Cycloproparenes: Synthesis, Structure, and Spectral Properties of Alkylidenecycloproparenes[1]

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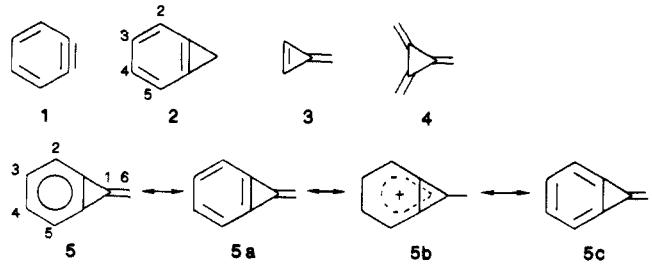
Abstract: 1*H*-Cyclopropa[*b*]naphthalene (**12**) and 1*H*-cyclopropabenzene (**2**) are converted for the first time into the 1-alkylidene-1*H*-cycloproparenes **17-22** and **27-30**, respectively, via cycloproparenyl anion generation and subsequent Peterson olefination. To date the reaction sequence fails to provide parent hydrocarbons **5** and **6**. The structure of (diphenylmethylene)cyclopropabenzene **27** has been established by X-ray crystallographic methods [crystal data for $C_{20}H_{14}$: space group $P2_1/n$, a = 17.579 (5) Å, b = 7.909 (3) Å, c = 10.298 (4) Å, β = 94.06 (2)°, V = 1428.0 Å^3, 1200 reflections ($I/\sigma(I) \geq 3.0$), and R = 0.049]. The spectral data of the alkylidene compounds are discussed in terms of a contribution to their structures from the dipolar form **5b**.

Strained organic molecules have continued to fascinate chemists for nearly a century. Because of their high energy and associated strain, such molecules possess unusual physical, spectral, and chemical properties which are of theoretical as well as synthetic interest and challenge.[3]

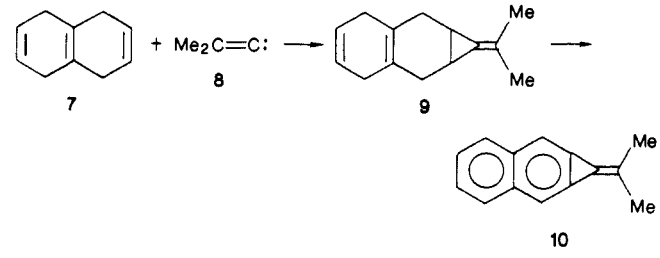
Among the more strained and intriguing class of molecules are the ortho-bridged aromatics. The parent member of the family, benzyne (**1**), is easily generated as a transient intermediate[4] but has been observed spectroscopically only at 8 K in an argon matrix.[5] The next homologue, cyclopropabenzene[6] (**2**), is a



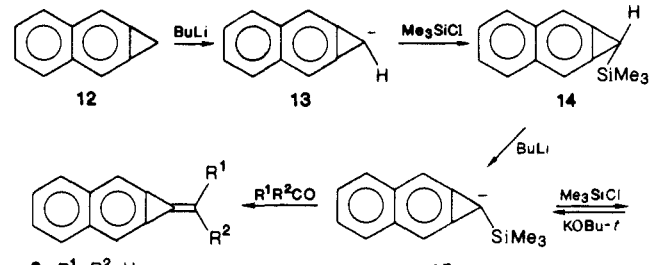
reasonably stable, isolable compound, despite the 68 kcal/mol of strain energy associated with the novel fused-ring system.[7,8] The cross-conjugated systems represented by the fulvenes and radialenes provide another alluring class of strained molecules. Although stable derivatives of the smallest fulvene, **3**, are known,[9] the recently reported[10] parent compound, methylenecyclopropene (**3**), decomposes above −75 °C. Likewise, the smallest parent radialene, trimethylenecyclopropane (**4**), polymerizes above 0 °C.[11]

A hitherto unknown and novel class of strained hydrocarbons which combine into a single molecule the features of the ortho-bridged benzenes **2**, as well as the cross-conjugated systems **3** and **4**, are the alkylidenecycloproparenes, e.g., **5**. Methylenecyclopropabenzene (**5**) is an exocyclic benzannulated **3** (with a predicted[12,13] strain energy of about 80 kcal/mol), a benzannulated trifulvene **5a**↔**5b**, and an unusual radialene **5c** all in one.

Scheme I



Scheme II



In this paper we wish to report the preparation, characterization, and properties of the first known[14] examples of this novel class of strained hydrocarbons, including an X-ray structure determination, along with derivatives of the cyclopropa[*b*]naphthalene analogue **6**.

Results and Discussion

Because of the unknown nature of **5** and its anticipated[10-12] possible instability, we concentrated our initial efforts on the

(1) Studies in the cycloproparene series. For the previous part see: Dent, B. R.; Halton, B., submitted for publication in *Aust. J. Chem.*

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(12) It is well-known (see ref. 13) that replacement of an sp^3-hybridized carbon with an sp^2-carbon adds approximately 12 kcal/mol of strain to a hydrocarbon; hence 68 kcal/mol for **2** (see ref. 8) plus 12 kcal/mol predicts a strain of 80 kcal/mol for the parent **5**.

(13) See ref. 3 and: Schleyer, P. V. R.; Williams, Jr., J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377-2386.

(14) A preliminary communication reporting our early results has appeared Halton, B.; Randall, C. J.; Stang, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 6108-6110.

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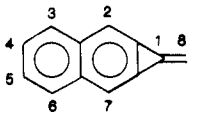
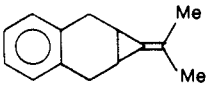


6

preparation of derivatives of **6**. Since strained derivatives of naphthalene are known[3] to be more stable than those of benzene, and since alkyl or aryl substituents stabilize double bonds, our initial attempts were directed toward the preparation of **10** via a seemingly simple, logical two-step process as outlined in Scheme I. Addition of isopropylidenecarbene[15] (**8**) to tetrahydronaphthalene (**7**) is known[16] to give adduct **9** in reasonable yield. However, attempted oxidation of **9** with numerous reagents under a variety of conditions failed to give the desired **10**; only unchanged starting material, the partially oxidized hydrocarbon **11**, and/or polymers were observed. The structure of compound **11** was confirmed by independent synthesis from 1,4-dihydronaphthalene.



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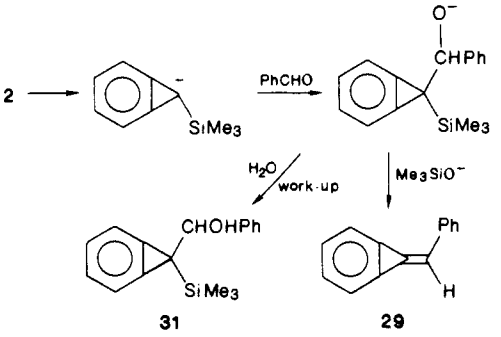
An alternative approach to **6** commencing with a preformed ring system is based upon the known[17] acidity of the benzylic protons of **2**. Thus metalation (BuLi) of **2** provides the cyclopropabenzenyl anion which can be captured by chlorotrimethylsilane. This, coupled with the facility of silicon to stabilize an α-anion[18] and the synthetic utility of the Peterson olefination,[18,19] suggested that alkylidenecycloproparenes (e.g., **6**) may be available by the route depicted in Scheme II. Treatment of **12** (readily available from naphthalene in three steps[20]) with butyllithium and chlorotrimethylsilane gives the bis(silyl) derivative **16** and not **14**. With carefully controlled addition of the base (1 molar equiv) and the chlorosilane, **16** (47%) is still obtained and starting material **12** (39%) is recovered. Because of the stabilization available to anion **15** by the silicon atom, we suggest that monosilyl **14** is deprotonated immediately upon formation by residual **13** to give **15** and to regenerate **12** (Scheme II). Subsequent reaction of **15** with chlorotrimethylsilane accounts for **16**. Despite many variations in the experimental procedure we have been unable to successfully synthesize **14**. However, this is of little consequence since the removal of the trimethylsilyl moiety is well documented[18] and bis(silyl) **16** appears to be an equally useful progenitor for **6** and its derivatives. In light of this, the synthesis of **16** has been improved upon by treating **12** sequentially with base and chlorotrimethylsilane *3 times* with 1.0, 0.5, and 0.25 molar equiv of the reagents, respectively. In this way **16** is obtained in 66% yield[21] free from **12**.

