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Studies in the cyclopropabenzene series: chemistry of 1-acyl-1*H*-cyclopropa[*b*]naphthalenes and synthesis of cyclopropa[*b*]naphthalenylidene enol ethers

Brian Halton,[a,*] Carissa S. Jones[a] and Davor Margetic[b]

[a]*School of Chemical and Physical Sciences, Victoria University of Wellington, P.O. Box 600, Wellington, New Zealand*
[b]*Centre for Molecular Architecture, Central Queensland University, Rockhampton, Queensland 4702, Australia*

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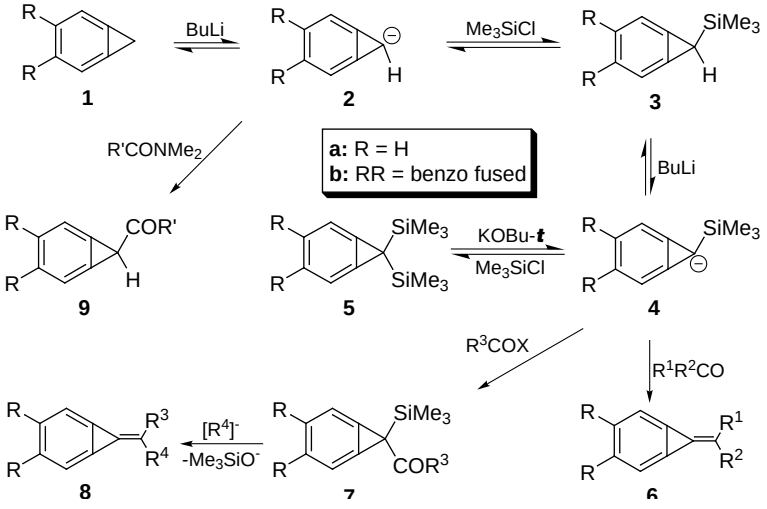
Abstract—The 1*H*-cyclopropa[*b*]naphthalenyl anion reacts with *N*,*N*-dimethylamides to provide C-1 acyl derivatives in good yield in what are rare examples of mono-substitution in the cyclopropabenzene series. The availability of these acylcyclopropabenzenes provides for subsequent benzylic proton abstraction and enolate ion interception to give *O*-silyl and *O*-phosphinate derivatives. This reaction sequence leads to the first cyclopropa[*b*]naphthalenylidene enol ethers and provides the only example of exocyclic alkene formation taking place in one step from the benzylic centre. Protonation of the acyl derivatives by mineral acid triggers three-membered ring opening to 2,3-disubstituted naphthalenes rather than 2-monosubstituted analogues that typically arise from protonation at the aromatic ring. Upon thermolysis ring expansion to a naphthofuran occurs.

Although the chemistry of the cyclopropabenzenes, e.g. **1**, has received significant attention over the past years,[1–6] the number of examples of compounds carrying a single C-1 substituent are remarkably few. Thus while Eaborn and co-workers[7,8] were able to isolate the monosilyl cyclopropabenzene derivative **3a**, all attempts to obtain the equivalent naphthalene analogue **3b** led to the disilane **5b** instead (Scheme 1).[6,9,10] Base-induced proton abstraction of **3a** and desilylation of **5a** and **5b** gives the silicon-stabilized anions **4a** and **4b** that have been used in a range of Peterson olefinations to provide C-1 exocyclic alkenes **6** (alkylidenecyclopropabenzenes) in what has become the major pathway to this class of compounds.[6,11–13] An alternative route to such compounds[14] involves trapping **4b** with a modified carbonyl



Scheme 1.

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* Corresponding author. Tel.: +64-4-463-5954; fax: +64-4-463-5241; e-mail: brian.halton@vuw.ac.nz

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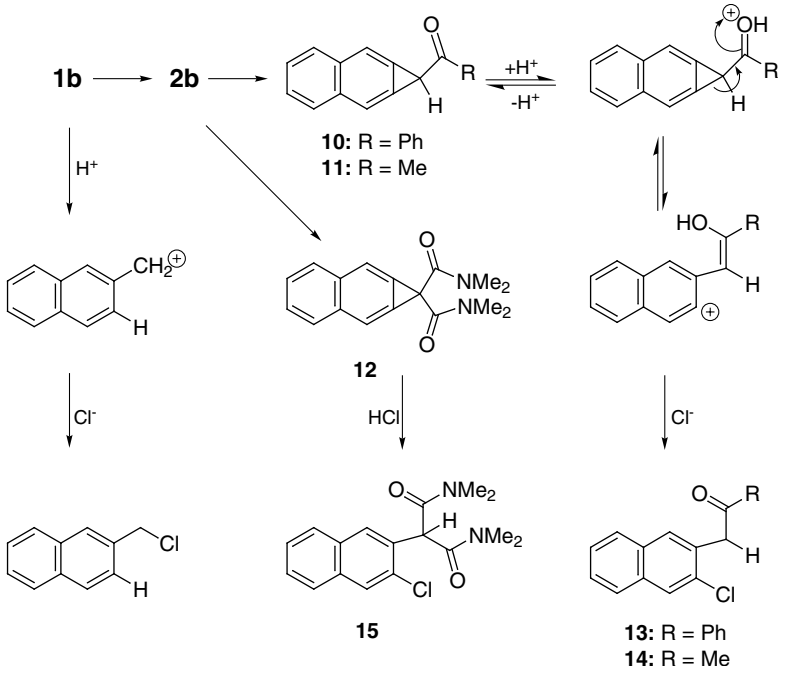


