N_2 was added DIBAH (1.04 mL of a 1 M solution in hexanes, 1.04 mmol) and the resulting solution was stirred for 3 h. Water (2 mL) was added and the reaction mixture was stirred for 10 min followed by addition of 5% HCl (5 mL). Further workup afforded the crude products. Preparative TLC (99:1 CH_2Cl_2–CH_3OH) gave 52 mg (74% yield) of an oil containing **2d** and **2c** (79:21 ratio by NMR).

Reduction of Dihydroisoxazole 1b with BH_3–THF. To a cold (0–5 °C) solution of **1b** (0.04 g, 0.15 mmol) in THF (4 mL) under N_2 was added borane in THF (0.9 mL of a 1 M solution) and the resulting solution was stirred for 4 h. Water–THF (2 mL, 1:1) was added followed by 1% HCl (2 mL). Further workup afforded the crude products. Preparative TLC (99:1 CH_2Cl_2–CH_3OH) gave 37 mg (95% yield) of an oil containing **2d** and **2c** (52:48 ratio by NMR).

Reduction of Dihydroisoxazole 1b with 9-BBN. To a cold (0–5 °C) solution of **1b** (0.04 g, 0.15 mmol) in THF (5 mL) under N_2 was added 9-BBN (3 mL of an 0.5 mM solution in THF, 1.5 mmol) and the resulting solution was stirred for 210 min at 0–5 °C and at ambient temperature for 1 h. Volatiles were removed at reduced pressure, benzene (2 mL) followed by ethanolamine (0.092 mL) were added, and the resulting solution was stirred overnight at room temperature. Dichloromethane (10 mL) was added and the mixture was filtered. The filtrate was worked up to afford crude product. Preparative TLC (20:80 EtOAc–hexanes) gave 36 mg (90% yield) of an oil containing **2d** and **2c** (93:7 ratio by NMR).

Conversion of Oxirane 7 to Alcohol 2c. To a cold (0–5 °C) solution of oxirane **7**[8] (0.02 g, 0.08 mmol) in THF (2 mL) under N_2 was added lithium triethylborohydride (0.20 mL of a 1 M solution in THF, 0.20 mmol) and the resulting solution was stirred for 15 min. Water–THF (1 mL, 1:1) was added and then 5% HCl (5 mL). Further workup afforded the crude products. Preparative TLC (35:625 EtOAc–hexanes) gave 14 mg (68% yield) of **2c** free of any isomeric **2d**.

Supplementary Material Available: Calculated bond lengths for **8** (s-trans and s-cis conformers), ^1H NMR spectrum of **5a**, ORTEP drawing of **2f**, crystal data for **2f**, tables of refined positional and thermal parameters for **2f**, and tables of bond lengths and bond angles for **2f** (7 pages). Ordering information is given on any current masthead page.

Studies in the Cyclopropabenzene Series: ^{13}C NMR Correlations for Alkylidenecyclopropabenzenes

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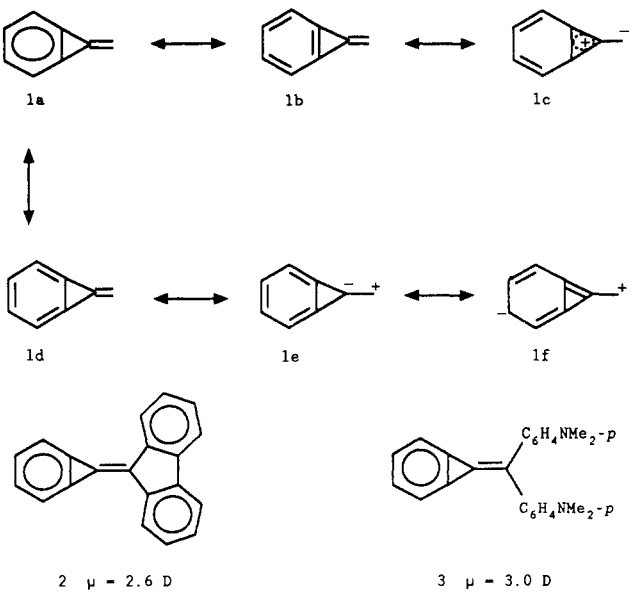
The ^{13}C NMR spectra of a series of (arylmethylene)- and (diarylmethylene)-1*H*-cyclopropa[*b*]naphthalenes, **6** and **8**, and -cyclopropabenzenes, **7** and **9**, have been analyzed. A systematic change in the ^{13}C chemical shifts of the cyclopropabenzenyl carbon atoms is induced by remote para substituents R which correlate linearly with the corresponding Hammett constant σ_p^+. Depending upon the nature of R the cyclopropabenzenyl unit accepts more or donates less π-electron density.