Attempts to convert **16** into **17** employing fluoride ion promoted cleavage of a Si–C bond[18] in the presence of ketone have failed; **12** is formed almost quantitatively. The difficulties associated with drying tetrabutylammonium fluoride imply the presence of HF_2^- in the medium,[22] thereby providing the necessary proton source (after F^- loss) for the observed conversion. The efficacy of the silyl Wittig olefination[19] stems from the formation of a strong Si–O bond, and this has provided the necessary impetus

Scheme III



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for effective desilylation with *tert*-butoxide under anhydrous conditions.[23] Thus treatment of **16** with potassium *tert*-butoxide in dry tetrahydrofuran containing benzophenone brings about the desired Peterson reaction, and the alkylidenecyclopropa[*b*]naphthalene **17** is obtained quantitatively as a stable, yellow, crystalline solid. The reaction sequence (Scheme II) has been extended to provide analogues **18–21** (10–70%) as stable compounds and the *tert*-butyl derivative **22** as an air-sensitive solid. However, the sensitivity of the carbonyl compounds necessitates generation of anion **15** at low temperature prior to their addition. Despite such precautions **6**, **23**, and **24** are not obtained even after many variations in the procedure. With paraformaldehyde and *p*-nitrobenzaldehyde, complex product mixtures ensue, but **6** and **23**, respectively, are not present. With acetone, enolate anion formation appears to dominate since **12** (85%) is obtained at the expense of **24**.

In light of these results analogous studies have been carried out with parent **2**,[24] and the bis silyl derivative **26** obtained. Reaction of **26** with *tert*-butoxide and benzophenone in a manner strictly analogous to that for the conversion **16** → **17** leads to alkylidenecyclopropabenzene **27** which is also a stable, yellow, crystalline solid, but the yield is only 24%. In extending this study

25, R = H
26, R = Me_3Si

27, $R^1 = R^2 = Ph$
28, $R^1 = Ph$, $R^2 = Me$
29, $R^1 = Ph$, $R^2 = H$
30, $R^1 = p$-MeO-C_6H_6, $R^2 = H$

we have found it to be more efficient to convert **2** into **27–30** in a "one-pot" procedure which bypasses **26** and avoids having to isolate the known[17] monosilyl **25** (c.f. **12** → **17**, Scheme II). Thus **27** is available in 38% yield and **28–30** in yields of **10–33%**. It is notable that in each case the conversion of **2** into the alkylidenecyclopropabenzene is less efficient than for the corresponding cyclopropa[*b*]naphthalene. However, **28–30** are significantly less thermally stable than their naphthalene analogues, and while satisfactory high-resolution mass data have been obtained from the molecular ions, attempted purification leads to significant decomposition. Furthermore, the conversion **2** → **29** requires a long reaction period for optimum product yield (33%) compared with analogous **12** → **20**. After a short period, workup provides **29** (13%) accompanied by an unstable oil proposed as **31** (40%) (Scheme III) from its spectral data. The mass spectrum of this latter compound at 18 eV gives the molecular ion (*m/e* 268) as the base peak, the ^1H NMR spectrum displays singlets for the trimethylsilyl (–0.29 ppm), hydroxyl (2.13 ppm), and benzylic (5.11 ppm) protons, and the ^{13}C NMR spectrum exhibits 13 nonequivalent carbon resonances as expected for structure **31** (Experimental Section). β-Hydroxy silane **31** must result from protonation of the Peterson intermediate during workup.

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(21) On occasions the yield of **16** has been as high as 76%.
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Table I. ^{13}C NMR Parameters for Some 1-Alkylidene-1*H*-cyclopropa[*b*]naphthalenes[a]

compd	C1	C1a/C7a	C2/C7	C2a/C6a	C3/C6	C4/C5	C8
12	18.6	123.5	112.3	136.8	128.4	125.5	
17	112.0	ns[b]	107.3	138.9 or 139.6	128.8	126.7 or 127.4	120.8
18	110.3	129.0[c]	106.6, 106.9	138.1, 138.7	128.6, 128.7	125.1 or 126.4	113.8
19	118.5	na[d]	110.9, 111.4	139.8, 140.2	129.4, 129.5	127.8, 127.9	ns[e]
20	111.9	125.6, 127.8	108.2, 108.3	138.4, 139.1	128.8, 128.9	126.7, 126.8	107.1
21	110.2	125.9, 127.0	107.2, 107.5	138.3, 139.0	128.7, 128.8	126.4, 126.5	107.5
22	109.6	128.1	107.6, 107.8	137.9, 138.2	128.6, 128.7	126.1	119.5

[a] Recorded at 20.00 MHz for deuteriochloroform solutions with Me_4Si as internal standard. The shifts due to the substituents at C8 are given in the Experimental Section. Chemical shifts are ±0.05 ppm. [b] Signal overlapped and not seen. [c] Only one singlet observed. [d] Signal not easily assignable but in the range 124–134 ppm. [e] The expected quartet from coupling to ^{19}F was too weak for observation.

Table II. ^{13}C NMR Parameters for Some 1-Alkylidene-1*H*-cyclopropabenzenes[a]

compd	C1	C1a/C5a	C2/C5	C3/C4	C6
2	18.4	125.4	114.7	128.8	
27	113.3	132.7	110.7	133.2	111.2
28	111.4	134.1[b]	110.2, 110.5	132.0, 132.7	103.9
29	113.1	131.1, 133.3	111.5, 111.6	132.8, 133.8	98.2
30	111.6	131.3, 131.4	111.0, 111.1	132.3, 133.4	98.1

[a] Recorded at 20.00 MHz for deuteriochloroform solutions with Me_4Si as internal standard. The shifts due to the substituents at C6 are given in the Experimental Section. Chemical shifts are ±0.05 ppm. [b] Only one singlet observed.

The assignment of the alkylidenecycloproparene structure to **17–22** and **27–30** follows from the spectral data. Thus each compound provides a molecular ion at the expected *m/e* value in the mass spectrum, and the ^1H NMR data reflect the presence of the exocyclic double-bond substituents. However, it is the ^{13}C NMR data that are particularly informative in that each compound shows distinctive resonances in the range 106.6–111.6 ppm for the aromatic carbons adjacent to the fused three-membered ring (C2/C7 of **17–22**, Table I; C2/C5 of **27–30**, Table II). Such shielding is diagnostic of the cyclopropabenzene ring system[7] (**2**, 114.7 ppm; **12**, 112.3 ppm) and is also demonstrated by **16** (107.9 ppm), **26** (111.8 ppm), and **31** (115.4, 115.8 ppm). It is noteworthy that alkylidenecyclopropanaphthalenes **17–22** have C2/C7 *more* shielded than the corresponding carbons of the cyclopropabenzenes **27–30** by ~3.5 ppm, a difference which is somewhat greater than is observed for parents **12** and **2**. The unsymmetrical nature of **18–22** and **28–30** is evidenced by distinct resonances for C2/C7 and C2/C5, respectively ($\Delta\delta$ 2–6 Hz) (Tables I and II). The presence of the exocyclic double bond is reflected by a vinylic singlet resonance for C1 at ~112 ppm (except for trifluoromethyl-substituted **19**, 118.5 ppm) which is affected by the exocyclic double-bond substituents to the same extent in both series of compounds. Moreover, the small variations recorded agree with expectations from comparably substituted ethenes.[25] Confirmation of the assigned structures is provided by an X-ray crystallographic analysis of the cyclopropabenzene **27**.

Structural Study of 27. (i) Collection and Reduction of X-ray Intensity Data. Approximate unit cell dimensions for **27** were obtained from preliminary precession photographs (0*kl*, 1*kl*, 2*kl*, and *h*0*l*) which showed systematic absences (*h*0*l*, $h + l = 2n + 1$; 0*k*0, $k = 2n + l$) corresponding uniquely to the space group $P2_1/n$. Accurate cell dimensions together with estimated standard errors and the crystal orientation matrix were obtained from 25 high-order reflections [17° < 2θ (Mo Kα) < 25°] on a Nicolet R3m diffractometer which was used for data collection. Details of crystal data and data collection are provided in Table III.

Throughout the data collection the intensities of three reflections (0,4,−2; 14,0,0; and 004) were recorded as a measure of crystal and instrument stability. A maximum variation of <2% was noted, and no decay correction was applied. Intensities were corrected for Lorentz and polarization effects;[26] no correction was made for absorption (μ 0.73 cm^{-1}).