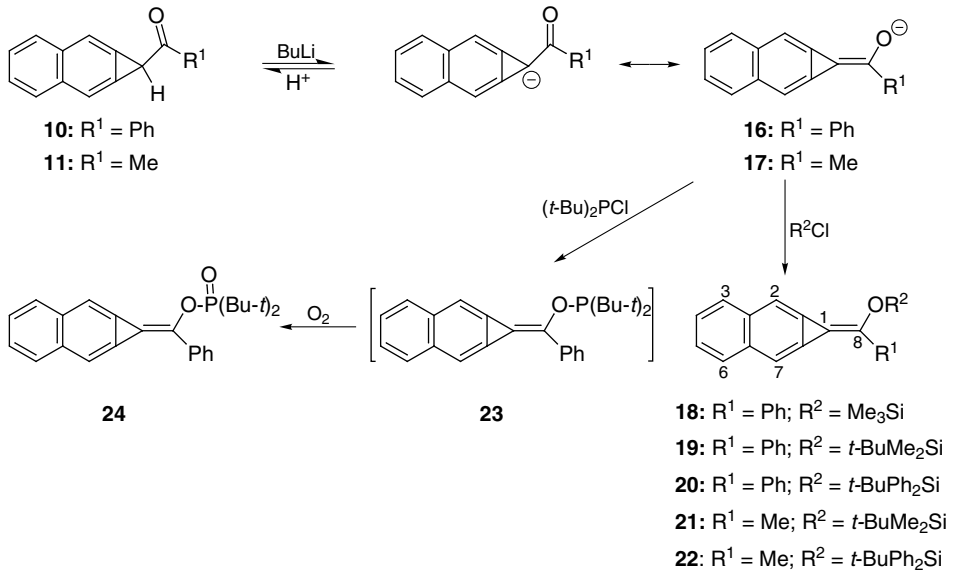
Scheme 2.

compound to give a 1-acyl-1-trimethylsilyl derivative **7b** which, in turn, reacts with an appropriate nucleophile at the carbonyl carbon atom to induce deoxysilylation and formation of alkene **8b**.

The capture of **2** or **4** with electrophilic species other than those described above has proved more difficult. The studies have attracted less attention but they have shown that the chemistry of the C-1 cyclopropanaphthalenyl anion is frustrated by its fast protonation and by the formation of monosubstituted derivatives that are difficult to isolate.[15–17] Nonetheless, monosilyl **3b** has been isolated from the desilylation of **5b** and protonation of **4b**, although particular care was needed.[15] A modification of the reaction procedure from **1b** also provided[15] 1-acetyl and 1-benzoyl (and 1,1-dicarboxamido) derivatives, cf. **9b**, via the interception of **2b** (Scheme 2). It is the chemistry of these last compounds that forms the basis of the present paper. The location of electron withdrawing functionality adjacent to the cyclopropanyl C-1 centre in **9** opens up the possibility of chemistry in which the electron demand is reversed from that normally observed in the electrophilic opening of the cyclopropanene three-membered ring; this last path is illustrated for the formation of 2-(chloromethyl)naphthalene from **1b** in Scheme 2.[1–4] Furthermore, the presence of a benzylic α hydrogen atom in **9** augurs well for enolate ion formation from C-1 with direct formation of an exocyclic olefin, while the location of the carbonyl group suggests that thermolysis and/or photolysis will provide naphtho[*b*]furans from cleavage of the three-membered ring.[18–20] We report herein on the ring opening reactions of 1-acylcyclopropa[*b*]naphthalenes and on the formation and characterization of cyclopropanylidene enol ethers.

1-Benzoyl- (**10**), 1-acetylcyclopropa[*b*]naphthalene (**11**), and the dicarboxamide derivative **12** were prepared from **1b** in moderate yields, as described previously.[15] On treatment with HCl these compounds undergo easy ring opening but do not provide the monosubstituted arenes expected on the basis of typical protonation of the cyclopropanene π framework (Scheme 2).[21–23] Rather, it is the electrophilic carbonyl group that is protonated, thereby facilitating cleavage of the three-membered ring which, in turn, requires capture of the nucleophile at the arene site; the 2-chloro-3-[(substituted)methyl]naphthalenes **13**–**15** are formed in yields of 60–74%. Although 2′-chlorophenylpropan-2-one[24–26] and 2-(2′-chlorophenyl)-1-phenylethanone[27,28] are known, the naphthalene analogues **13**–**15** have not been recorded previously. Their structures are assigned with confidence from the spectroscopic data (Section 1) and especially the appearance of broadened singlets for the (now) non-equivalent *para* protons H-1 (7.70–7.85 ppm) and H-4 (7.88–7.93 ppm), with their corresponding carbon resonances in the ranges 130.2–130.6 and 127.4–127.7 ppm, respectively. The benzylic protons for **13** and **14** appear at 4.59 and 4.00 ppm whereas the tertiary Ar**C**H$(CONMe_2)_2$ of **15** is at 5.56 ppm. The methyl groups of the bis(dimethylamido) derivative **15** appear as two six-proton singlets at 2.94 and 3.02 ppm, respectively, as is expected on the basis of restricted rotation about such CO–N bonds.[29–32]

In contrast to the behaviour described above, treatment of the cyclopropanenes **10** and **11** with base (BuLi) is expected to effect the removal of the benzylic proton H-1 and generate the enolate anions **16** and **17** (Scheme 3). As enolates can be captured by electrophiles at both carbon and oxygen, we sought to effect the latter since this would provide new and novel alkylidenecyclopropanenes generated for the first time in one step from the cyclopropanene simply by proton removal at C-1. As discussed above, the conventional method for preparation of methylidenecyclopropanenes is by Peterson olefination from the silyl derivatives employing a carbonyl-containing



Scheme 3.

