Studies in the Cyclopropanarene Series: Unexpected Products from Peterson Olefinations

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Reaction of tetraphenylcyclopentadienone with anion **8** derived by monodesilylation of 1,1-bis(trimethylsilyl)cyclopropa[*b*]naphthalene (**10**) gives the 1-(5′-cyclopentadienyl)-substituted cyclopropanarene **17** from simple anion addition to the carbonyl group rather than fulvalene **16** from loss of Me_3SiO^-. Reactions of anion **8** with *p*-(trifluoromethyl)benzaldehyde and thiophene-2-carbaldehyde give the expected exocyclic olefins **12a** and **12b**, respectively. In contrast, the 3,6-dimethoxy analogue **24**, obtained from cyclopropanarene **20**, gives the C1 unsubstituted cyclopropanarene **19** and the Tishchenko products, *p*-(trifluoromethyl)benzyl *p*-(trifluoromethyl)benzoate (**21**) and 2-thienylmethyl thiophene-2-carboxylate (**22**), respectively.

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Introduction

The class of strained aromatic hydrocarbons known as the cyclopropanarenes, and illustrated by parent 1*H*-cyclopropabenzene (**1**) and 1*H*-cyclopropa[*b*]naphthalene (**2**), has provided much fascinating chemistry[1,2] since Anet and Anet[3] reported the first authenticated derivative in 1964. The fact[4,5] that the pK_a of **1** is ca. 36 means that the C1 cyclopropabenzenyl anion **3** and its naphthalenyl analogue **4** can be generated with relative ease and used in synthesis. This has proved to be the case[6,7] as **3** and **4** have been used routinely in Peterson olefinations[8−11] to give exocyclic alkenes **11** and **12** (Scheme 1) of which there now exist well in excess of 100 examples.[1]

In the cyclopropabenzene series the reaction sequence can be performed as a one-pot operation for the transformation of **1** into **11**.[12] This contrasts with cyclopropa[*b*]-naphthalene where the transformation of **2** into disilane **10** because monosilane **6** is deprotonated under the reaction conditions by unconsumed **4,** regenerates **2** and gives **10** (via anion **8**) in equimolar quantities (Scheme 1).[6,11,12] Use of excess reagents leads to **10** in good yield (66%) and this stable, crystalline synthon can be stored in the refrigerator almost indefinitely. Desilylation of **10** with potassium *tert*-butoxide regenerates anion **8** and this is able to react with added aldehyde or ketone to give the desired exocyclic alkene **12**. In all but one of such reported Peterson olefinations[1] the sequences from **1** to **11**, and from **10** to **12**, proceed directly to the alkene; the only side product recorded has come from the transformation of **1** into **11** (R^1 = Ph; R^2 = H) employing benzaldehyde. In this instance, and after short reaction periods, an unstable oil was obtained in yields of up to 40% that was proposed as the β-hydroxysilane **13** (Scheme 1) from workup prior to the loss of trimethylsilyl oxide.[12] We provide here the first examples of attempted Peterson olefinations in the cyclopropanaphthalene series where the desired olefination is thwarted and unexpected products are obtained.

Results and Discussion

The provision of polar fulvalenes from **1** and **2** has been appropriately demonstrated[13] for derivatives of ring systems rather than for the parent molecules themselves. Thus, the fluorenylidene derivatives **14** and **15** are available in good yields[14] although no simpler cyclopentadienylidene analogues are known − the facile thermal dimerisation of cyclopentadienone has precluded its use. In our study of "push-pull' electronic effects in the cyclopropanarenes,[15] we attempted to prepare the tetracyclone derivative **16** for use as a model compound by employing what are now conventional procedures and workup. While an orange solid was isolated it proved not to be the alkylidene derivative **16**, but alcohol **17** resulting from nucleophilic addition of anion **8** to the tetracyclone >C=O bond and subsequent protonation. The presence of ^{1}H NMR singlets at δ = 0.22 ppm (Me_3Si) and 5.20 ppm (OH) in a ratio of 9:1 together with an envelope of 26 aromatic protons in the range δ = 7.22−7.95 ppm is fully consistent with this (see Exp. Sect.). That the cyclopropa[*b*]naphthalenyl moiety had been retained was clearly evident from the diagnostic[1,16] shielding of the C2/C7 arene carbon atoms adjacent to the three-