Since the first derivatives of methylenecyclopropabenzene (**1**) were reported[1] in 1984, many interesting physical[2,3] and chemical[4,5] properties of this novel series of hydrocarbons have emerged.[6] Not least among these is the ambiphilic character of the cyclopropabenzenyl component of **1** and the ability this has to stabilize both positive and negative charge as illustrated by the polar derivatives **2** and **3**, respectively.[7] Thus when substituted with electron-withdrawing groups at the exocyclic center, contributions to the structure from **1a–c** appear to dominate whereas with electron-donating substituents the alternative forms **1d–f** are important. In the singlet excited state these features are even more significant, and fluorescence with marked Stokes shifts and high quantum efficiency have been recorded.[8]

The range of alkylidenecyclopropabenzenes that is now available allows for the assignment of the ^{13}C NMR resonances of the cyclopropabenzenyl moiety and these are now reported. The effects of the substituents in the *p*-aryl derivatives **6a–f** and **7a,b** and the *p,p'*-diaryl derivatives **8a–e** and **9a–d** are felt in the cyclopropabenzenylidene unit and excellent correlations with the Hammett σ_p^+ constants are found.



Experimental Section

Compounds. The compounds studied were prepared from cyclopropabenzene (**4**) or cyclopropa[*b*]naphthalene (**5**) by silyl-Wittig olefination as previously reported.[1,3-9]

^{13}C NMR Spectra. The ^{13}C NMR spectra were recorded for $CDCl_3$ and DMSO-d_6 solutions (~10% solutions) where possible,

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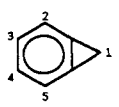
and chemical shifts are relative to Me_4Si (δ 0.00). The spectra were recorded at 20.00 MHz on a Varian Associates FT80A instrument except for the dinitrocyclopropa[*b*]naphthalene derivative **8e** ($CDCl_3$: Bruker AC300 operating at 75.470 Mz; DMSO-d_6 Bruker AC400 operating at 100.624 MHz). Pulse sequences to enhance quaternary carbons, SFORD, and routine spin-echo techniques were employed to establish the multiplicity of the resonance lines.

Results and Discussion

Detailed analyses[10,11] of the ^{13}C NMR chemical shifts of the ortho fused aromatics reveal that the carbon atoms adjacent to the sites of ring fusion in cyclopropabenzene (**4**, C2/C5) are significantly shielded (δ 114.7) due to the unusual bonding associated with the three-membered ring. The appearance of these methine signals in the range 110–115 ppm is diagnostic of the ring system. Moreover, the fusion centers (C1a/C5a) appear at δ 125.4 which, while in the usual aromatic region, represents an abnormal shielding when compared with the higher homologues (cyclobutabenzene, 145.6; indan, 144.0 ppm) that is a direct consequence of their cyclopropenyl[12] nature (cyclopropene HC=, 108.7 ppm). By comparison the remaining more remote methine centers (C3/C4) are essentially unaffected by fusion and resonate at 128.8 ppm. The data for cyclopropa[*b*]naphthalene (**5**) are comparable (C2/C7, 112.3; C1a/C7a, 123.4; C2a/C6a, 136.7 ppm) and have been similarly assessed.[10,13]



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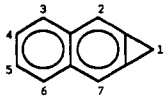
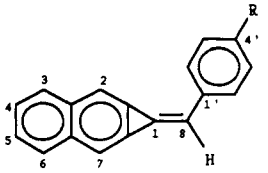


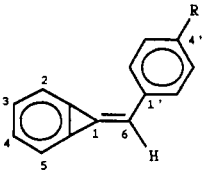
5

The NMR spectral data of the alkylidenecyclopropparenes are fully compatible with species sustaining a diamagnetic ring current. However, the ^1H NMR data are not easily amenable to analysis because all of the stable derivatives have aromatic substituents attached to the exocyclic center and the signals are overlapped within the usual aromatic range. By comparison the ^{13}C NMR spectra provide insights to the nature of these fulvenes, and the data are collected in Tables I–III. It should be noted that the Peterson olefination procedure from **4** employing aldehydes is significantly less efficient than with **5** and that the ensuing (arylmethylene)-1*H*-cyclopropabenzenes **7** are noticeably less stable; the result is that data are available for **7a,b** only.