compound and it has yielded almost one hundred exocyclic alkene derivatives.[6,10,33] In the event, use of the base with **10** followed by addition of chlorotrimethylsilane led to an unstable solid that provided spectroscopic data compatible with enol ether **18**. In particular, the C-1 benzylic proton of **10** (5.34 ppm) was absent, the formerly equivalent H-2/7 (7.78 ppm) were non-equivalent and shifted to 7.31 and 7.41 ppm and the protons of the new trimethylsiloxy group appeared at 0.46 ppm. The ^{13}C NMR spectrum showed the absence of the carbonyl carbon of the substrate **10** (189.6 ppm) but provided characteristically shielded and distinct signals for C-2 (*Z* with respect to the silyloxy group) and C-7 (*E* with respect to the silyloxy group) of **18** at 104.2 and 104.9 ppm, respectively, that provide adequate proof for retention of the cyclopropanaphthalene framework.[1–6,11,12] In addition, a shielded C-1 olefinic resonance was recorded at 96.0 ppm and the trimethylsiloxy carbons resonated at 0.90 ppm. Unfortunately all attempts to isolate the pure compound resulted in its decomposition, likely from traces of water, as it is well known that trimethylsilyl enol ethers are very sensitive to it and to acid.[34]

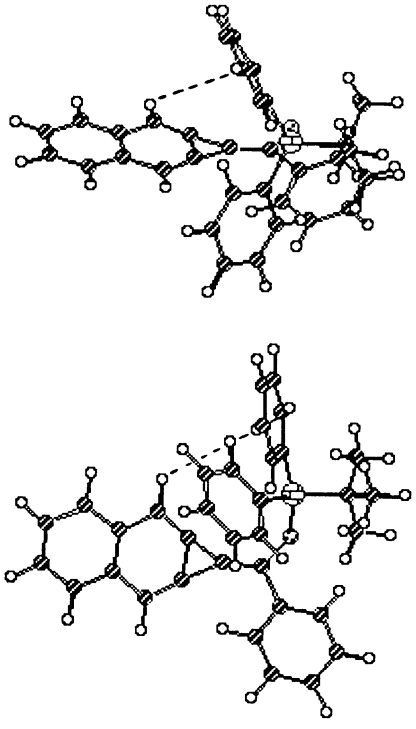
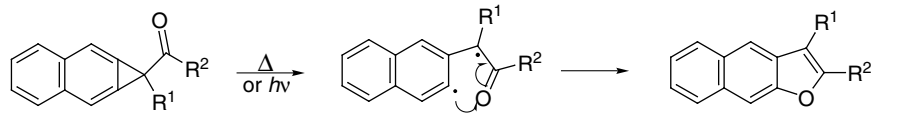


Figure 1. Two views of the favoured conformation of siloxyalkene **20** showing the shielding of H-2 by an Si-Ph group; the distance H-2 to ring centre is 411 ppm.

By employing sterically more demanding *t*-butyldimethyl- and *t*-butyldiphenyl-chlorosilanes with **10** the siloxyalkenes **19** and **20** were isolated in yields of 57 and 60%, respectively; the acetyl derivative **11** is likewise transformed into enol ethers **21** and **22** but they are markedly less stable (Section 1). The structures of these methylidenecyclopropanaphthalenes follow from their spectroscopic data. The bright yellow *t*-butyldimethyl derivative **19** displays methyl proton resonances at δ 0.48 ($OSiMe_2$) and 1.19 (OSiBu-*t*) while the C-8 silyl ether and phenyl substituents cause non-equivalence in H-2/7 which appear at δ 7.29/7.40; the corresponding carbon resonances are at 104.1/104.9 while C-1 and C-8 appear at 95.9 and 135.8 ppm, respectively. The data recorded for the yellow *t*-butyldiphenyl derivative **20** have many similarities and show an OSiBu-*t* (δ 1.30) and shielded and deshielded olefinic carbons (C-1 and C-8: δ 97.5 and 136.9), but it is the non-equivalence of H-2 and H-7 that shows the most dramatic change; H-2 (*Z* to the O atom) resonates 1.5 ppm to higher field than H-7 (δ 5.78 vs 7.27). The C-2/7 resonances differ in chemical shift by 1 ppm (δ 104.9/103.9), a value somewhat larger than normal.[6] Because of the large chemical shift difference between H-2 and H-7, HMBC correlations for the assignment of H-3 and H-6 (and their respective carbon resonances) are straightforward (Section 1). It is abundantly clear that the dramatic difference in the environment of H-2 and H-7 in **20** is a result of the sterically very demanding diphenyl(*t*-butyl)silyl group. Semiempirical calculations at the restricted Hartree–Fock level using the AM1



10: R^1 = H; R^2 = Ph
11: R^1 = H; R^2 = Me
12: R^1 = $CONMe_2$; R^2 = NMe_2

26: R^1 = H; R^2 = Ph
27: R^1 = H; R^2 = Me
28: R^1 = $CONMe_2$; R^2 = NMe_2

Scheme 4.

method[35,36] place H-2 in the shielding cone of one of the silicon phenyl substituents in the most favoured conformer (546 kJ mol^{-1}), as shown in Fig. 1. The distance from the centre of this pendant phenyl ring to H-2 is 411 ppm and it is twisted 70° with respect to the plane carrying the cyclopropyarenyl moiety. The range of isomers derived from rotations about the C-8–O, O–Si, and Si–C_{ipso} bonds of this flexible molecule all fall within ca. 12 kJ mol^{-1}. The electronic absorption spectra of these brightly coloured compounds show little solvatochromy between hexane and acetonitrile but there seems little doubt that the molecules typify the polar alkylidenecyclopropyarenes and have charge separation.[6] The assignment of structure to the analogous, though sterically somewhat less crowded, *t*-butyldimethylsilyl enol ether **21** from the acetyl-substituted **11** follows by analogy but the compound undergoes easy oxidation during attempted purification. In contrast, the more bulky diphenyl derivative **22** (δ_H 5.99, H-2; 7.04, H-7) is formed in only low yield and could not be obtained pure prior to its decomposition. It seems likely that the presence of the enolizable MeCO-centre also provides for alternative, competing reaction pathways.