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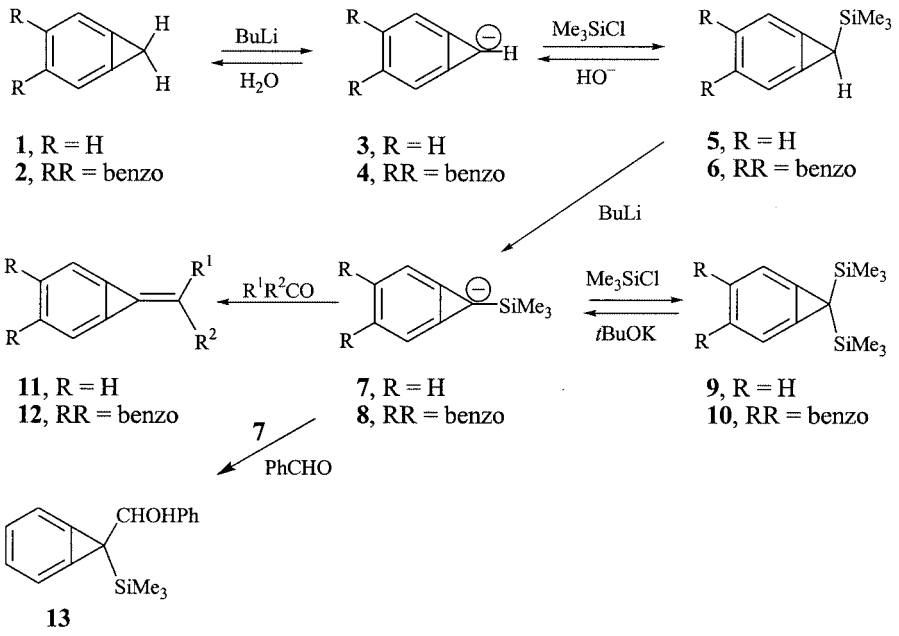
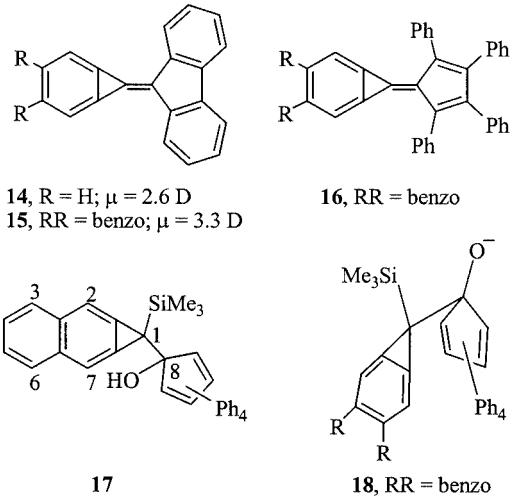


1, R = H
2, RR = benzo
3, R = H
4, RR = benzo
5, R = H
6, RR = benzo
11, R = H
12, RR = benzo
7, R = H
8, RR = benzo
9, R = H
10, RR = benzo
13

Scheme 1

membered ring (δ = 113.6 ppm). Confirmation of the composition as $C_{43}H_{36}OSi$ has come from high-resolution mass measurement and the compound is confidently assigned as the 1,1-disubstituted cycloproparene **17**. The formation of alcohol is quite understandable when one considers the unfavourable geometrical constraints that are present in the *syn*-periplanar transition structure **18** needed for the ejection the trimethylsilyloxy anion in the additionelimination pathway. The formation of alcohols under the Peterson protocol is well documented and can be the normal outcome if the alkene is not stabilized.[17] Moreover, subsequent alkene formation can often be brought about by dehydroxysilation under acid conditions. However, treatment of **17** with acid does not lead to the sought after exocyclic alkene. The cycloproparenes and their alkylidene derivatives are known to be sensitive to acids[18] and the complex mixture of products formed is thought to be due to this. A comparable outcome was obtained from attempted Peterson olefination of the 3,6-dimethoxycyclopropanaphthalene **19** by way of disilane **20**. However, in this instance the reaction product, assumed to be the 3,6-dimethoxy-substituted alcohol corresponding to **17** was not isolated as it proved to be light and air sensitive; it decomposed during attempted purification.

The behaviour of the unsubstituted disilane **10** towards *p*-(trifluoromethyl)benzaldehyde in the presence of base is in agreement with expectation (Scheme 2)[1] in that exocyclic alkene **12a** (R = *p*-$CF_3C_6H_4$) is obtained as bright yellow needles in 62% yield, although this quantity is obtained only after variations in the reaction conditions (see Exp. Sect.). Spectroscopic data that are fully in agreement with the assigned structure were obtained, but these do not justify discussion here. Similarly, anion **8** is known to react with thiophene-2-carbaldehyde to give conjugated alkene **12b** (R^1 = H; R^2 = 2-thienyl), but only in low (34%) yield



14, R = H; μ = 2.6 D
15, RR = benzo; μ = 3.3 D
16, RR = benzo
17
18, RR = benzo

(Scheme 2).[11] In contrast, comparable reactions employing the 3,6-dimethoxy-substituted analogue **20** result in different outcomes that are less easily explained.

Following chromatography, the reaction of **20** with *tert*-butoxide in the presence of *p*-(trifluoromethyl)benzaldehyde leads to yellow platelets that bear all the obvious external characteristics of a coloured, crystalline alkylidenecycloproparene. However, the NMR spectra immediately exclude such a structure since the ^1H spectrum shows an absence of methoxy protons and the ^{13}C analogue has no shielded cycloproparene C2/C7 aromatic carbon atoms.[1] Not only is a derivative of **12** discounted, but also is any compound in which the elements of the cycloproparenyl moiety were to have become involved. This was confirmed from subsequent continued chromatography, which provided the desilylated dimethoxycycloproparene **19** in almost quantitative yield.