Table III. Crystal Data and Experimental Details for 1-(Diphenylmethylene)-1*H*-cyclopropabenzene (**27**)

formula	$C_{20}H_{14}$
fw	254.3
a, Å	17.579 (5)
b, Å	7.909 (3)
c, Å	10.298 (4)
β, deg	94.06 (3)
V, Å^3	1428.0
Z	4
space group	$P2_1/n$
ρ(calcd), g cm^{-3}	1.18
crystal dimensions, mm	0.23 × 0.20 × 0.23
radiation	Mo Kα(λ = 0.71073 Å)
temp, °C	21
monochromator	graphite
2θ limits, deg	2.0–47.0
scan type	θ, 2θ
total no. of reflns	2477
total reflns used ($I > 3\sigma(I)$)	1200
final no. of variables	237
R	0.049
R_{wf}	0.050

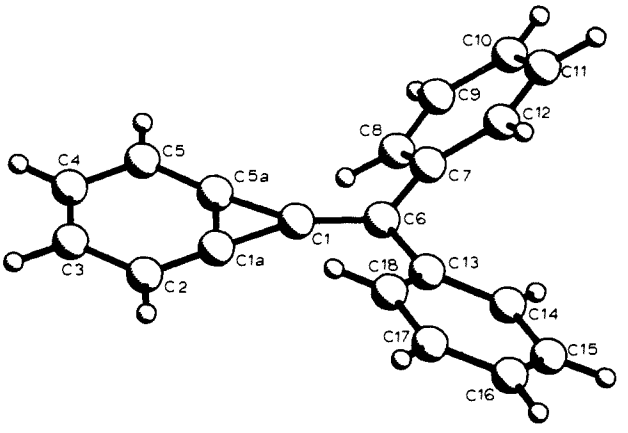

Figure 1. Molecular structure of 1-(diphenylmethylene)-1*H*-cyclopropabenzene (**27**), $C_{20}H_{14}$.

(ii) Solution and Refinement of the Structure. The structure was solved by direct methods using the MULTAN77 package but without including the known phenyl rings in the normalization procedure.[27] The top 20 peaks in the resulting E map were assigned correctly to the carbon atoms, and the non-hydrogen atoms were determined from subsequent difference Fourier calculations. The function minimized by full-matrix least-squares refinement was $\sum w(F_o - |F_c|)^2$ with the weighting factor *w* equal to $[\sigma^2(F_o) + 0.0003F_o^2]^{-1}$. All carbon and hydrogen atoms were refined with anisotropic and isotropic thermal parameters, re-

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Table IV. Atomic Coordinates for 1-(Diphenylmethylene)-1*H*-cyclopropabenzene (**27**)

atom	x/a	y/b	z/c
C1	0.607 23 (17)	0.3062 (4)	0.5474 (3)
C1a	0.567 36 (18)	0.3354 (5)	0.6611 (4)
C5a	0.525 58 (18)	0.2942 (4)	0.5500 (3)
C2	0.536 27 (24)	0.3799 (5)	0.7762 (4)
C3	0.457 35 (27)	0.3729 (6)	0.7676 (5)
C4	0.415 09 (25)	0.3256 (6)	0.6545 (6)
C5	0.447 40 (21)	0.2847 (5)	0.5400 (5)
C6	0.671 88 (16)	0.3028 (4)	0.4853 (3)
C7	0.667 49 (17)	0.2649 (4)	0.3439 (3)
C8	0.613 24 (20)	0.1541 (5)	0.2892 (4)
C9	0.605 68 (26)	0.1252 (6)	0.1566 (5)
C10	0.652 94 (28)	0.2074 (6)	0.0756 (5)
C11	0.707 73 (25)	0.3176 (6)	0.1272 (4)
C12	0.714 39 (21)	0.3462 (5)	0.2606 (4)
C13	0.745 12 (17)	0.3396 (4)	0.5602 (3)
C14	0.813 21 (18)	0.2665 (5)	0.5265 (4)
C15	0.880 74 (21)	0.2951 (5)	0.5989 (4)
C16	0.882 75 (24)	0.3986 (6)	0.7062 (4)
C17	0.816 16 (24)	0.4709 (6)	0.7416 (4)
C18	0.748 65 (22)	0.4436 (5)	0.6684 (4)
H2	0.567 2 (20)	0.412 (5)	0.856 (3)
H3	0.429 4 (22)	0.392 (5)	0.850 (4)
H4	0.362 0 (22)	0.329 (5)	0.651 (3)
H5	0.419 4 (20)	0.257 (5)	0.462 (4)
H8	0.578 3 (17)	0.096 (4)	0.342 (3)
H9	0.568 9 (23)	0.036 (6)	0.119 (4)
H10	0.650 3 (20)	0.194 (5)	−0.015 (4)
H11	0.743 9 (20)	0.384 (4)	0.073 (3)
H12	0.750 5 (15)	0.413 (3)	0.295 (3)
H14	0.812 8 (16)	0.192 (4)	0.451 (3)
H15	0.927 1 (18)	0.243 (4)	0.571 (3)
H16	0.930 3 (20)	0.416 (4)	0.758 (3)
H17	0.817 6 (20)	0.542 (5)	0.821 (4)
H18	0.702 8 (16)	0.500 (4)	0.694 (3)

spectively. Atomic scattering factors for carbon atoms were taken from ref 29 while those for hydrogen came from the compilation of Stewart et al.[30] In the final cycle of refinement, no individual parameter shift was greater than 0.003 of the corresponding estimated standard deviation. No unusual trends were then observed in an analysis of $\sum w(F_o - |F_c|)^2$ as a function of either sin θ/λ or E_o.

The atomic coordinates for **27** together with their estimated standard deviations are listed in Table IV. A listing of observed and calculated structure factors [×10 (electrons)], final thermal parameters, and mean plane data are available in the supplementary material.

(iii) Discussion. The crystal structure of **27** consists of independent molecules of the title compound, as illustrated in Figure 1. There are no closer contacts between the molecules than those indicating weak van der Waals interactions (C···H and H···H ≥ 2.77 and 2.57 Å, respectively). Details of the molecular conformation are provided in Table V, which lists selected bond lengths, interbond angles, and dihedral angles.

The distortions found in the fused six-membered ring of **27** are identical in type with those found in 1,1-dichloro-2,5-diphenylcyclopropabenzene.[31] Thus the effects of diphenylmethylene substitution at C1 of the cyclopropabenzene framework are indistinguishable from those of dichloro substitution in the latter compound. Although the resolution of the present structure is better than for those of other cyclopropabenzenes reported previously,[31-33] no significant bond localization is evident in the fused

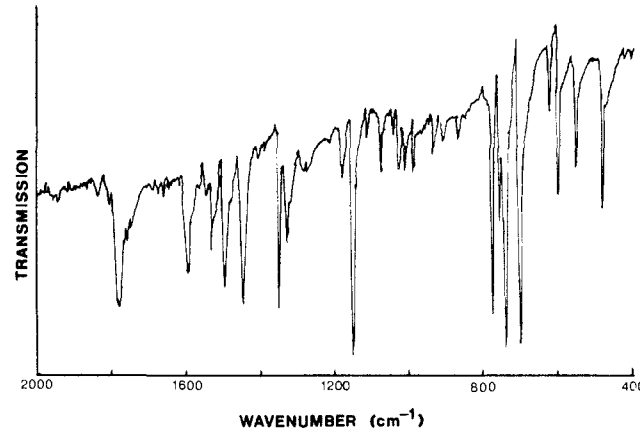

Figure 2. Infrared spectrum (KBr) of 1-(diphenylmethylene)-1*H*-cyclopropabenzene (**27**).

six-membered ring. Moreover, the length of the exocyclic double bond (C1–C6, 1.343 (4) Å) is in the normal range for double bonds[34] and provides no evidence for charge separation, c.f. **5b**. The short fused bond (C1a–C5a, 1.355 (4) Å) induces considerable compression as in other cyclopropabenzenes,[31-33] and this is illustrated by the angles at C5 and C2 of 113.1 (4)° and 112.9 (4)°, respectively (c.f. 108° and 110°, respectively, for 1,1-dichloro-2,5-diphenylcyclopropabenzene[31]). The weighted mean-plane data for the fused cyclopropabenzene moiety show a mean out-of-plane deviation of 0.009 Å compared with 0.001 and 0.004 Å, respectively, for C7–C12 and C13–C18 of the pendant phenyl rings. A further similarity of **27** to the 1,1-dichloro analogue[31] lies in the interplanar angle between the fused six- and three-membered rings. A value of 3.7° is noted here which compares well with the 3.4° previously recorded.[31] The phenyl substituents of **27** make angles of 36.0° and 29.0° to the plane containing atoms C5a, C1a, C1, C6, C7, and C13. This is expected to alleviate close nonbonding contacts between the phenyl rings and the cyclopropabenzene framework.