Despite the drawbacks associated with acetylcyclopropyarene **11**, di-*t*-butylchlorophosphine intercepts phenyl substituted enolate **16**. Work-up in a manner analogous to that employed for the siloxy ethers **19** and **20** provides product, but it is not the phosphinous acid ester **23** that is isolated. Rather the phosphonic acid ester **24** is the bright yellow solid obtained and its formation is presumed to result from aerial oxidation[37] of initially formed **23**. The two *t*-butyl groups exhibit a phosphorus-coupled proton doublet ($^3J_{P-H}$=14.7 Hz) in the ^{1}H NMR spectrum and the C–H(2/7) groups appear at δ 7.53/106.6 and 7.65/108.6; the phosphorus resonance is at 68.6 ppm.

Upon thermolysis and/or photolysis 1,1-diester-substituted cycloproparenes are known to provide benzofurans from ring expansion involving the carbonyl group.[18–20] Comparable reactions of the acylcycloproparenes **10**–**12** described herein, therefore, should result in novel and new naphtho[*b*]furans (Scheme 4). This is borne out from refluxing a solution of the diamide **12** in benzene. Rearrangement occurs to give the aminofuran **28** quantitatively (Section 1). At ambient temperature rotation about the CO–N bond[29–32] in this compound is comparable with the time-scale of NMR measurement in *d*-chloroform solution as the $CONMe_2$ protons appear as a broad singlet (δ 3.17) but the resonance of the methyl carbons is not discernible above the baseline. HSQC and HMBC experiments allow for the location of this chemical shift at δ ca. 35.2. At −20°C rotation is slowed and the signals are clearly evident in the expected 1:1 ratios (δ_H 3.18 and 3.19; δ_C 35.2 and 39.3). In the same way, the C-1 acetyl derivative **11** provides the known[38,39] analogous product **27** but the yield is only 20%. With this and the phenyl substituted substrate **10**, added scope likely exists for alternative reactions at least formally through diradical **25**. Thus dimerizations[40,41] and involvement of the C-8 phenyl group of **10** through radical insertions[42–44] become relevant. It is not surprisingly, therefore, that the 2-phenylnaphthofuran **26** is isolated in low (7%) yield but it proved to be the only identifiable product from a multi-component mixture formed upon thermolysis of **10** at 80°C. In contrast, reaction in the solid state at 101°C gives some 17% of **26** while the photo-rearrangement (254 nm) provides the same product in a meagre 5% yield.

In conclusion, we have demonstrated that the novel C-1 acylcycloproparenes **10**–**12** undergo ring opening in an acid medium. The *ortho*-disubstituted products are formed in reactions triggered by enol formation. This contrasts with electrophilic addition to the aromatic π framework and opening to a benzylic cation as observed in simpler cycloproparenes. The formation of enolate ion upon base removal of the C-1 hydrogen atom has been demonstrated from trapping with sterically congested chlorosilanes. This has provided the first example of cycloproparenylidene enol ethers whose ultraviolet absorptions are compatible with extended conjugation and 'push–pull' character within the molecules. The thermal behaviour of these acyl derivatives compares well with that of C-1 esters reported some 30 years ago and has provided new and novel naphthofurans. We continue to explore the chemistry of the cycloproparene framework and in particular the development of more extended conjugation through less common functionality at C-1.

1. Experimental

1.1. General

Microanalyses were performed by the Analytical Facility of Otago University, Dunedin. Accurate mass measurements were recorded by Mr O. Zubkov on a PE Biosystems Mariner spectrometer operating in electrospray mode except where stated otherwise. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity INOVA 300 MHz instrument for *d*-chloroform solutions using the residual solvent peak as internal standard; the ^{31}P NMR spectrum (same instrument) used the P atom of 10% phosphoric acid in D_2O as 0.00 ppm. NMR multiplicities are defined by the usual notation and coupling constants are in hertz. The assignments of ^{13}C and ^{1}H NMR resonances were made with the aid of

DEPT and ^1H–^1H COSY and ^{13}C–^1H HSQC experiments, and heteronuclear multiple bond connectivity (HMBC) experiments. IR spectra of solid samples were recorded for KBr disks using a Biorad FTS 7 spectrophotometer. UV measurements were acquired from a Hewlett–Packard 8452A diode array spectrophotometer. Melting points were determined on a Reichert hot-stage melting point apparatus and are uncorrected.

Thin layer chromatographic (TLC) analyses were performed using Merck Kieselgel (Alufoilen) 60 F_{254} to a thickness of 0.2 mm. Components were detected under an ultraviolet lamp at 254 or 350 nm, or in an iodine chamber. Preparative TLC plates were coated with Merck Kieselgel GF_{254} to a thickness of 0.75 mm and radial chromatography plates were coated with Merck Kieselgel 60 GF_{254} to a thickness of 2.0 or 4.0 mm. Column chromatography employed Riedel de Haën silica gel S (230–400 ASTM) unless otherwise stated.

1.1.1. Reaction of the 1-acyl-1*H*-cyclopropa[*b*]naphthalenes with mineral acid. To the stirred 1-acyl-1*H*-cyclopropa[*b*]naphthalene (57–100 mg, 0.31–0.41 mmol) in THF (5 ml) under nitrogen was added HCl (2 M, 1 ml, 2 mmol) and the stirring continued at ambient temperature until the reaction was complete (TLC). The yellow product mixture was poured into CH_2Cl_2/H_2O (1:1; 100 ml), the phases were separated, and the aqueous phase extracted (CH_2Cl_2, 3×15 ml). The combined organic layers were washed (H_2O, 50 ml), dried ($MgSO_4$), and concentrated under reduced pressure to an oily yellow solid that was purified by radial chromatography.