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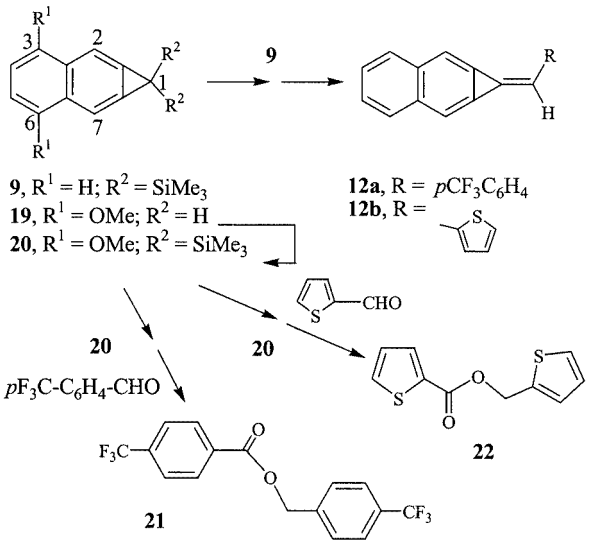


Scheme 2

The nature of the unexpected product became more obvious from observation of a conjugated carbonyl stretching vibration at 1685 cm^{-1} in the IR spectrum and a molecular ion as the base peak of the E.I. mass spectrum at m/z = 356. Furthermore, the presence of two independent *para* disubstituted benzene rings each carrying a CF_3 group (with appropriate long range $^{19}F,^{13}C$ couplings from distinct *p*-CF_3 moieties at δ = 130.3 ppm and 134.7 ppm, respectively − see Exp. Sect.) and a benzylic function (δ_H: 5.48 ppm; δ_C: 66.2 ppm) are evident from the 2-D NMR spectra recorded. The product is confirmed as *p*-trifluoromethybenzyl *p*-(trifluoromethyl)benzoate (**21**; 41%; Scheme 2) from single-crystal X-ray structure determination. The details of the analysis have been deposited (see Exp. Sect.) and Figure 1 shows an ORTEP plot of the molecule at 50% probability. The recorded bond lengths and angles fall within expectation for such a routine structure but the six fluorine atoms are disordered over two sites with an occupancy at 0.5 each.

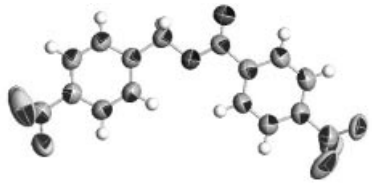
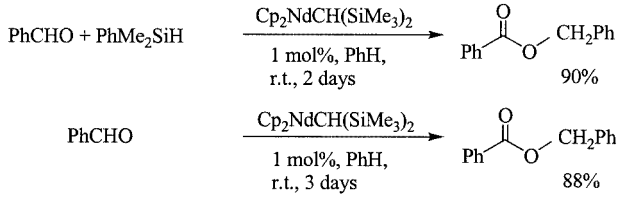


Figure 1. ORTEP plot of *p*-(trifluoromethyl)benzyl *p*-(trifluoromethyl)benzoate (**21**) at 50% probability

In a similar vein, the reaction between **20** and base in the presence of thiophene-2-carbaldehyde does not give anticipated exocyclic analogue of **12b**. It also yields the desilylated diether **19** (91%) this time accompanied by 2-thienylmethyl thiophene-2-carboxylate (**22**) (45%), the latter displaying spectroscopic data that match those recently published.[19]

The reaction of an aldehyde to give an ester that carries the acid component from oxidation and the alcohol moiety from reduction is the known as the Tishchenko reaction,[20] and it is catalysed by early lanthanoid reagents; $Cp_2LaH(SiMe_3)_2$ is particularly effective. It has analogy to the Cannizzaro reaction inasmuch as an aldehyde with no α hydrogen atom has half an equivalent reduced and the other half oxidized. However, unlike the Cannizzaro reaction, an ester is obtained instead of an acid and an alcohol. Of particular relevance here is the fact that attempted hydrosilation of benzaldehyde with dimethylphenylsilane and catalyst provided the Tishchenko "dimer" benzyl benzoate in 90% yield.[19] Moreover, when the silane was omitted, the same yield of dimer (88%) was obtained (Scheme 3). Under such catalysis, Tanaka and co-workers report a quantitative conversion of thiophene-2-carbaldehyde into ester **22**.[19]