Spectroscopic Properties. The geometry of **27** reflects distortions which attempt to relieve the strain associated with the fusion of the cyclopropene ring, and these occur primarily at the fusion sites. As with other cyclopropabenzenes, the geometry is determined by π- and σ-effects, and it does not necessarily reflect bond fixation or delocalization in the π-framework.[35] It cannot be taken to imply or refute contributions to **27** from resonance structures analogous to **5a–c**. It is the spectral properties which are most influenced by π-electron characteristics, and it is from these that contributions to the structure from charge separation (e.g., **5b**) should become apparent.

The infrared spectra of the triafulvenes generally show two characteristic bands in the regions 1810–1880 and 1510–1550 cm^{-1} which are believed to result from strong coupling of the exo- and endocyclic double bonds.[9] Parent **3** shows[10] maxima at 1770 and 1519 cm^{-1}, and this shift to a lower wavenumber of the high-energy transition is also consistent with dipolar structure (c.f. **5b**). Each of the alkylidenecyclopropabenzenes reported herein displays infrared bands in the ranges 1765–1795 and 1510–1550 cm^{-1} (Figure 2). However, the transitions for naphthalenes **17–22** are weaker than those for the cyclopropabenzenes **27–30**. A contribution from the dipolar form (c.f. **5b**) seems likely.

The ultraviolet absorption spectra of **27–30** display maxima at ca. 250, 375, and 395 nm (Figure 3a), while **17–21** have λ_{max} at ca. 230, 250, 395, and 425 nm (Figure 3b). The alkyl-substituted **22** has its λ_{max} at 231, 273, 351, and 371 nm. When the medium is changed from cyclohexane to acetonitrile *hypsochromic shifts* are recorded for all compounds. The short-wavelength absorptions (<300 nm) are affected by 2–3 nm and the two long-wavelength maxima by 3–5 and 5–7 nm, respectively. Al-

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Table V. Selected Bond Distances, Interbond Angles, and Dihedral Angles for 1-(Diphenylmethylene)-1*H*-cyclopropabenzene (**27**)

(a) Bond Distances, Å

C1–C1a	1.426 (5)	C1–C5a	1.441 (4)	C15–C16	1.374 (5)	C16–C17	1.375 (5)
C1–C6	1.343 (4)	C1a–C5a	1.355 (4)	C17–C18	1.377 (5)		
C1a–C2	1.385 (5)	C5a–C5	1.373 (5)	C2–H2	0.98 (3)	C3–H3	1.02 (4)
C2–C3	1.385 (6)	C3–C4	1.388 (6)	C4–H4	0.93 (4)	C5–H5	0.94 (4)
C4–C5	1.383 (6)	C6–C7	1.483 (4)	C8–H8	0.96 (3)	C9–H9	1.02 (4)
C6–C13	1.482 (4)	C7–C8	1.385 (4)	C10–H10	0.94 (4)	C11–H11	1.03 (4)
C7–C12	1.389 (4)	C8–C9	1.382 (5)	C12–H12	0.88 (3)	C14–H14	0.97 (3)
C9–C10	1.381 (6)	C10–C11	1.378 (6)	C15–H15	0.98 (3)	C16–H16	0.97 (3)
C11–C12	1.388 (5)	C13–C14	1.395 (4)	C17–H17	1.00 (4)	C18–H18	0.97 (3)
C13–C18	1.382 (4)	C14–C15	1.375 (5)				

(b) Interbond Angles, deg

C5a–C1–C1a	56.4 (2)	C6–C1–C1a	151.1 (3)	C8–C7–C6	120.9 (3)	C12–C7–C6	121.4 (3)
C6–C1–C5a	152.4 (3)	C5a–C1a–C1	62.3 (2)	C12–C7–C8	117.6 (4)	C9–C8–C7	121.5 (4)
C2–C1a–C1	172.2 (4)	C2–C1a–C5a	124.1 (3)	C10–C9–C8	120.0 (5)	C11–C10–C9	119.9 (5)
C1a–C5a–C1	61.3 (2)	C5–C5a–C1	174.5 (4)	C12–C11–C10	119.5 (4)	C11–C12–C7	121.6 (4)
C5–C5a–C1a	123.8 (4)	C3–C2–C1a	112.9 (4)	C14–C13–C6	121.2 (3)	C18–C13–C6	121.6 (3)
C4–C3–C2	122.6 (4)	C5–C4–C3	123.4 (4)	C18–C13–C14	117.2 (3)	C15–C14–C13	121.3 (4)
C4–C5–C5a	113.1 (4)	C7–C6–C1	118.9 (3)	C16–C15–C14	120.4 (4)	C17–C16–C15	119.2 (4)
C13–C6–C1	118.8 (3)	C13–C6–C7	122.2 (3)	C18–C17–C16	120.4 (4)	C17–C18–C13	121.5 (4)

(c) Selected Dihedral Angles,[a] deg

A B C D		A B C D	
C5a–C1–C1a–C2	−146.6	C13–C6–C7–C12	−36.7
C6–C1–C1a–C5a	176.1	C1–C6–C13–C14	149.7
C6–C1–C1a–C2	29.5	C1–C6–C13–C18	−28.4
C1a–C1–C5a–C5	159.5	C7–C6–C13–C14	−31.2
C6–C1–C5a–C5	−16.4	C7–C6–C13–C18	150.7
C1a–C1–C6–C7	−175.3	C6–C7–C8–C9	176.2
C1a–C1–C6–C13	3.8	C12–C7–C8–C9	−0.1
C5a–C1–C6–C7	−2.3	C6–C7–C12–C11	−176.6
C5a–C1–C6–C13	176.8	C8–C7–C12–C11	−0.3
C1–C1a–C5a–C5	−177.7	C7–C8–C9–C10	0.0
C2–C1a–C5a–C1	174.8	C8–C9–C10–C11	0.3
C2–C1a–C5a–C5	−2.9	C9–C10–C11–C12	−0.6
C1–C1a–C2–C3	145.8	C10–C11–C12–C7	0.6
C5a–C1a–C2–C3	1.9	C6–C13–C14–C15	−177.4
C1–C5a–C5–C4	−156.8	C18–C13–C14–C15	0.8
C1a–C5a–C5–C4	1.5	C6–C13–C18–C17	176.8
C1a–C2–C3–C4	0.1	C14–C13–C18–C17	−1.4
C2–C3–C4–C5	−1.4	C13–C14–C15–C16	−0.7
C3–C4–C5–C5a	0.6	C14–C15–C16–C17	1.1
C1–C6–C7–C8	−33.8	C15–C16–C17–C18	−1.7
C1–C6–C7–C12	142.4	C16–C17–C18–C13	1.9
C13–C6–C7–C8	147.2		

[a] The angle is positive if the rotation of bond A–B around bond B–C is clockwise to eclipse bond C–D.

though small, these shifts are in the opposite sense to those expected[36] for $\pi \rightarrow \pi^*$ transitions with this solvent change and are uniformly larger for **27–30** than for **17–22**. This negative solvatochromy argues for a contribution to the structures from dipolar **5b** in the more polar medium with a greater contribution in the cyclopropabenzenes that in the cyclopropanaphthalenes. Initially, a "masking" effect of the changes in the λ_{max} values was thought possible due to the aryl substituents of **17–21** and **27–30**, but this seems unlikely since the changes recorded for alkyl-substituted **22** are essentially the same.