(a) From **10**[15] (100 mg, 0.41 mmol) after 40 h was obtained **2-phenylnaphtho[2,3-b]furan (26)** (3.8 mg, 4%—see below) as a white solid from radial chromatography (light petroleum elution). Further elution (dichloromethane) gave **2-(3-chloro-2-naphthalenyl)-1-phenylethanone (13)** (90 mg, 79%) as a white solid and the major component; an analytical sample was obtained (THF) as lustrous, fluffy white needles, mp 164–166°C (Found: C, 76.8; H, 4.6; Cl, 12.6; $[M+H]^+$ 281.0728. $C_{18}H_{13}ClO$ requires: C, 77.0; H, 4.7; Cl, 12.6%; $[M+H]^+$ 281.0739). ν_{max} 3055, 3034, 3025, 1694, 1319, 1209, 976, 764, 750, 687 cm^{-1}. λ_{max} (MeCN) 229 (4.80), 250 sh (4.26), 271 (3.84), 280 (3.82), 290 nm (log ϵ 3.62). ^1H NMR δ 4.59 (s, CH_2), 7.44–7.54 (m, H6/7 and H13/15), 7.59–7.64 (app tt, J=7.3, 1.7 Hz, H14), 7.74 (bs, H1), 7.75–7.79 (m, H5/8), 7.93 (bs, H4), 8.08–8.12 (m, H12/16); ^{13}C NMR δ 43.5 (CH_2), 126.3/126.6 (C6 and C7), 126.7/127.5 (C5 and C8), 127.6 (C4), 128.4 (C12/16), 128.7 (C13/15), 130.6 (C1), 131.0 (q), 132.0 (q), 132.3 (q), 133.2(5) (q), 133.3(2) (C14), 136.5 (C11), 196.6 (CO).

(b) From **11**[15] (57 mg, 0.31 mmol) after 36 h was obtained **1-(3-chloro-2-naphthalenyl)propan-2-one (14)** (41 mg, 60%) as a pale yellow solid from radial chromatography (dichloromethane/light petroleum elution, 1:1). An analytical sample was obtained (same solvent mixture) as colourless plates, mp 87–88°C (Found: C, 71.5; H, 5.1; $[M+H]^+$ 219.0571. $C_{13}H_{11}OCl$ requires: C, 71.4; H 5.1%; $[M+H]^+$ 219.0571). ν_{max} 3045, 2922, 2903, 2853, 1721, 1588, 1492, 1402, 1361, 1334, 1319, 1165, 1135, 1006, 966, 888, 763 cm^{-1}. λ_{max} (MeCN) 229 (5.00), 263 (3.58), 272 (3.67), 281 (3.67), 290 nm (log ϵ 3.49). ^1H NMR δ 2.26 (s, Me), 4.00 (s, CH_2), 7.47–7.50 (m, H6/7), 7.70 (bs, H1), 7.73–7.80 (m, H5/8), 7.90 (bs, H4); ^{13}C NMR δ 29.7 (Me), 48.6 (CH_2), 126.4/126.7(2) (C6 and C7), 126.7(7)/127.4 (C5 and C8), 127.7 (C4), 130.6 (C1), 130.7 (C2 or C3), 131.9 (C8a or C4a), 132.2 (C3 or C2), 133.2 (C4a or C8a), 205.3 (CO).

(c) From **12**[15] (100 mg, 0.35 mmol) after 168 h was obtained **2-chloro-3-[bis(*N*,*N*-dimethylcarboxamido)-methyl]naphthalene (15)** (84 mg, 74%) as a pale yellow solid from radial chromatography (ethyl acetate elution); an analytical sample was obtained from dichloromethane/light petroleum (1:1) as colourless blocks, mp 145–146°C (Found: C, 63.7; H, 6.0; N, 8.8; Cl, 10.9; $[M+H]^+$ 319.1223. $C_{17}H_{19}O_2N_2Cl$ requires: C, 64.0; H, 6.0; N, 8.8; Cl, 10.0%; $[M+H]^+$ 319.1208). ν_{max} 3059, 2924, 2854, 1656, 1495, 1455, 1439, 1385, 1352, 1271, 1205, 1129, 1054, 1017, 959, 880, 851, 755 cm^{-1}. λ_{max} (MeCN) 231 (4.67), 276 nm (log ϵ 3.55). ^1H NMR δ 2.94 (s, 2×NMe), 3.02 (s, 2×NMe), 5.56 (s, ArC**H**), 7.42–7.49 (m, H6/7), 7.70–7.73 (m, H5), 7.79–7.83 (m, H8), 7.84 (bs, H1), 7.88 (bs, H4); ^{13}C NMR δ 36.0 (2×NMe), 37.2 (2×NMe), 51.3 (ArCH), 126.3/126.9 (C6 and C7), 126.4 (C5), 127.4 (C4), 128.1 (C8), 129.9/131.0 (C2 and C3), 130.2 (C1), 131.9/133.3 (C4a and C8a), 167.7 (2×CO).

1.1.2. Preparation of enol ethers from 1-acyl-1*H*-cyclopropa[*b*]naphthalenes. To a stirred solution of the 1-acyl-1*H*-cyclopropa[*b*]naphthalene (100–150 mg, 0.41–0.61 mmol) in anhydrous THF (15 ml) at −78°C under argon was added BuLi (2.5 M, 0.16–0.25 ml, 1 mol equiv.). The dark mixture was stirred at this temperature for 30 min prior to the dropwise addition of alkyl halide (1 mol equiv.). The mixture was warmed to ambient temperature overnight, poured into Et_2O/H_2O (1:1; 100 ml) and the phases separated. The aqueous phase was extracted (ether, 3×15 ml) and the combined organic layers were washed (H_2O, 50 ml), dried ($MgSO_4$) and concentrated under reduced pressure to a thick yellow oil which was purified by radial chromatography.