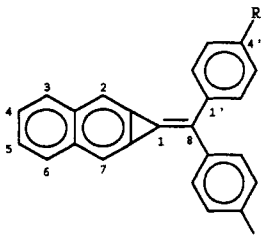
Like the precursor cyclopropparenes the alkylidene derivatives display shielded methine resonances in the range 98–112 ppm (Tables I–III), and these are compatible only with the carbon atoms adjacent to the sites of ring fusion. However, the shielding is greater than is observed for **4** and **5** by 4–5 ppm (C2/7: **5**, 112.3; **8a**, 107.3 ppm (Table II)). On the other hand the quaternary bridge carbons (C1a/C7a of **6** and **8**; C1a/C5a of **7** and **9**) are deshielded by about 7 ppm when compared with the parent cyclopropparene (C1a/C5a: **4**, 128.8; **9a**, 132.7 ppm (Table III)). The



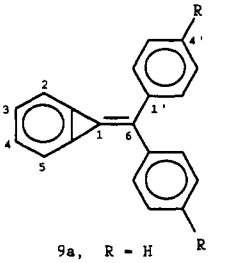
6a, R = H
b, = OMe
c, = NMe_2
d, = SMe
e, = NO_2
f, = Cl



7a, R = H
b, = OMe



8a, R = H
b, = OMe
c, = NMe_2
d, = $^+NMe_3$ I^-
e, = NO_2



9a, R = H
c, = NMe_2
b, = OMe
d, = $^+NMe_3$ I^-

arylmethylene derivatives **6** and **7** provide a clear distinction between the quaternary cyclopropparenyl center C1 and the exocyclic methine site (**6**, C8; **7**, C6) (Table I). The diaryl homologues **8** (Table II) and **9** (Table III) each have two quaternary carbon resonances in the range 105–122 ppm. One of these is at essentially the same position as C1 in **6** and **7**, respectively, e.g. **6b**, 110.2, and **8b**, 109.5; **6c**, 108.2, and **8c**, 107.0, and is assigned likewise while the other signal is shifted to a lower field than the exocyclic vinylic methine resonance of **6** or **7** by at least 10 ppm, e.g. **6e**, 104.1; **8e**, 114.2, and is assigned as the sp^2 diarylmethylene center. The assignment of C1 is compatible with the mesomerism possible (vide infra) and that of the exocyclic center is nicely consistent with the change from Cα of styrene (PhC*H*=, δ 136.7) to C1 of 1,1-diphenylethene (Ph_2C=, δ 150.2).[14] The lack of symmetry in **6** and **7** is reflected in distinct but closely spaced pairs of lines for the distinguishable centers (Table I), e.g. **6a**, C2/C7, 108.2 and 108.3; **7b**, C2/C5, 111.0 and 111.1 ppm, respectively; no attempt is made to differentiate these signals. The assignment of resonances due to the carbon atoms of the pendant aryl substituents is made using the well-established substituent effects in monosubstituent benzenes.[15]

In 3-methylenecyclopropene (**10**)[16] the exocyclic sp^2 center displays its carbon resonance at δ 59.6 while the endocyclic olefinic carbons appears at δ 132.9. Together with the ^1H NMR data the shielding of the exocyclic carbon atom is taken as support for significant charge separation in the molecule with a substantial contribution to **10** from the delocalized 2π-cyclopropenyl cation form.