Scheme 3

Of all the aldehydes and ketones that have reacted with disilane **20** in the presence of base[15,21] only *p*-(trifluoromethyl)benzaldehyde and thiophene-2-carbaldehyde have afforded Tishchenko dimers and regenerated the original cycloproparene hydrocarbon **19**. The regeneration of parent **2** upon desilylation of disilane **10** has been the subject of a detailed investigation in these laboratories.[6] The reaction is base catalysed and requires one equivalent each of base and water to effect monodesilylation and subsequent protonation of the α-silyl anion. Proton capture releases hydroxide ion for the removal of the second trimethylsilyl group and protonation upon workup completes the sequence. The same process is presumed to operate for the analogous **20** → **19** transformation. The involvement of water in the Tishchenko reactions in which **21** and **22** are formed has been discounted, however, from the results of a dual reaction in which both *p*-(trifluoromethyl)- and *p*-methoxybenzaldehyde can react with α-silyl anion **24** from **20**. Thus, reaction of 2 mol. equiv. each of disilane **20** and potassium *tert*-butoxide with a mixture of 1 mol. equiv. of each aldehyde leads to the isolation of hydrocarbon **19** (47%), Tishchenko dimer **21** (40%), and the normal exocyclic alkene **23** from anisaldehyde (77%; cf. 83% from a dedicated procedure with *p*-anisaldehyde alone − Exp. Sect.; Scheme 4).

A Cannizzaro reaction of *p*-(trifluoromethyl)benzaldehyde to give a 1:1 mixture of acid (from oxidation) and alcohol (from reduction) in 90% overall yield is effected by aqueous NaOH over 30 minutes. In contrast, potassium *tert*-butoxide is ineffective and returns unchanged aldehyde almost quantitatively under conditions that match those

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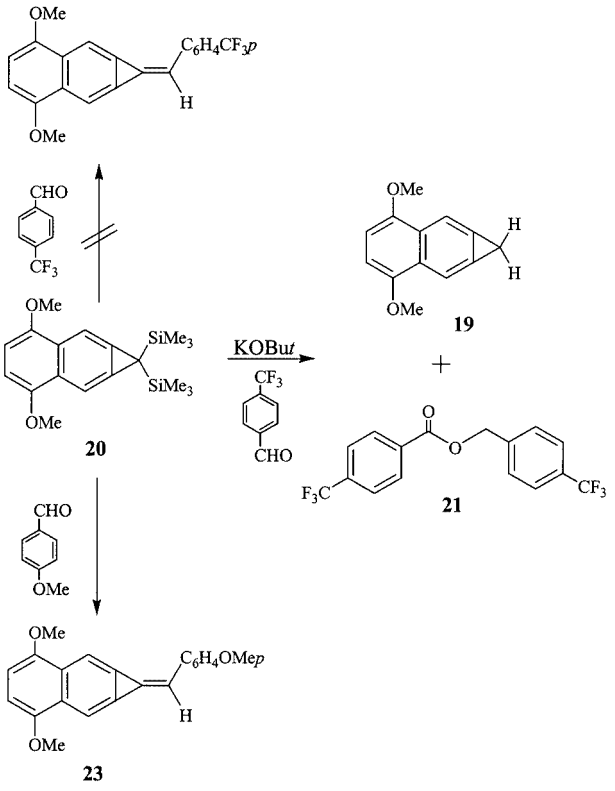
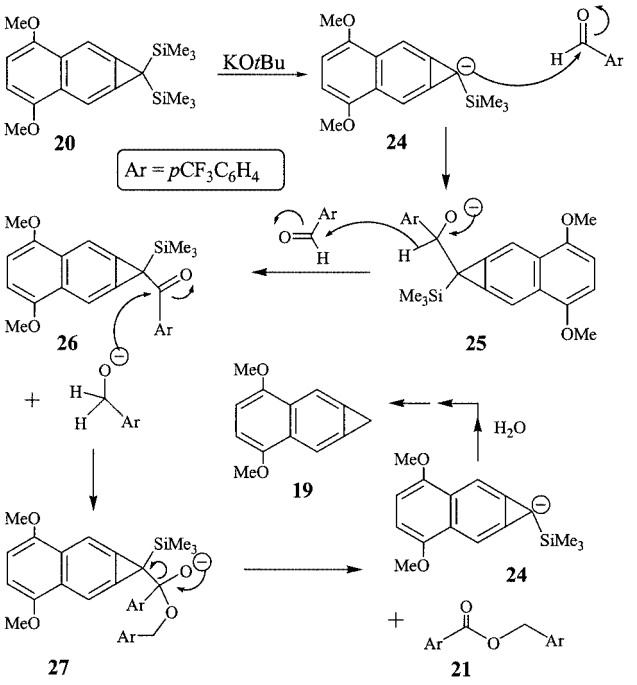


Scheme 4



Scheme 5

from which Tishchenko dimer is obtained. Furthermore, ester **21** is not hydrolysed by *tert*-butoxide in dry THF under the conditions of its formation. Given these data, we conclude that the two Tishchenko reactions recorded herein result from attack of cycloproparenyl anion **24** on the aldehydic carbon of the added aldehyde to give anion **25**, as shown in Scheme 5 for the trifluoromethyl compound. Intermolecular hydride ion transfer to aldehyde then generates acylcycloproparene **26** and alkoxide. In turn, this can then react at the acyl carbonyl centre in an addition-elimination sequence to liberate the Tishchenko dimer **21** and regenerate anion **24** which affords hydrocarbon **19** from base-induced desilylation.