(a) From 1-benzoyl-1*H*-cyclopropa[*b*]naphthalene (**10**)[15] (120/150 mg, 0.49/0.61 mmol): (i) with trimethylsilyl chloride (0.08 ml, 0.61 mmol) was obtained a bright yellow solid (84 mg) after radial chromatography (dichloromethane/light petroleum, 1:1) that contained (^1H NMR) **1-[(trimethylsiloxy)phenylmethylidene]-1*H*-cyclopropa[*b*]-naphthalene (18)** and unchanged **10** in a 17:3 ratio. Attempts to obtain the pure compound resulted in its decomposition. Partial NMR data for **18** abstracted from spectra are: ^1H NMR δ 0.55 (s, Me_3Si), 7.30–7.31 (d, J∼1 Hz, 1H), 7.37–7.43 (app tt, J=7.3, 1.7 Hz, 1H), 7.41–7.42 (d, J∼1 Hz, 1H), 7.47–7.50 (BB′, 2H), 7.51–7.57 (app t, J=7.6 Hz, 2H), 7.84–7.89 (AA′, 2H), 8.05–8.09 (app d, J=8.5 Hz, 2H); ^{13}C NMR δ 0.90 (Me_3Si), 96.0 (q), 104.2 (CH), 104.9 (CH), 124.7 (2×CH), 127.0 (CH), 126.2 (CH), 127.8 (CH), 128.1(5) (CH), 128.2(6) (CH), 128.3 (2×CH).

(ii) With *t*-butyldimethylsilyl chloride (93 mg, 0.61 mmol) in THF (2 ml) was obtained **1-[(*t*-butyldimethylsiloxy)-phenylmethylidene]-1*H*-cyclopropa[*b*]naphthalene (19)**

(125 mg, 57%) as a bright yellow solid from radial chromatography (dichloromethane/light petroleum, 1:4). An analytical sample was obtained as bright yellow plates from dichloromethane/light petroleum (1:1), mp 104–106°C (Found: C, 80.5; H, 7.2(5); $[M+H]^+$ (APCI) 359.1826. $C_{24}H_{26}OSi$ requires: C, 80.4; H, 7.4%; $[M+H]^+$ 359.1807). ν_{max} 3041, 2948, 2925, 2854, 1785, 1592, 1549, 1509, 1487, 1419, 1311, 1292, 1251, 1177, 1160, 1138, 1074, 841, 783, 763, 747, 689, 608, 553 cm^{-1}. λ_{max} (hexane) 230 (4.58), 246 sh (4.25), 254 (4.15), 291 (4.28), 368 (4.07), 374 (4.14), 393 (4.56), 422 nm (log ϵ 4.82); UV λ_{max} (MeCN) 230 (4.56), 246 sh (4.25), 254 (4.14), 291 (4.26), 368 (4.03), 372 (4.07), 392 (4.49), 420 nm (log ϵ 4.72). ^{1}H NMR δ 0.48 (s, Me_2Si), 1.19 (s, Me_3CSi), 7.29 (d, J=1.5 Hz, H2 or H7), 7.37–7.42 (app tt, J=7.3, 1.7 Hz, H12), 7.40 (d, J=1.5 Hz, H7 or H2), 7.45–7.50 (BB′, H4/5), 7.51–7.56 (t, J=7.6 Hz, H11/13), 7.84–7.88 (AA′, H3/6), 8.07–8.10 (app d, J=8.6 Hz, H10/14); ^{13}C NMR δ −3.7 (Me_2Si), 18.4 (Me_3**C**), 25.9 (**Me**$_3$CSi), 95.9 (C1), 104.1/104.9 (C2 and C7), 114.6 (C1a or C7a), 124.7 (C10/14), 126.1(5)/126.2 (C4 and C5), 126.4 (C7a or C1a), 127.8 (C12), 128.1/128.2 (C3 and C6), 128.3 (C11/13), 135.8 (C8), 137.1 (C9), 137.7/137.8 (C2a and C6a).

(iii) With *t*-butyldiphenylsilyl chloride (0.13 ml, 0.49 mmol) was obtained from radial chromatography (dichloromethane/light petroleum, 1:4) an analytical sample of **1-[(*t*-butyldiphenylsiloxy)phenylmethylidene]-1*H*-cyclopropa[*b*]naphthalene (20)** (150 mg, 63%) as a viscous tar which solidified after scratching, mp 134–140°C (Found: C, 84.5(5); H, 6.5; $[M+H]^+$ (APCI) 483.2139. $C_{34}H_{30}OSi$ requires: C, 84.6; H, 6.3%; $[M+H]^+$ 483.2140). ν_{max} 3071, 3050, 2927, 2855, 1589, 1547, 1506, 1486, 1471, 1445, 1418, 1386, 1287, 1151, 1132, 1114, 1073, 1025, 886, 828, 762, 742, 701, 620, 602, 552, 503, 490, 469 cm^{-1}. λ_{max} (hexane) 227 (4.73), 254 sh (4.33), 282 (4.23), 292 (4.39), 369 (4.16), 374 (4.22), 394 (4.64), 422 nm (log ϵ 4.90); λ_{max} (MeCN) 228 (4.58), 254 sh (4.19), 282 (4.09), 292 (4.24), 368 (4.01), 374 (4.08), 393 (4.47) 421 nm (log ϵ 4.71). ^{1}H NMR δ 1.30 (s, Me_3CSi), 5.78 (d, J=1.2 Hz, H2), 7.27 (d, J=1.2 Hz, H7), 7.33–7.52 (m, 10H), 7.61–7.66 (bd t, J=7.7 Hz, H11/13), 7.74 (bd d, J=8.1 Hz, H6), 7.99–8.03 (m, 4H), 8.27–8.31 (bd d, J=7.3 Hz, H10/14); ^{13}C NMR δ 19.5 (Me_3**C**Si), 26.5 (**Me**$_3$CSi), 97.5 (C1), 103.9 (C7), 104.9 (C2), 124.6 (C10/14), 125.5 (C1a or C7a), 125.7/125.8 (C4 and C5), 126.4 (C7a or C1a), 127.7 (2×CH), 127.8 (CH), 127.9 (CH), 128.2 (CH), 128.5 (C11/13), 129.8 (C18), 133.3 (C15), 134.6 (C8), 135.1 (2×CH), 136.9 (C9), 137.5/137.7 (C2a and C6a).