10

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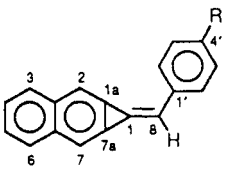
Table I. ^{13}C NMR Chemical Shifts of 1-(Arylmethylene)-1*H*-cycloproparenes[a]

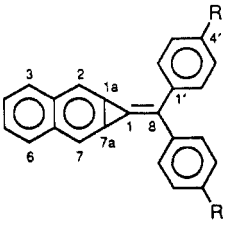


compound	C1	C8	C1a/C7a	C2/C7	C2a/C6a	C3/C6	C4/C5	C1′	C2′/C6′	C3′/C5′	C4′	R
6a, R = H	111.9	107.1	125.6	108.2	138.4	128.8	126.7	137.9[b]	126.5	128.7	126.9	
			127.8	108.3	139.1[b]	128.9	126.8					
6b, R = OMe	110.2	107.2[c]	125.9	107.2	138.3	128.7	126.5	130.9	127.8	114.5	159.1	55.4
			128.0	107.5[c]	138.9	128.8	126.6					
6c, R = NMe_2	108.2	108.4	126.6	106.4	138.2	128.6	126.2	126.6	127.8	112.8	149.9	40.4
			–[d]	106.5	138.9	128.7	126.4					
6d, R = SMe	111.3	106.5	125.4	108.0	138.3	128.8	126.7	134.8	126.9[c]	126.8[c]	136.9	16.0
			–[d]	108.1	139.0	128.9	126.8					
6e, R = NO_2	116.2	104.1	–[d]	109.7	139.1	129.2	126.2	–[d]	127.6	124.3	144.9	
				111.1	139.8	129.3						
6f, R = Cl	112.4	105.6	125.3	108.5	138.4	128.9	126.9	136.4	128.9	127.4	132.5	
				108.6	139.1		127.0					

	C1	C6	C1a/C5a	C2/C5	C3/C4					
7a, R = H	113.1	98.2	131.1	111.5	132.8	138.6	125.5	128.6	125.5	
			133.5	111.6	133.8					
7b, R = OMe	111.6	98.1	131.3	111.0	132.3	–[d]	126.6	114.4	158.1	55.4
			131.4	111.1	132.4					

[a] Recorded for $CDCl_3$ solutions with Me_4Si as internal standard to ±0.05 ppm. [b] Quaternary carbon assignments could be reversed. [c] Methine carbon assignments could be reversed. [d] A dash is used to signify not seen.

Table II. ^{13}C NMR Chemical Shifts of (Diarylmethylene)cyclopropa[*b*]naphthalenes[a]



compound	solvent	C1	C8	C1a/C7a	C2/C7	C2a/C6a	C3/C6	C4/C5	C1′	C2′/C6′	C3′/C5′	C4′	R
8a, R = H	$CDCl_3$	112.0	120.8	–[b]	107.3	138.9[c]	128.8	126.7[d]	139.6[c]	128.5[d]	128.2[d]	127.4[d]	
	DMSO-d_6	111.3	118.9	127.3	107.4	138.3[c]	129.7	126.2[d]	138.6[c]	128.7[d]	127.6[d]	127.0[d]	
8b, R = OCH_3	$CDCl_3$	109.5	119.8	127.8	106.0	138.6	128.5	126.4	132.2	129.4	113.9	159.1	55.3
	DMSO-d_6	108.6	119.2	126.7	106.0	138.0	128.5	126.7	131.0	128.9	114.1	158.9	55.1
8c, R = $N(CH_3)_2$	$CDCl_3$	107.0	121.8	127.9	104.5	138.5	128.3	126.0	128.7	129.4	112.2	149.9	40.5
	DMSO-d_6	105.4	121.5	127.6	104.0	137.8	128.1	126.2	126.2	128.7	112.0	149.8	39.9
8d, R = $N^+(CH_3)_3I^-\cdot H_2O$	DMSO-d_6	114.2[c]	114.4[c]	125.1	109.0	138.7	129.1	127.7	139.7	128.6	121.2	146.0	56.5
8e, R = NO_2	$CDCl_3$	117.8	114.2	125.7	109.8	139.7	129.3	128.0	145.4[c]	128.3	124.2	146.6[c]	
	DMSO-d_6	117.0	114.1	125.0	110.0	139.2	129.2	128.0	144.6[c]	128.3	124.1	146.1[c]	

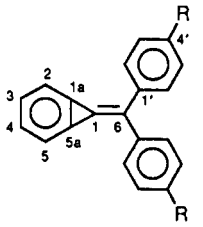
[a] Recorded with Me_4Si as internal standard to ±0.05 ppm. [b] Not seen. [c] Quaternary carbon assignments could be reversed. [d] Methine carbon assignments could be reversed.