While the sequence of Scheme 5 adequately accounts for the formation of the observed products, it offers little to account for the anomalous behaviour of the two aldehydes in question. The fact that exocyclic alkenes *are* obtained using the *same* aldehydes with non-ether **10** argues strongly for the electron donating capacity of the methoxy groups of **20** to influence subtly the course of reaction. This appears most likely, as differences in steric demand at the reaction sites of **10** and **20** should not be large. We continue to explore the chemistry of these novel compounds.

Experimental Section

General: The Analytical Facility of Otago University, Dunedin, performed all microanalyses. Mr. O. Zubkov recorded mass measurements with high resolution coming from a PE Biosystems Mariner 5158 TOF spectrometer operating in electrospray mode, and 70 eV data from a Hewlett−Packard 5995C instrument. ^{1}H and ^{13}C NMR spectra were recorded with a Varian Unity INOVA 300 MHz instrument for [D]chloroform solutions using the residual solvent peak as internal standard. The usual notations define NMR multiplicities and coupling constants are in Hertz. The assignment of ^{13}C and ^{1}H NMR resonances was made with the aid of DEPT and ^{1}H-^{1}H COSY and ^{13}C-^{1}H 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 while UV/Vis spectra were measured with a Hewlett−Packard 8452A diode array spectrophotometer. Melting points were determined with a Reichert hot-stage melting point apparatus and are uncorrected.

Thin-layer chromatographic (TLC) analyses were performed using Merck Kieselgel (Alufolien) 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. Radial chromatography plates were coated with Merck Kieselgel 60 GF_{254} to a thickness of 2.0 or 4.0 mm.

General Method for the Synthesis of Alkylidene-1*H*-cyclopropa[*b*]-naphthalenes: To a stirred solution of disilane[11] **10** or **20** (1 equiv.) and the carbonyl compound (1 equiv.) in anhydrous THF (ca. 10 mL), cooled to −70 °C and under nitrogen, was added dropwise via syringe needle to a solution of freshly sublimed potassium *tert*-butoxide (1 equiv.) in the same anhydrous solvent (ca. 10 mL). The mixture was stirred at −70 °C for 1 h then warmed to ambient temperature overnight. The mixture was quenched (satd. $NaHCO_3$; 30 mL) and the organic phase extracted with dichloromethane (3 × 20 mL). The combined organic extracts were washed (water; 3 × 20 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a crude product that was purified by radial chromatography.

1-(5-Hydroxytetraphenylcyclopenta-1,3-dienyl)-1-trimethylsilyl-1*H*-cyclopropa[*b*]naphthalene (17): Treated as described above, disilane **20** (100 mg. 0.35 mmol),[21] tetracyclone (135 mg, 0.35 mmol) and potassium *tert*-butoxide (40 mg, 0.35 mmol) gave an orange-brown

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solid, which upon radial chromatography (light petroleum/dichloromethane, 4:1) gave 1*H*-cyclopropa[*b*]naphthalene[14] (**2**) as the most mobile fraction. Yield 8 mg, (16%). The second fraction comprised of **17**. Yield 94 mg, (45%). Orange powder, m.p. 106.0−107.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.22 (s, 9 H, $SiMe_3$), 5.20 (broad s, 1 H, OH), 7.22 (tt, $^3J_{AB}$ = 7.5, $^4J_{AC}$ = 1.6 Hz, 2 H), 7.32 (t, $^3J_{AB}$ = 7.8 Hz, 4 H), 7.33 (tt, $^3J_{AB}$ = 7.5, $^4J_{AC}$ = 1.6 Hz, 2 H), 7.42−7.55 (m, 8 H), 7.61−7.76 (m, 8 H, 2 × 14/18-H, 4/5-H and 2/7-H), 7.91−7.95 (BB′ of AA′BB′, 2 H, 3/6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.2 ($SiMe_3$), 36.3 (C1), 83.8 (C8), 113.6 (C2/7), 125.3(C1a/7a), 126.8 (C4/5) 127.1(C3/6), 128.1 (C22), 128.6 (C10/11), 128.8 (C9/12), 129.7 (C16), 130.5 (C21/23), 130.6 (C20/24), 130.7 (C15/17), 131.5 (C14/18), 132.7 (C19), 133.1 (C13), 136.5 (C2a/6a) ppm. HRMS (positive APCI) calcd. for $C_{43}H_{36}OSi$ [M + H$^+$] 597.2613; found 597.2608 (−0.84 mmu). MS (70 eV): *m/z* (%) = 597 (52) [M + 1$^+$] 596 (100) [M$^+$], 582 (23), 581 (45), 568 (19), 525 (33), 524 (80), 522 (11), 496 (23), 105 (17). IR (KBr): $\tilde{\nu}_{max}$ = 3440, 3051, 2968, 2923, 2169, 1685, 1561, 1438, 1384, 1293, 1231, 1132, 1095, 1028, 955 cm^{-1}. UV/Vis (cyclohexane): λ_{max} (log ε) = 226 (4.05), 284 (3.84), 340 (3.88) nm; (acetonitrile): λ_{max} = 226 (4.02), 286 (3.79), 340 (3.86) nm.