(iv) With di-*t*-butylchlorophosphine (0.09 ml, 0.49 mmol) was obtained after radial chromatography (ethyl acetate elution) a mixture of **di-*t*-butylphosphinic acid 8-[1-(phenylmethylidene)-1*H*-cyclopropa[*b*]naphthalene]-*O*-ether (24)** together with an unidentified phosphorous-containing compound as a yellow oil. Subsequent radial chromatography (ethyl acetate/dichloromethane elution, 6:1) gave an analytical sample of **24** (32 mg, 16%) as a bright yellow oil which solidified on standing, mp 158–161°C (Found: C, 76.7; H, 7.3; $[M+H]^+$ 405.1978. $C_{26}H_{29}O_2P$ requires: C, 77.2; H, 7.2%; $[M+H]^+$ 405.1990). ν_{max} 3053, 2924, 2854, 1770, 1742, 1713, 1632, 1469, 1448, 1423, 1384, 1274, 1231, 1143, 1115, 1074, 1011, 939, 889, 822, 748, 692, 672, 594, 476 cm^{-1}. λ_{max} (hexane) 230 (4.73), 252 sh (4.31), 290 (4.43), 3.71 sh (4.25), 392 (4.63) 420 nm (log ϵ 4.75); UV λ_{max} (MeCN) 230 (4.73), 252 sh (4.30), 290 (4.41), 3.69 sh (4.22), 391 (4.57), 418 nm (log ϵ 4.71). ^{1}H NMR δ 1.44 (d, $^3J_{P-H}$=14.7 Hz, 2×Me_3C), 7.33–7.37 (app tt, J=7.3, 1.2 Hz, H12), 7.42–7.47 (BB′, H4/5), 7.48–7.54 (app t, J=7.7 Hz, H11/13), 7.53 (d, J=1.7 Hz, H2 or H7), 7.65 (d, J=1.7 Hz, H7 or H2), 7.85–7.89 (AA′, H3/6), 7.95–7.99 (app d, J=8.5 Hz, H10/14); ^{13}C NMR δ 26.7 (2×**Me**$_3$C), 37.2 (d, $^1J_{P-C}$=80.6 Hz, 2×**Me**$_3$C), 99.9 (C1), 106.6/108.6 (C2 and C7), 124.0 (C10/14), 126.0 (d, $^4J_{P-C}$=1.0 Hz, C1a or C7a), 126.3(3)/126.3(8) (C4 and C5), 127.0 (d, $^4J_{P-C}$=1.0 Hz, C7a or C1a), 127.7 (C12), 128.4 (C3 or C6), 128.6 (C11/13), 128.9 (C6 or C3), 132.4 (d, $^2J_{P-C}$=12.6 Hz, C8), 135.5 (d, $^3J_{P-C}$=4.5 Hz, C9), 138.3/138.9 (C2a and C6a); ^{31}P NMR δ 68.6.

(b) From 1-acetyl-1*H*-cyclopropa[*b*]naphthalene (**11**)[15] (100 mg, 0.55): (i) with *t*-butyldimethylsilyl chloride (84 mg, 0.55 mmol) in THF (2 ml) was obtained after radial chromatography (dichloromethane/light petroleum elution, 1:4) a bright yellow oil (60 mg) that contained predominantly **1-[(1-*t*-butyldimethylsiloxy)ethylidene]-1*H*-cyclopropa[*b*]naphthalene (21)** (ca. 55 mg, ca. 35%). Subsequent attempts to purify compound **21** resulted in its decomposition. NMR data abstracted from the spectra of the crude product are: ^{1}H NMR δ 0.37 (s, Me_2Si), 1.05 (s, Me_3CSi), 2.29 (s, =CMe), 7.09/7.10 (2×bs, H2 and H7), 7.38–7.41 (BB′, H4/5), 7.73–7.77 (AA′, H3/6); ^{13}C NMR δ −3.9 (Me_2Si), 18.0 (Me_3**C**Si), 22.3 (=C**Me**), 25.6 (Me_3CSi), 95.4 (C1), 103.4/103.6 (C2/7), 125.6/125.7 (C4/5), 127.9/128.1 (C3/6), 126.2, 128.4, 136.7, 137.3, 137.5 (all q).

(ii) With *t*-butyldiphenylsilyl chloride (0.143 ml, 0.55 mmol) was obtained a thick yellow tar (150 mg) as the crude product of reaction. ^{1}H NMR analysis indicated the presence of olefin **22** from the presence of doublets (ca. J=1 Hz) at δ 5.99 (H2) and 7.04 (H7) with the shielding caused by a phenyl group in analogy with the lowest energy conformer of **20**. Attempts to isolate this product resulted in its decomposition.