^{13}C NMR shifts have been used routinely as a probe for the detection of charge.[37] However, their application to dipolar structures of the type **5b** has no strict analogy since simple alkyl- and aryl-substituted triafulvenes are unstable and data are lacking.[9] Parent **3** displays a signal at 59.6 ppm for the methylene carbon and at 132.9 ppm for the two equivalent ring carbons.[10] Together with the **1H** NMR data, the shielding of C4 in **3** argues strongly for a significant dipolar contribution to the structure. Delocalized cyclopropabenzenyl cations have been characterized, and their ^{13}C NMR spectra have been recorded.[38] Comparisons between the changes in the various carbon chemical shifts induced by ionization with those caused by converting a cyclopropabenzene into a 1-alkylidene derivative do not provide unqualified support for dipolar contributions to **17–22** and **27–30**. In particular **21** and **30**, which carry an electron-donating *p*-anisyl substituent, should oppose or reverse the polarity exhibited by their counterparts. In fact the ^{13}C NMR data recorded for these compound are remarkably similar to those obtained for the 1-phenylmethylene derivatives **20** and **29** (see Tables I and II). On the other hand the more intense C6 quaternary carbon resonance of **27** is shifted from 111.2 ppm in deuteriochloroform to 113.6 ppm in perdeuteriobenzene. The less intense C1 moves in the opposite direction ($CDCl_3$, 113.3 ppm; C_6D_6, 112.0 ppm) as expected for a decreased polar contribution.

Conclusions

We have shown that members of the novel and new class of hydrocarbons known as the alkylidenecyclopropabenzenes can be obtained with comparative ease (and in good satisfactory yield) from the parent cyclopropabenzene via Peterson olefination. Unfortunately, the procedure has failed thus far to provide the parent members of the benzene and naphthalene series. The stability

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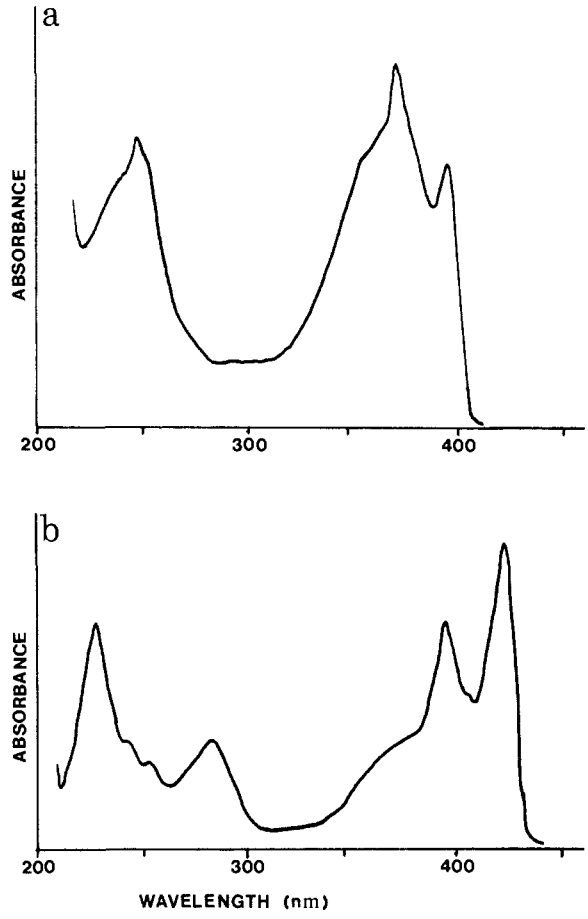

Figure 3. Ultraviolet spectra (in cyclohexane) of (a) 1-(phenylmethylene)-1*H*-cyclopropabenzene (**29**) and (b) 1-(phenylmethylene)-1*H*-cyclopropa[*b*]naphthalene (**20**).

of the cyclopropabenzene derivatives is less than that of their cyclopropa[*b*]naphthalene homologues. A crystallographic study of **27** has confirmed the structure assignment and shows that the ring system suffers the same bond-length and bond-angle deformations as other cycloproparenes; no abnormalities are recorded. The IR and UV data support some dipolar contribution to the structure of the alkylidenecycloproparenes akin to that in the triafulvenes. This is thought to be more extensive in the cyclopropabenzenes **27–30** than in the cyclopropa[*b*]naphthalenes **17–22**. The NMR data are less supportive and show that if such dipolar character exist, it is not as extensive as is observed for methylenecyclopropene. Further studies, and in particular the chemistry of these novel strained hydrocarbons, will be the subject of the future reports.

Experimental Section

Melting points were determined by using a Reichert hot-stage melting point apparatus and are uncorrected. Microanalyses were performed by the Microanalytical Unit, Otago University, Dunedin, New Zealand. High-resolution mass measurements were made by using an AEI MS902 instrument. NMR spectra were recorded for deuteriochloroform solutions with Me_4Si as internal standard by using a Varian Associates FT80A instrument operating at 20.00 MHz for ^{13}C and 79.56 MHz for ^1H. Infrared spectra were recorded for Nujol mulls or as thin films on a Pye Unicam SP3-100 unless otherwise stated and ultraviolet spectra on a Pye Unicam SP8-400 spectrophotometer. All reactions were performed unuder an oxygen-free nitrogen atmosphere.

1a,2,3,6,7,7a-Hexahydro-1-isopropylidene-1*H*-cyclopropa[*b*]naphthalene (9). To a stirred solution of 1,4,5,8-tetrahydronaphthalene (**7**) (2.95 g, 0.011 mol)[39] and 2-methylprop-1-enyl triflate (2.08 g, 0.01 mol of a 90% solution in glyme)[40] in glyme (16 mL) at −23 °C and under nitrogen was slowly added a suspension of potassium *tert*-butoxide (1.23 g, 0.011 mol) in glyme (25 mL) over 45 min. The solution, which formed a deep-yellow color, was stirred for a further 10 min, warmed to room temperature (1 h), and concentrated under vacuum to a pale-yellow oily solid (ca. 3 g). Vacuum sublimation (0.2 mmHg) at room temperature for 18 h gave a sublimate containing **7** (1.5 g, 51% recovery) contaminated with ~11% **9**. The residue (0.72 g) was shown by ^1H NMR to be a 1:3.5 inseparable mixture of **7** and **9**[16] (31% based on triflate). This was dissolved in dioxane (10 mL) and used for subsequent study.

1a,2,7,7a-Tetrahydro-1-isopropylidene-1*H*-cyclopropa[*b*]naphthalene (11). (A) **From 9.** To a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (113 mg, 0.5 mmol) in dioxane (2 mL) at 15 °C was added dropwise (syringe) the solution of **9** in dioxan (see above) (1.0 mL, ca. 37 mg, 0.2 mmol of **9**). The solution, which rapidly began to precipitate hydroquinone, was held at 15 °C for 10 min, warmed to room temperature, filtered, and concentrated under vacuum, and the residue was extracted with ether (2 mL). The solution was filtered through silica and concentrated to a colorless oil. Preparative TLC (silica, ether/hexane 1:9 elution) and extraction of the band R_f 0.60 gave an oily solid which was sublimed in vacuum (room temperature, 0.05 mmHg) to afford **1a,2,7,7a-tetrahydro-1-isopropylidene-1*H*-cyclopropa[*b*]naphthalene (11)**: 12 mg, 32% mp 52–53 °C; IR ν_{max} (KBr) 3060, 3017, 2970, 2915, 2835, 1776, 1493, 1454, 1443, 1435, 1368, 1304, 1280, 1174, 970, 750, 730 cm^{-1}; NMR δ (CCl_4) 1.60 (br s, Me_2C=), 1.80 (br m, 2 H), 2.97 (m, 4 H), 6.8–7.0 (br s, 4 H); mass spectrum (relative intensity), *m/e* 184 (13, M), 142 (21, M − C_3H_6), 141 (79, M − C_3H_7), 129 (26, M − C_4H_7), 116 (100, M − C_5H_8), 115 (46, M − C_5H_9). Anal. Calcd for $C_{14}H_{16}$: C, 91.2 (5); H, 8.7 (5). Found: C, 91.0; H, 8.8.

Other mobile fractions (R_f <0.6) provided decomposition material only, and separate reactions employing an excess of DDQ (5 molar equiv) under a variety of conditions provided no evidence for **10**.