This is confirmed by the high dipole moment (1.90 D) for the compound. The ^{13}C NMR data for **2** and its naphtho[*b*] analogue do not allow for reliable assignments in the 120–135 ppm range because of overlap of the aromatic signals. However, a 2D COSY experiment for the naphtho analogue (of **2**) links the two-proton singlet for H2/H7 (δ 7.87) with the high-field methine carbon resonance (δ 109.6) and establishes the assignment. C1 is assigned at 115.4 and C8 at 108.8 ppm, respectively, by comparison with **6e** and **8e**, and, coupled with the polarity of **2**, a significant contribution from the charge separated form equivalent to **10** (cf. **1c**) is inferred.

The remote para substituents of the (arylmethylene)-cycloproparenes **6–9** systematically influence the chemical shifts of the cycloproparenyl carbon atoms of the molecules. Electron-donating groups at C4′ cause high-field shifts of all but the bridge carbons (C1a/C7a of **6** and **8**, C1a/C5a of **7** and **9**; Tables I–III) of the cycloproparenyl moiety while the exocyclic olefin center has its resonance systematically shifted to lower field. These effects are illustrated in Figure 1 for C1, C2/C7, and C8 of **8**. The shifts are most noticeable for the *p,p′*-dimethylamino-substituted derivative **8c** (Δδ 2.6–5.9) and are fully consistent with mesomerism with the cycloproparenylidene as the "electron-sink".

In the quaternary ammonium salts **8d** and **9d** mesomerism is no longer possible and the shifts are in the opposite sense to those noted above, e.g. for C1 **8c** 105.4, **8d** 114.2 ppm. This change in the direction of the shifts is enhanced further by the only known[9] dinitro compound **8e**, which displays C1 at 117.0 ppm while C8 is at 114.1 ppm. These data are compatible with the ambiphilic cycloproparenyl

Table III. ^{13}C NMR Chemical Shifts of Some (Diarylmethylene)cyclopropabenzenes[a]



compound	solvent	C1	C6	C1a/C5a	C2/C5	C3/C4	C1'	C2'/C6'	C3'/C5'	C4'	R
9a, R = H	$CDCl_3$	113.3	111.2	132.7	110.7	133.2	140.1	127.6	128.4	126.3	
	DMSO-d_6	112.8	109.9	131.5	111.0	134.2	139.2	127.1	128.5	126.4	
9b, R = OCH_3	$CDCl_3$	110.7	111.2	132.8	110.0	132.6	132.8	128.8	113.9	158.4	55.3
	DMSO-d_6	109.8	110.4	131.7[b]	110.1	133.3	131.7[b]	128.2	114.0	158.0	55.1
9c, R = $N(CH_3)_2$	CD_2Cl_2	109.2[c]	112.6	133.7	109.2[c]	132.3	128.7	128.8	112.8	149.8	40.7
	DMSO-d_6	108.0	111.6	131.2	108.8	132.4	127.6	127.9	112.3	149.1	40.0
9d, R = $N^+(CH_3)_3I^-$	DMSO-d_6	115.9	105.7	130.7	112.2	135.8	140.3	127.9	120.9	145.2	56.5

[a] Recorded with Me_4Si as internal standard to ±0.05 ppm. [b] δ 131.68 and 131.73. [c] δ 109.15 and 109.24, respectively.