Reaction of Silanol 17 with Dilute Hydrochloric Acid: During the space of 1 min an aqueous solution of HCl (10% v/v, 0.5 mL) was added dropwise to silanol **17** (30 mg, 0.05 mmol) in refluxing THF (20 mL). The mixture was refluxed for 30 min whereupon the colour changed from orange to black-brown. Following workup and concentration, the components of the resultant brown solid proved inseparable by radial chromatography. The ^{13}C NMR spectrum of the crude product showed no shielded C2/7 centres and ring opening of the cycloproparene is presumed to have taken place.[1]

1-(*p*-Trifluoromethylphenyl)methylidene-1*H*-cyclopropa[*b*]-naphthalene (12a): Although *p*-(trifluoromethyl)benzaldehyde is stable to the reaction conditions (see below), the best yield of alkene **12a** resulted from a variation in the general procedure. Thus *p*-(trifluoromethyl)benzaldehyde (0.78 mL, 61 mg, 0.35 mmol) was added to anion **8**, preformed by reacting disilane **10** (100 mg, 0.35 mmol)[21] with potassium *tert*-butoxide (40 mg, 0.35 mmol) at −70 °C. Workup according to the general procedure gave a yellow solid, which upon radial chromatography (light petroleum elution) yielded from the most mobile fraction the title alkene **12a**. Yield: 64 mg (62%). Bright yellow needles (light petroleum), m.p. 162.5−164.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.57 (s, 1 H, 8-H), 7.49−7.55 (AA′, 2 H, 4/5-H), 7.63−7.66 (m, 2 H, 11/13-H), 7.71 (d, J_{para} = 1.7 Hz, 1 H, 7-H), 7.78 (d, J_{para} = 1.7 Hz, 1 H, 2-H), 7.88 (d, $^3J_{AB}$ = 8.3 Hz, 2 H, 10/14-H), 7.92−7.98 (BB′, 2 H, 3/6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 104.9 (C8), 109.0 (C7), 109.3 (C2), 114.0 (C1), 124.2 (q, $^1J_{C,F}$ = 272 Hz, CF_3), 124.9 (C7a), 125.6 (q, $^3J_{C,F}$ = 4 Hz, C11/13), 127.0 (C1a), 127.1(0) (C10/14), 127.1(5) (C5), 127.2 (C4), 129.0 (C6), 129.2 (C3), 129.0 (q, $^2J_{C,F}$ = 32 Hz, C12), 138.5 (C6a), 138.6 (C9), 139.2 (C2a) ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3235, 2926, 2853, 2170, 1773, 1636, 1616, 1406, 1325, 1161, 1111, 1067, 1006, 860, 752, 610 cm^{-1}. UV/Vis (cyclohexane): λ_{max} (log ε) = 286 (3.32), 394 (3.40), 422 (3.51) nm; (acetonitrile): λ_{max} = 286 (3.30), 394 (3.41), 418 (3.46) nm. MS (70 eV): *m/z* (%) = 297 (22) [M + 1$^+$], 296 (100), [M$^+$], 275 (10), 246 (8), 226 (31) [M − CF_3], 123 (11). μ (21 °C) = 3.02 D. $C_{19}H_{11}F_3$ (296.08): calcd. C 77.0, H 3.7; found C 77.1; H 3.6.

1-(2′-Thienyl)methylidene-1*H*-cyclopropa[*b*]naphthalene (12b) was synthesised in the same yield and with the same spectroscopic data as described previously.[11]