(B) **From 1,4-Dihydronaphthalene.** To a solution of 1,4-dihydronaphthalene[41] (2.6 g, 0.02 mol) in glyme (10 mL), contained in a three-necked flask (50 mL) equipped with a mechanical stirrer and a nitrogen inlet/outlet system, was added in one portion a solution of tetrabutylammonium fluoride in glyme (3.93 g, 0.015 mol; 18 mL of a 0.843 M solution). The resultant solution was cooled to −20 °C and 2-methyl-1-(trimethylsilyl)prop-1-enyl triflate[40] (2.41 g, 0.009 mol) in glyme (10 mL) added dropwise with continuous stirring over 35 min, and the mixture was stirred for 30 min while warming to room temperature. The solution was concentrated under vacuum to a viscous oil which was extracted with pentane (3 × 30 mL). The combined fractions were washed (H_2O, 1 × 20 mL), dried ($MgSO_4$), and concentrated to yield 2.32 g of pale-yellow oil which was distilled under vacuum through a 5-cm column of glass beads. The fraction (bp 87–90 °C/10 mmHg) contained (^1H NMR) ca 38% **11** together with unchanged substrate and naphthalene. Preparative GLC afforded a pure sample of **11** (33 mg; mp 53–54 °C) identical in all respects with that obtained in (A) above.

1,1-Bis(trimethylstlyl)-1*H*-cyclopropa[*b*]naphthalene (16). To a stirred solution of cyclopropa[*b*]naphthalene (**12**)[20] (1.0 g, 7.1 mmol) in dry THF (30 mL) cooled to −70 °C and under oxygen-free nitrogen was slowly added butyllithium (7.1 mmol) in hexane (2.6 mL). The bath temperature was allowed to rise to −40 °C, maintained there for 1.5 h, and then returned to −70 °C. Chlorotrimethylsilane (0.90 mL, 7.1 mmol) was added slowly and the reaction mixture allowed to warm to −40 °C before being returned to −70 °C. The metalation and silylation procedure was repeated twice more, the first time with 1.3 mL of a hexane solution of butyllithium (3.5 mmole and 0.45 mL of chlorotrimethylsilane (3.5 mmol) and the second time with 0.65 mL of a hexane solution of butyllithium (1.75 mmol) and 0.23 mL of chlorotrimethylsilane (1.75 mmol). After the final silylation the reaction mixture was allowed to warm to room temperature (2 h). Aqueous sodium bicarbonate (50 mL) was added and the mixture extracted with light petroleum (2 × 75 mL). The combined organic extracts were washed with water (3 × 75 mL), dried ($MgSO_4$), and concentrated under vacuum to give a brown solid. The major and most mobile component was separated by column chromatography (silica gel, light petroleum elution) and recrystallized (light petroleum, −20 °C) to give **1,1-bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene (16)**: 1.33 g, 66%; mp 95–96 °C, IR ν_{max} 1680, 1402, 1250, 1038, 900, 740, 635 cm^{-1}; ^1H NMR δ 0.01 (s, 18 H, Me_3Si), 7.05 (s, H2/H7), 7.30 (m, H4/H5), 7.65 (m, H3/H6); ^{13}C NMR δ −1.3 (q, Me_3Si), 29.3 (s, C1), 107.9 (d, C2/C7), 124.7 (d, C4/C5), 127.4 (d, C3/C6), 131.3 (s, C1a/C7a), 136.2 (s, C2a/C6a); mass spectrum (relative intensity), *m/e* (18 eV) 284 (16, M), 283 (42, M − H). Anal. Calcd for $C_{17}H_{24}Si_2$: C, 71.8; H, 8.5. Found: C, 72.3; H, 8.75.

1-(Diphenylmethylene)-1*H*-cyclopropa[*b*]naphthalene (17). A stirred solution of **16** (60 mg, 0.21 mmol) and benzophenone (58 mg, 031 mmol) in anhydrous THF (9 mL) under oxygen-free nitrogen was cooled to −70

(39) We thank Prof. E. Vogel, University of Cologne, for a gift of this compound.

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°C, and potassium *tert*-butoxide (48 mg, 0.42 mmol) in THF (3 mL) was added slowly. The resultant clear-yellow solution was allowed to warm to room temperature (2 h). Water (15 mL) was added and the aqueous mixture extracted with dichloromethane (2 × 30 mL). The combined organic extracts were washed with water (3 × 30 mL), dried ($MgSO_4$), and concentrated under vacuum. The resultant crude oil was subjected to preparative TLC (light petroleum/ethyl acetate elution, 9:1) and the major and more mobile band (R_f 0.7) extracted (CH_2Cl_2, 100 mL) to give **1-(diphenylmethylene)-1*H*-cyclopropa[*b*]naphthalene (17)** (66 mg, 100%) as a bright-yellow solid. Recrystallization from light petroleum gave yellow needles: 95%; mp 110–111 °C; IR ν_{max} (KBr) 3050, 1765, 1590, 1540, 1485, 1440, 1410, 1340, 1130, 843, 838, 760, 750, 740, 690 cm^{-1}; UV λ_{max} (cyclohexane) 230 (4.82), 250 (4.54), 258 (sh, 4.52), 269 (sh, 4.48), 291 (4.32), 412 (4.69), 438 nm (log ϵ 4.73); UV λ_{max} (acetonitrile) 228 (4.73), 249 (4.48), 287 (4.31), 409 (4.62), 433 nm (log ϵ 4.65); ^1H NMR δ 7.1–7.4 (complex m, 10 H), 7.5–7.8 (complex m, 6 H); ^{13}C NMR (Table I) δ 126.7 or 127.4 (d, C12/C18), 128.2 and 128.5 (both d, C10/C14, C16/C20, C11/C13, C17/C19), 138.9 or 139.6 (C9/C15); mass spectrum (relative intensity), *m/e* (70 eV) 304 (100, M). Anal. Calcd for $C_{24}H_{16}$: C, 94.7; H, 5.3. Found: C, 95.0; H, 5.15.

Alkylidenecyclopropa[*b*]naphthalenes 18–22. General Procedure. To a stirred solution of **16** (150 mg, 0.53 mmol) in anydrous THF (10 mL) at −70 °C and under oxygen-free nitrogen was slowly added potassium *tert*-butoxide (72 mg, 0.643 mmol) in the same solvent (3 mL). The temperature was raised to −30 °C, maintained there for 1.5 h (during which time the reaction solution developed a dark coloration), and then returned to −70 °C. Anion **15** thus generated was quenched at −70 °C with the appropriate carbonyl compound (1.1 molar equiv) and the resultant clear-orange solution warmed to room temperature (1.5 h). Water (10 mL) was added, the aqueous mixture was extracted with dichloromethane (2 × 40 mL), and the combined organic extracts were washed with water (3 × 40 mL), dried ($MgSO_4$), and concentrated under vacuum to an orange solid. Column chromatography (silica gel), eluting with light petroleum, afforded the corresponding alkylidenecyclopropanaphthalene.

(i) **From 16 and Acetophenenone. 1-(1-Phenylethylidene)-1*H*-cyclopropa[*b*]naphthalene (18)**: 52 mg, 42%, recrystallized from light petroleum as yellow needles (39%); mp 94–95 °C; IR ν_{max} (KBr) 3050, 2980, 1775 (w), 1590, 1550, 1505, 1490, 1440, 1415, 1245, 1175, 1155, 1145, 845, 760, 745, 690 cm^{-1} UV λ_{max} (cyclohexane) 230 (4.70), 242 (sh, 4.38), 253 (sh, 4.24), 289 (4.38), 377 (sh, 4.32), 394 (4.62), 412 (sh, 4.49), 422 nm (log ϵ 4.72); UV λ_{max} (acetonitrile) 229 (4.62), 241 (sh, 4.31), 252 (sh, 422, 288 (4.43), 373 (sh, 4.27), 391 (4.56), 417 nm (log ϵ 4.66); ^1H NMR δ 2.52 (s, MeCO), 7.1–7.4 (complex m, 7 H), 7.7–8.0 (complex m, 4 H); ^{13}C NMR (Table I) δ 18.9 (q, Me), 125.1 or 126.4 (d, C10/C14), 126.8 (d, C12), 128.4 (d, C11/C13), 139.6 (s, C9); mass spectrum (relative intensity), *m/e* (18 eV) 242 (100, M). Anal. Calcd for $C_{19}H_{14}$: C, 94.2; H, 5.8. Found: C, 94.1; H, 5.65.

