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

20. The existence of compounds 3-6 has been disclosed in ref. 4 but only yield and mp were recorded – see entries 17-20 in Table 1, ref. 4.