***p*-(Trifluoromethyl)benzyl *p*-(Trifluoromethyl)benzoate (21):** The general procedure described above employing disilane **20** (100 mg, 0.29 mmol)[21] and *p*-(trifluoromethyl)benzaldehyde (51 mg, 0.29 mmol) gave a bright yellow solid that was radially chromatographed (3:1 light petroleum/dichloromethane elution). The most mobile fraction provided title benzoate **21**. Yield: 50 mg (41%). Yellow platelets (light petroleum), m.p. 61.0−62.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.48 (s, 2 H, 8-H), 7.57 (d, $^3J_{AB}$ = 8.1 Hz, 2 H, 2′/6′-H), 7.65 (d, $^3J_{AB}$ = 8.1 Hz, 2 H, 3′/5′-H), 7.72 (d, $^3J_{AB}$ = 8.1 Hz, 2 H, 3/5-H), 8.19 (d, $^3J_{AB}$ = 8.1 Hz, 2 H, 2/6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 66.2 (C8), 123.5 (q, $^1J_{C,F}$ = 273 Hz, C10), 123.9 (q, $^1J_{C,F}$ = 273 Hz, C9), 125.5 (q, $^3J_{C,F}$ = 3 Hz, C3/5), 125.7 (q, $^3J_{C,F}$ = 3 Hz, C3′/5′), 128.3 (C2′/6′), 130.1 (C2/6), 130.3 (q, $^2J_{C,F}$ = 33 Hz, C4′), 132.9 (C1), 134.7 (q, $^2J_{C,F}$ = 33 Hz, C4), 139.5 (C1′), 165.0 (C7) ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2934, 2374, 1724, 1513, 1445, 1413, 1324, 1276, 1166, 1125, 1109, 1065, 1016, 860, 774 cm^{-1}. UV/Vis (cyclohexane): λ_{max} (log ε) = 234 (4.21), 268 (3.68), 272 (3.65), 284 nm (3.62) nm; (acetonitrile): λ_{max} = 236 (4.12), 270 (3.71), 274 (3.65) nm. MS (70 eV): *m/z* (%) = 357 (25) [M + 1$^+$], 356 (100) [M$^+$], 342 (15), 341 (71), 327 (13), 326 (56), 313 (6), 298 (18), 270 (11). $C_{16}H_{10}F_6O_2$ (316.06): calcd. C 55.2, H 2.9, F 32.7; found C 55.5, H 2.7, F 32.9.

Further radial chromatography (light petroleum elution) provided 3,6-dimethoxy-1*H*-cyclopropa[*b*]naphthalene (**19**) identical to that previously prepared and with spectroscopic data in agreement with those published.[21] Yield: 55 mg (95%).

Reactions of *p*-(Trifluoromethyl)benzaldehyde with Bases

i) With Potassium *tert*-Butoxide: Under conditions analogous to those employed above but in the absence of cycloproparene, *p*-(trifluoromethyl)benzaldehyde (51 mg, 0.29 mmol) was recovered quantitatively from attempted reaction with potassium *tert*-butoxide (34 mg, 0.29 mmol).

ii) With Aqueous Sodium Hydroxide: When stirred for 30 min at ambient temperature, *p*-(trifluoromethyl)benzaldehyde (102 mg, 0.58 mmol) and aqueous sodium hydroxide (50% w/w, 1.0 mL) provided a 1:1 mixture of *p*-(trifluoromethyl)benzoic acid and *p*-(trifluoromethyl)benzyl alcohol in 90% overall yield.

Reactions of Ester 21 with Bases

i) With Potassium *tert*-Butoxide: Ester **21** (50 mg, 0.14 mmol) and potassium *tert*-butoxide (19 mg, 0.14 mmol) were refluxed for 1 h in THF. Workup gave recovered ester in quantitative yield.

ii) With Aqueous Sodium Hydroxide: Ester **21** (50 mg, 0.14 mmol) and aqueous sodium hydroxide (50% w/w, 1.0 mL) were refluxed for 1 h in THF. A 1:1 mixture of *p*-(trifluoromethyl)benzoic acid and *p*-(trifluoromethyl)benzyl alcohol was isolated in 90% overall yield.

In situ Reaction of Disilane 20 with Potassium *tert*-Butoxide in the Presence of *p*-(Trifluoromethyl)benzaldehyde and *p*-Methoxybenzaldehyde: Disilane **20** (200 mg, 0.58 mmol),[21] potassium *tert*-butoxide (68 mg, 0.58 mmol), *p*-(trifluoromethyl)benzaldehyde (51 mg, 0.29 mmol) and *p*-methoxybenzaldehyde (39 mg, 0.29 mmol) were reacted in anhydrous THF (30 mL) as described above. Workup and radial chromatography gave:

3,6-Dimethoxy-1-(*p*-methoxyphenyl)methylidene-1*H*-cyclopropa-[*b*]naphthalene (12c): Yield: 71 mg (77%). Yellow needles (light petroleum), m.p. 148.5−151.0 °C (see below),

***p*-(Trifluoromethyl)benzyl *p*-(trifluoromethyl)benzoate (21):** Yield: 48 mg (40%). Yellow platelets (light petroleum), m.p. 60.0−62.0 °C, and

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3,6-Dimethoxy-1*H*-cyclopropa[*b*]naphthalene (19): Yield: 55 mg (95%). Clear prisms, m.p. 129.0−131.0 °C. No evidence was obtained for 1-(*p*-trifluoromethylphenyl)methylidene-3,6-dimethoxy-1*H*-cyclopropa[*b*]naphthalene.