(ii) **From 16 and α,α,α-Trifluoroacetophenone. 1-(1-Phenyl-2,2,2-trifluoroethylidene)-1*H*-cyclopropa[*b*]naphthalene (19)**: 15 mg, 10%, yelow crystalline solid; IR ν_{max} 1790, 1595, 1550, 1500, 1320, 1215, 1140, 1090, 885, 760, 740, 680 cm^{-1}; UV λ_{max} (cyclohexane) 227 (4.63), 236 (sh, 4.35), 253 (4.29), 263 (4.24), 281 (sh, 4.07), 396 (4.50), 420 nm (log ϵ 4.36); UV λ_{ma}x (acetonitrile) 226 (4.63), 252 (4.39), 2.65 (4.38) (sh, 4.25), 393 (4.55), 414 nm (sh, log ϵ 4.40); ^1H NMR δ 7.2–7.5 (complex m, 6 H), 7.8–8.0 (complex m, 5 H); ^{13}C NMR (Table I) δ 126.0 (d, C12), 127.8, (d, C10/C14), 128.8 (C11/C13); mass spectrum (relative intensity), *m/e* (70 eV) 296 (100 M); exact mass calcd for $C_{19}H_{11}F_3$ 296.081 277, found 296.079 900.

(iii) **From 16 and Benzaldehyde. 1-(Phenylmethylene)-1*H*-cyclopropa[*b*]naphthalene (20)**: 82 mg, 68%, recrystallized from light petroleum as yellow needles (59); mp 114–117 °C; IR ν_{max} 1775 (w), 1545 (w), 1590, 1250, 1040, 850, 740, 685 cm^{-1}; UV λ_{max} (cyclohexane) 229 (4.60), 245 (4.19), 284 (4.29), 376 (sh, 4.28), 394 (4.61), 406 (sh, 4.42 nm (log ϵ 4.73); UV λ_{max} (acetonitrile) 228 (4.59), 252 (sh, 4.20), 283 (4.34), 373 (sh, 4.29), 391 (4.60), 417 nm (log ϵ 4.69); ^1H NMR δ 6.53 (s, 1 H, CH=C), 7.15–8.03 (complex m, 11 H); ^{13}C NMR (Table I) δ 126.5 (d, C10/C14), 126.8 (d, C12), 128.7 (d, C11/C13), 137.9 (s, C9); mass spectrum (relative intensity), *m/e* (70 eV) 228 (100, M). Anal. Calcd for $C_{18}H_{12}$: C, 9.47; H, 5.3. Found: C, 94.8; H, 5.2.

(iv) **From 16 and *p*-Methoxybenzaldehyde. 1-((4-Methoxyphenyl)-methylene)-1*H*-cyclopropa[*b*]naphthalene (21)**: 71 mg, 52%, yellow needles from light petroleum; mp 115–118 °C; IR ν_{max} 1750 (w), 1600, 1550, 1515, 1500, 1245, 1170, 1030, 855, 745 cm^{-1}; UV λ_{max} (cyclohexane) 232 (4.72), 250 (4.43), 259 (sh, 4.42), 287 (4.30), 300 (sh, 4.17), 386 (sh, 4.33), 403 (4.71), 423 (sh 4.52), 432 nm (log ϵ 4.86); UV λ_{max} (acetonitrile) 231 (4.75), 248 (sh, 4.45), 283 (4.36), 379 (sh, 4.41), 400 (4.75), 427 nm (log ϵ 4.84); ^1H NMR δ 3.81 (s, 3 H, MeO), 6.50 (s, 1 H, CH=C), 6.89–7.91 (complex m, 10 H); ^{13}C NMR (Table I) δ 55.4 (q, MeO), 114.5 (d, C11/C13), 127.8 (d, C10/C14), 130.9 (s, C9), 159.1 (s, C12); mass spectrum (relative intensity), *m/e* (70 eV) 258 (100 M). Anal. Calcd for $C_{19}H_{14}O$: C, 88.3; H, 5.5. Found: C, 88.3, H, 5.6.

(v) **From 16 (4 mmol) and 2,2-Dimethylpropanal (5 mmol) with Anion Generation at −50 °C and Flash Chromatography. 1-(2,2-Dimethylpropylidene)-1*H*-cyclopropa[*b*]]naphthalene (22)**:[42] 554 mg, 68%, pale-yellow waxy solid; mp 59–60 °C; IR ν_{max} (KBr) 3032, 2948, 2886, 2854, 1774, 1588, 1498, 1448, 1422, 1380, 1350, 1350, 1240, 1186, 1130, 940, 844, 808, 736, 632 cm^{-1}; UV λ_{max} (cyclohexane) 231 (4.50), 273 (4.17), 335 (sh, 3.73), 351 (4.01), 361 (3.95), 371 nm (log ϵ 4.27); UV λ_{max} (acetonitrile) 230 (4.59), 272 (4.24), 332 (sh, 3.82), 349 (4.09), 359 (4.04), 369 nm (log ϵ 4.32); ^1H NMR δ 1.29 (s, 9 H, Me_3C), 5.64 (s, CH=C), 7.25–7.45 (m, 2 H), 7.35 (s, H2/H7), 7.65–7.85 (m, 2 H); ^{13}C NMR (Table I) δ 30.1 (q, Me_3C), 34.0 (s, Me_3C); mass spectrum (relative intensity), *m/e* (70 eV) 208 (31, M), 193 (100, M − Me); exact mass calcd for $C_{16}H_{16}$ 208.1252, found 208.1247.

1,1-Bis(trimethylsilyl)cyclopropabenzene (26). To a stirred solution of cyclopropabenzene[24] (**2**) (300 mg, 3.3 mmol) in dry THF (12 mL) at −70 °C under oxygen-free nitrogen was slowly added butyllithium (3.3 mmol) in hexane (1.23 mL). The external temperature was allowed to rise to to −30 °C, maintained there for 1.5 h, and then returned to −70 °C. Chlorotrimethylsilane (0.42 mL, 3.3 mmol) was added slowly and the reaction mixture allowed to warm up to −40 °C before being returned to −70 °C. The metalation and silylation procedure were repeated with 1 molar equiv of butyllithium and chlorotrimethylsilane, after which the reaction mixture was allowed to warm to room temperature (1.5 h). Aqueous sodium bicarbonate (20 mL) was added, the mixture was extracted with pentane (2 × 40 mL), and the combined organic extracts were washed with water (3 × 30 mL), dried ($MgSO_4$), and concentrated under vacuum to a yellow oil. Column chromatography (silica gel, pentane elution) furnished **1,1-bis(trimethylsilyl)cyclopropabenzene (26)** (580 mg, 75%) as a clear colorless oil: IR ν_{max} 2940, 2910, 1580, 1485, 1445, 1242, 860, 840, 690 cm^{-1}; ^1H NMR δ 0.01 (s, 18 H, Me_3Si), 6.91 (br s, 4 H); ^{13}C NMR δ −1.3 (q, Me_3Si), 29.5 (s, C1), 111.8 (d, C2/C5), 126.45 (d, C3/C4), 132.9 (s, C1a/C5a). Anal. Calcd for $C_{13}H_{22}Si_2$: C, 66.6; H, 9.5. Found: C, 66.7; H, 9.7.

Alkylidenecyclopropabenzenes 27–30. General Procedure. To a stirred solution of cyclopropabenzene (**2**) (250 mg, 2.8 mmol) in dry THF (8 mL) under oxygen-free nitrogen and at −70 °C was slowly added butyllithium (2.8 mmol) in hexane (1.04 mL). The bath temperature was raised to −30 °C for 1.5 h and then returned to −70 °C, whereupon chlorotrimethylsilane (0.36 mL, 2.8 mmol) was added slowly. The reaction mixture was warmed to −30 °C before being returned to −70 °C. The metalation procedure with butyllithium (2.8 mmol) was repeated and the resultant α-silyl carbanion solution quenched with the relevant carbonyl compound (2.8 mmol) in THF (2 mL) at −70 °C. The product mixture was warmed to −20 °C until the dark solution decolorized to clear orange, whereupon aqueous sodium bicarbonate (15 mL) was added, the mixture was extracted with dichloromethane (2 × 40 mL), and the combined organic extracts were washed with water (3 × 30 mL), dried ($MgSO_4$), and concentrated under vacuum to an orange oil. Column chromatography provided the most mobile component as a yellow solid which was recrystallized from light petroleum.