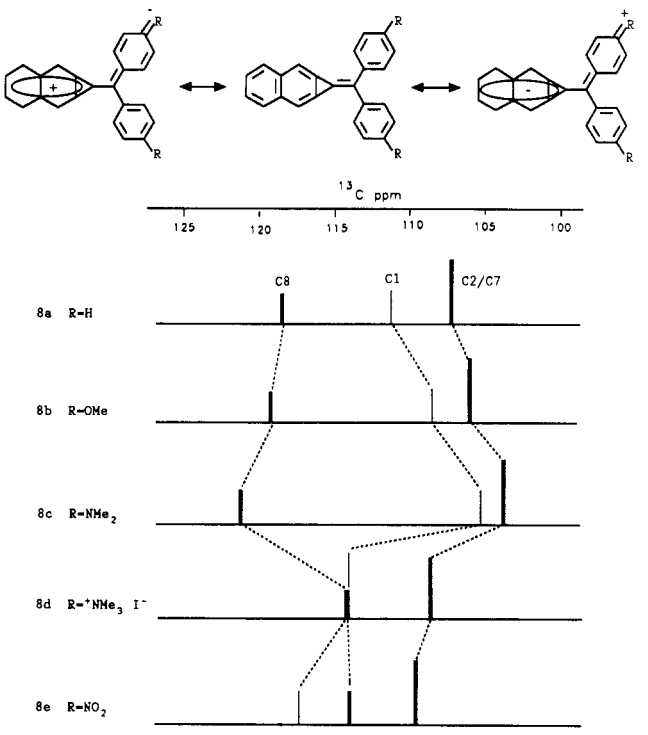


Figure 1. ^{13}C NMR shifts of 1-(diarylmethylene)-1*H*-cyclopropa[*b*]naphthalenes, **8**.

moiety now behaving as the electron source that contributes to the structure from the "push–pull" form **1c** (or **2**).

Carbon-13 chemical shifts are ideal probes for investigating substituent effects in aromatic molecules with comparable steric environments. Thus in monosubstituted benzenes the observed chemical shifts of the para carbon atoms correlate well with the total charge density calculated by the CNDO/2 method[17] and with the appropriate Hammett σ-constant.[18] As σ_p^+ values best represent resonance contributions[18] these have been used with much effect by Neuenschwander and co-workers[19] to correlate the ^{13}C chemical shifts of the five-membered ring carbons of various para-substituted 6-arylpentafulvenes. Plots of

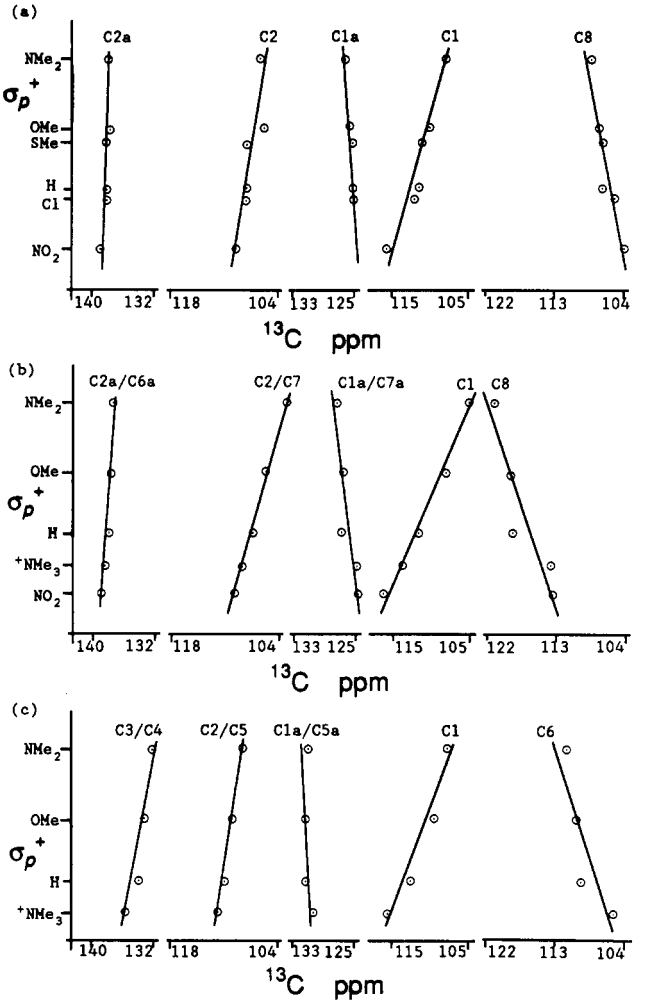


Figure 2. Plot of Hammett substituent constants σ_p^+ against ^{13}C chemical shifts for (a) 1-(arylmethylene)-1*H*-cyclopropa[*b*]-naphthalenes, **6**, (b) 1-(diarylmethylene)-1*H*-cyclopropa[*b*]-naphthalenes, **8**, and (c) 1-(diarylmethylene)-1*H*-cyclopropabenzenes, **9**.