1.1.3. Preparation of naptho[2,3-*b*]furans 26–28. (a) A solution of the requisite 1-acyl-1*H*-cyclopropa[*b*]naphthalene (100–340 mg, 0.35–1.87 mmol) was refluxed in dry benzene (5 ml) under argon for 16 h. The residue obtained by concentration to dryness was purified as described.

(i) 1-Benzoyl-1*H*-cyclopropa[*b*]naphthalene (**10**) (120 mg, 0.49 mmol) gave **2-phenylnaphtho[2,3-*b*]furan (26)** (8 mg, 7%) as cream plates from radial chromatography (light petroleum elution), mp 204°C (sub.), 225–233°C (sublimate vapourizes) (Found: C, 86.8; H, 4.8; $[M+H]^+$ 245.0953. $C_{18}H_{12}O$ requires: C, 88.5; H, 4.9 (5)%; $[M+H]^+$ 245.0961). ν_{max} 3059, 3039, 1564, 1490, 1448, 1264, 1018, 902, 867, 761, 742, 719, 689, 478 cm^{-1}. λ_{max} (MeCN) 222 (4.77), 272 (4.77) 279 (4.71), 330sh (4.59), 340 (4.64), 356sh nm (log ϵ 4.25). ^{1}H NMR δ 7.15 (d, J~1 Hz, 1H), 7.41–7.52 (m, 5H), 7.92–7.97 (m, 5H), 8.04 (bs, 1H); ^{13}C NMR δ 100.7 (CH), 106.6 (CH) 118.5 (CH) 124.0 (CH), 124.7 (CH), 125.3 (2×CH), 127.8 (CH), 127.9 (CH), 128.8 (2×CH), 129.1 (CH), 130.1 (C), 130.2 (C), 130.7 (C), 131.5 (C), 153.9 (C), 158.1 (C).

When **10** (50 mg, 0.20 mmol) was slowly heated to its melting point (101°C) the sample decomposed violently. The cooled black residue was dissolved in acetone and filtered though silica gel in a micropipette. The eluent was purified by radial chromatography (light petroleum) to give naphthofuran **26** (8.6 mg, 17%) identical to the sample obtained above.

(ii) 1-Acetyl-1*H*-cyclopropa[*b*]naphthalene (**11**) (340 mg, 1.87 mmol) gave 2-methylnaphtho[2,3-*b*]furan (**27**) (67 mg, 20%) from radial chromatography (dichloromethane/light petroleum elution, 1:1) as a white solid, mp 73–74°C (lit.[39] 71–72°C). ^{1}H NMR δ 2.54 (d, $J\sim1$ Hz, Me), 6.50 (t, $J\sim1$ Hz, H3), 7.43–7.47 (m, H6/7), 7.84 (bs, H9), 7.93–7.96 (m, H4 and H5/8); ^{13}C NMR δ 14.3 (Me), 102.2 (C3), 106.0 (C9), 117.4 (C4), 123.7/124.3 (C6 and C7), 127.7 (6)/127.7 (9) (C5 and C8), 130.4 (C3a and C4a or C8a), 130.8 (C8a or C4a), 154.0 (C9a), 158.1 (C2).

(iii) Bis(*N*,*N*-dimethyl)-1*H*-cyclopropa[*b*]naphthalene-1,1-dicarboxamide (**12**) (100 mg, 0.35 mmol) gave **2-*N*,*N*-dimethylamino-3-*N*,*N*-dimethylamidobenzo[2,3-*b*]furan (28)** (100 mg, 100%) as a brown wax. Recrystallization (dichloromethane/light petroleum, 1:1) gave an analytical sample as brown plates, mp 135–136°C (Found: C, 71.5; H, 6.6; N, 9.9 (5); $[M+H]^+$ 283.1442. $C_{17}H_{18}O_2N_2$ requires: C, 72.3; H, 6.4; N 9.9%; $[M+H]^+$ 283.1441). ν_{max} 3053, 2924, 1643, 1633, 1607, 1579, 1430, 1416, 1370, 1042, 857 cm^{-1}. λ_{max} (MeCN) 222 (4.56), 272 (4.56), 292 (3.83), 305 (4.01), 318 (4.15), 353 nm (log ϵ 4.11). ^{1}H NMR δ 3.15 (s, $=CNMe_2$), 3.17 (bs, $CONMe_2$), 7.29–7.40 (m, H6/7), 7.42 (bs, H4), 7.58 (bs, H9), 7.79–7.82 (m, H5/8); ^{13}C NMR δ 35.2[†] ($CONMe_2$), 39.4 ($=CNMe_2$), 85.7 (C3), 104.9 (C9), 113.2 (C4), 123.2/124.1 (C6 and C7), 126.9 (C5), 127.6 (C8), 129.1/131.3 (C4a and C8a), 130.8 (C3a), 149.0 (C9a), 160.6 (C2), 166.9 (CO). The chemical shift data for the formally non-equivalent $CONMe_2$ methyl groups were resolved at −20°C giving δ_H 3.18 (s, 3H) and 3.19 (s, 3H), and δ_C 35.2 and 39.3.

(b) A solution of benzoyl-1*H*-cyclopropa[*b*]naphthalene (**10**) (80 mg, 0.33 mmol) in MeCN (30 ml) was irradiated at 254 nm for 16 h in a Rayonette RP203 preparative photochemical reactor in a quartz tube fitted with a reflux condenser. Concentration to dryness and purification of the orange residue by radial chromatography (light petroleum) gave naphthofuran **26** (3.6 mg, 5%) as a cream solid identical to that obtained above.

1.2. Computational methods

Semiempirical calculations were performed at the restricted Hartree–Fock level using the AM1 method.[35,36] Calculations were performed using SPARTAN[45] on an R5000 Silicon Graphics workstation.

[†] This chemical shift value was obtained from the HSQC and gHMBC spectra as no signal was observed in the ^{13}C NMR experiment.

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