(i) **From 2 and Benzophenone. 1-(Diphenylmethylene)-1*H*-cyclopropabenzene (27)**: 273 mg, 38%, yellow needles; mp 89–91 °C IR ν_{max} (KBr) 3055, 1775, 1595, 1530, 1495, 1440, 1350, 1150, 775, 738, 695 cm^{-1}; UV λ_{max} (cyclohexane) 249 (4.34), 265 (sh, 4.25), 385 (4.41), 405 nm (sh, log ϵ 4.32); UV λ_{max} (acetonitrile) 246 (4.34), 262 (sh, 4.20), 381 (4.43), 398 nm (sh, log ϵ 4.31); ^1H NMR δ 7.0–7.8 (complex m); ^{13}C NMR ($CDCl_3$) (Table II) δ 126.3 (d, C10/C16), 127.6 (d, C8/C12 and C14/C18), 128.4 (d, C9/C11 and C15/C17), 140.1 (s, C7/C13); ^{13}C NMR (C_6D_6) δ 110.8 (d, C2/C5), 112.0 (s, C1), 113.6 (s, C6), 133.0 (s, C1a/C5a), 133.2 (d, C3/C4), 140.7 (s, C7/C13); ^{13}C NMR (CD_3CN) δ 111.6 (s, C6), 111.7 (d, C2/C5), 114.2 (s, C1), 127.4 (d, C10/C16), 128.4 (d, C8/C12 and C14/C18), 129.4 (d, C9/C11 and C15/C17), 140.7 (s, C7/C13); mass spectrum (relative intensity), *m/e* (100, M). Anal. Calcd for $C_{20}H_{14}$: C, 94.5; H, 5.5. Found: C, 94.2; H, 5.5.

(ii) **From 2 and Acetophenone. 1-(1-Phenylethylidene)-1*H*-cyclopropabenzene (28)**: 52 mg, 10% unstable clear yellow oil; IR ν_{max} 3085, 2940, 1797, 1595, 1545 (w), 1495, 1460, 1455, 1365, 1343, 1155, 765, 748, 700 cm^{-1}; UV λ_{max} (cyclohexane) 242 (4.04), 249 (4.09), 256 (sh, 3.95), (sh, 4.15), 371 (4.26), 394 nm (log ϵ 4.12); ^1H NMR δ 2.37 (s, Me), 7.0–7.5 (complex m, 9 H); ^{13}C NMR (Table II) δ 18.3 (q, Me), 124.3 (d, C8/C12), 125.6 (d, C13), 128.4 (d, C9/C11), 140.3 (s, C7); exact mass calcd for $C_{15}H_{12}$ 192.093 896, found 192.093 570.

(iii) **From 2 and Benzaldehyde. (a) 1-(Phenylmethylene)-1*H*-cyclopropabenzene (29)**: 65 mg, 13% pale-yellow solid, yielded after the

(42) We are grateful to Dr. S. J. Buckland and Qui Mei for the preparation of this compound.

mixture stirred at room temperature for 1.5 h followed by flash chromatography; IR ν_{max} 1775, 1600, 1515, 1345, 1250, 835, 730, 695 cm^{-1}; UV λ_{max} (cyclohexane) 236 (sh, 3.84), 242 (3.89), 248 (3.94), 357 (sh, 3.92), 362 (sh, 3.96), 3.70 (4.04), 380 (sh, 3.89), 394 nm (log ϵ 3.90); UV λ_{max} (acetonitrile) 236 (3.86), 246 (3.85), 355 (sh, 3.83), 366 (3.90), 387 nm (log ϵ 3.73); ^1H NMR δ 6.16 (C_6D_6, 6.21; CD_3CN, 6.12) (s, 1 H, CH=C), 6.8-7.8 (complex m, 9 H); ^{13}C NMR (Table II) δ 125.5 (d, C8/C10/C12), 128.6 (d, C9/C11), 138.6 (s, C7); mass spectrum (relative intensity), *m/e* (70 eV) 178 (100, M); exact mass calcd for $C_{14}H_{10}$ 178.078247, found 178.077960.[43]

Subsequent fractions gave an unstable clear yellow oil proposed as **1-(hydroxyphenylmethyl)-1-(trimethylstlyl)cyclopropabenzene (31)**: 302 mg, 40%; ^1H NMR δ -0.29 (s, Me_3Si), 1.42 (s, OH), 5.09 (s, ArC*h*OH), 7.0-7.4 (complex m, 9 H); ^{13}C NMR δ -2.2 (q, Me_3Si), 44.6 (s, C1), 75.4 (d, Ar*c*HOH), 115.4 and 115.8 (both d, C2/C5), 127.2, 127.9, 128.3, 128.5, and 128.7 (all d, aromatic CH), 130.9 and 131.8 (both s, C1a/C5a), 142.9 (s, phenyl); mass spectrum (relative intensity), *m/e* (18 eV) 268 (100, M).

(b) **29**: 166 mg, 33%, yielded after the mixture stirred at room temperature for 16 h; identical with the compound obtained in (a) above as the sole isolable product.

(iv) **From 2 and *p*-Methoxybenzaldehyde. 1-((4-Methoxyphenyl)-methylene)-1*H*-cyclopropabenzene (30)**: 181 mg, 31%, yellow crystalline solid; IR ν_{max} 1780, 1600, 1510, 1300, 1250, 1030, 838, 735 cm^{-1}; UV λ_{max} (cyclohexane) 238 (sh, 3.88), 258 (3.94), 361 (sh, 3.93), 377 (4.09), 387 (sh, 3.95), 401 nm (log ϵ 4.00); UV λ_{max} (acetonitrile) 257 (4.08), 356 (sh, 4.11), 372 (4.24), 393 nm (log ϵ 4.12); ^1H NMR δ 3.80 (s, OMe), 6.12 (C_6D_6, 6.24; CD_3CN, 6.13) (s, 1 H, CH=C), 6.91 (d, J = 8.7 Hz, H8/H12), 7.08-7.47 (complex m, 4 H), 7.55 (d, J = 8.7 Hz, H9/H11); ^{13}C NMR (Table II) δ 55.4 (q, OMe), 114.4 (d, C9/C11), 126.6 (d, C8/C12), 158.1 (s, C10); mass spectrum (relative intensity), *m/e* (70 eV) 208 (100, M); exact mass calcd for $C_{15}H_{12}O$ 208.088 810, found 208.087 740.[43]

(43) As attempted recrystallization leads to decomposition, no melting point data are available; see text.

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Supplementary Material Available: Tables VI and VII listing thermal vibration parameters for non-hydrogen atoms and weighted mean planes (2 pages); tables of calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

2,4,6-Tris(2,6-di-*tert*-butyl-4-substituted-phenoxy)-1,3,5,2,4,6-trioxatriphosphorinanes. Synthesis, Characterization, X-ray Structure, and Solid-State ^{31}P NMR of a Novel Family of Phosphorus(III)-Oxygen Heterocycles

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Abstract: The reaction of 2,6-di-*tert*-butylphenyl phosphorodichloridite or its para-substituted derivatives with 1 equiv of water in the presence of 2 equiv of trialkylamine forms a family of novel P(III)-O heterocycles, the 1,3,5,2,4,6-trioxatriphosphorinanes. These cyclic trianhydrides of substituted phosphorus acids are formed in 40-80% yields. The *p*-methyl derivative crystallizes in the $P\bar{1}$ space group of the triclinic crystal system with two molecules per unit cell (a = 10.896 (1) Å, b = 22.391 (3) Å, c = 9.785 (2) Å, α = 95.14 (1)°, β = 99.17 (1)°, and γ = 90.38 (1)°). The X-ray crystal structure of the *p*-methyl (and *p*-*tert*-butyl) derivative reveals that the P_3O_3 heterocycle exists in a distorted boat conformation with the three phosphorus atoms in nonequivalent environments. Two of the substituents are trans axial to one another while the third substituent is intermediate between axial and equatorial. The high-resolution solid-state ^{31}P NMR spectra confirm that each of the compounds examined in this study possesses three nonequivalent phosphorus atoms in the solid state. However, the ^{31}P NMR solution spectra of these compounds show that two of the phosphorus atoms are equivalent. This implies that the molecules each have a plane of symmetry in solution. While the compounds are stable to air or water, they melt with decomposition.

There has been a recent flurry of activity[1] in the isolation and characterization of novel trivalent phosphorus compounds **1** which owe their formation to sterically hindering ligand groups. For example, hindering groups prevent alternative reactions from occurring and effectively stabilize (protect) the labile P-P double bond[2] during the synthesis of **1**. We now report the synthesis and characterization of a new class of *trivalent* phosphorus compounds **2** which also owe their stability to steric hindrance. These are formally cyclic anhydrides of monosubstituted phosphorous acids and belong to the tris(aryloxy)-1,3,5,2,4,6-trioxatriphosphorinane family.

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