^{13}C chemical shifts against σ_p^+ for one remote cyclopropenyl substituent of **6**, **8**, and **9** are shown in Figure 2, parts a–c, respectively, and remarkably good linear correlations are found. For **6** the carbon atoms C1a, C2, and C2a that are cis with respect to the aryl substituent are assumed to have the higher field signal of the C1a/C7a, C2/C7, and C2a/C6a pair, respectively; equally good plots

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(not shown) are obtained using the lower field signal. The parent compounds **6a-9a** generally give a poor fit, and this is consistent with the small, but measureable, permanent dipoles recorded (**8a** and **9a**, μ = 0.4 and 1.0 D respectively)[3] for the molecules and the fact that this is not recognized by the zero value of the Hammett substituent constant for H. The most sensitive centers to substituent effects are the exocyclic olefinic carbons. As the electron-donating capacity of the remote para substituent increases, the electron density at C1 and the centers adjacent to the ring fusion is enhanced and the centers are shielded. Although the more remote positions (**6** and **8**: C2a/C6a; C7 and C9; C3/C4) are also influenced, the effect is smaller (Figure 2, Tables I-III). Because the electron density of the exocyclic double bond is directed toward C1 the influence of the electron-rich para substituent upon the arylmethylene center (C8/C6) is notably the opposite to that for C1, and a deshielding effect is recorded. This is in precisely the opposite direction to shifts recorded for C1 of *p,p'*-disubstituted 1,1-diarylethenes. In DMSO-d_6 C1 of 1,1-diphenylethene resonates at δ 149.2 but the *p,p'*-dimethoxy, dimethylamino, and trimethylammonio derivatives have this same signal at 148.2, 149.0, and 145.4 ppm, respectively. However, as Sardella and co-workers[20] have shown, the effect of a remote aryl substituent upon the exocyclic olefinic centers of 6-aryl-6-methylfulvene is primarily due to π-polarization because of a marked (~70°) twist angle of the aryl ring to the flat cyclopentadienylidene moiety. This results in a π-electron excess or deficiency at the C1' ipso-center as a result of the C4' substituent. An attenuation of the resonance effect is involved, and the dominance of π-polarization accounts for the major changes in the exocyclic olefinic resonances and the reversal in slope of the fulvene C6 correlation. A similar effect is likely in **8** and **9** since **8c** has a twist angle for the aryl substituent of 28° in the solid state.[21] The situation in **6** and **7** is less obvious as the twist angle of the aryl substituent is only 5° in **6c**. It appears therefore that the cyclopropparenyl moieties of **6-9** either behave as electron acceptors or donate *less* π-electron density when electron donors are located at the remote para positions. It is notable that the nitro substituted compounds **6e** and **8e** provide chemical shift data which match expectations from the plots of Figure 2. These serve to support the ambiphilicity of the cyclopropparenyl moiety.

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5-Methylene-2(5*H*)-furanone as a Dienophile in Diels-Alder Cycloadditions: Site Selectivity and Regioselectivity

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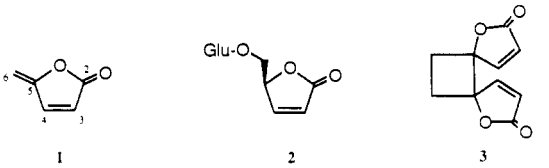
Site selectivity and regioselectivity in Diels-Alder reactions of 5-methylene-2(5*H*)-furanone (**1**) with several acyclic dienes have been investigated. We have found that **1** consistently reacts specifically at the exocyclic double bond, giving spiro adducts in good yields. Excellent regioselectivity has also been found in either catalyzed or uncatalyzed reactions with unsymmetrically substituted dienes. A kinetic study of the reaction with isoprene has revealed that the observed regioselectivity is a direct consequence of kinetic control over the process. Theoretical calculations have been carried out in order to interpret these experimental results.

The blistering property and antibiotic activity of many plants belonging to the natural order Ranunculaceae are well-known.[1] These physiological activities are attributable to protoanemonin (**1**), an α,β-unsaturated lactone that is released in the plant upon crushing of the tissues with enzymatic splitting of the glucoside ranunculin (**2**).[2-5] Protoanemonin easily dimerizes through a [2 + 2] head-to-head cycloaddition to anemonin (**3**), the crystalline product normally isolated from Ranunulaceae.

Chart I



1 **2** **3**

Although **1** is easily prepared from levulinic acid,[6] its potential reactivity as a multifunctional C_5 synthon has scarcely been explored, and few explanations have been advanced for its physiological activity.[7] Its electrophilic

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