3,6-Dimethoxy-1-(*p*-methoxyphenyl)methylidene-1*H*-cyclopropa-[*b*]naphthalene (23): Disilane **12** (100 mg, 0.29 mmol)[11] and *p*-methoxybenzaldehyde (40 mg, 0.29 mmol) gave a yellow solid, which upon radial chromatography (light petroleum/dichloromethane, 4:1) provided from the most mobile fraction the title compound **23**. Yield: 76 mg (83%). Yellow needles (light petroleum), m.p. 148.5−150.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.86 (s, 3 H, C12−OMe), 3.89 (s, 3 H, C3/6−OMe), 3.89 (s, 3 H, C6/3−OMe), 6.44 (s, 1 H, 8-H), 6.70 (s, 2 H, 4/5-H), 7.00 (d, $^3J_{AB}$ = 8.3 Hz, 2 H, 11/13-H), 7.61 (d, $^3J_{AB}$ = 8.3 Hz, 2 H, 10/14-H), 7.81 (d, J_{para} = 1.7 Hz, 1 H, 7-H), 7.85 (d, J_{para} = 1.7 Hz, 1 H, 2-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.1 (C12−OMe), 55.9 (C3/6−OMe), 102.0 (C7), 102.0(5) (C2), 104.2 (C5), 104.3 (C4), 105.8 (C8), 111.1 (C1), 112.5 (C11/13), 125.8 (C7a), 127.7 (C1a), 127.8 (C10/14), 130.4 (C6a), 130.5 (C2a), 131.2 (C9), 150.4 (C6), 150.5 (C3), 157.2 (C12 ppm. HRMS (positive APCI) calcd. for $C_{21}H_{18}O_3$ [M + H$^+$] 319.1334; found 319.1338 [+1.2(5) mmu]. IR (KBr): $\tilde{\nu}_{max}$ = 3054, 2965, 2929, 2856, 1931, 1774 (w), 1660, 1646, 1598, 1254, 1165, 1034, 866, 822, 787 cm^{-1}. UV/Vis (cyclohexane): λ_{max} (log ε) = 312 (3.77), 320 (3.82), 416 (4.01), 440 (4.10) nm; acetonitrile): λ_{max} = 314 (3.71), 320 (3.80), 414 (3.99), 436 nm (4.05). μ (21 °C) = 0.92 D. $C_{21}H_{18}O_3$ (319.13): calcd. C 79.2, H 5.7. found C 79.1, H 5.5(5).

Reaction of Disilane 20 with Potassium *tert*-Butoxide in the Presence of 2-Thiophenecarbaldehyde: Disilane **20** (100 mg, 0.29 mmol)[21] and 2-thiophenecarboxaldehyde (33 mg, 0.39 mL, 0.29 mmol) produced from application of the general procedure, a bright yellow solid. Radial chromatography (light petroleum/dichloromethane, 3:1) provided from the most mobile fraction 2-thienylmethyl thiophene-2-carboxylate (**22**).[19] Yield: 29 mg (45%). Yellow needles (light petroleum), m.p. 72.0−72.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.49 (s, 2 H, 7-H), 7.02 (dd, $J_{2,3}$ = 3.4, $J_{1,2}$ = 5.1 Hz, 1 H, 4-H), 7.10 (dd, $J_{2,3}$ = 3.9, $J_{1,2}$ = 4.9 Hz, 1 H, 4′-H), 7.18−7.19 (m, 1 H, 5′-H), 7.35 (dd, $J_{1,3}$ = 1.2 Hz, $J_{1,2}$ = 5.1 Hz, 1 H, 3′-H), 7.56 (dd, $J_{1,3}$ = 1.2, $J_{1,2}$ = 4.9 Hz, 1 H, 3-H), 7.83 (dd, $J_{1,3}$ = 1.2, $J_{2,3}$ = 3.9 Hz, 1 H, 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 61.0 (C7), 126.9 (C4′), 127.0 (C3′), 127.8 (C4), 128.4 (C5′), 132.7 (C3), 133.4 (C1′), 133.8 (C5′), 137.7 (C1), 161.9 (C6) ppm. HRMS (positive APCI) calcd. for $C_{10}H_8O_2S_2$ [M + H$^+$] 223.9966; found 223.9959 (−3.1 mmu). MS (70 eV): *m/z* (%) = 225 (2) [M + 1$^+$], 224 (14) [M$^+$], 179 (3), 111 (59) [M − O-thienylmethyl$^+$], 97 (100), 57 (13), 53 (18), 39 (55). IR (KBr): $\tilde{\nu}_{max}$ = 2930, 1852, 1670, 1564, 1329, 1107, 956, 823 cm^{-1}. UV/Vis (cyclohexane): λ_{max} (log ε) = 230 (4.00), 268 (3.77), 346 (3.65) nm; (acetonitrile): λ_{max} = 230 (4.01), 270 (3.72), 348 (3.63) nm.

Further radial chromatography (light petroleum elution) provided **3,6-dimethoxy-1*H*-cyclopropa[*b*]naphthalene** (**19**) identical to an authentic sample.[21] Yield: 53 mg (91%).

X-ray Structure Determination of *p*-(Trifluoromethyl)benzyl *p*-(Trifluoromethyl)benzoate (21): CCDC-213488 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystalographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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