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The Preparation of Exocyclic Functionalised Alkylidenecycloproparenes Via a New Procedure

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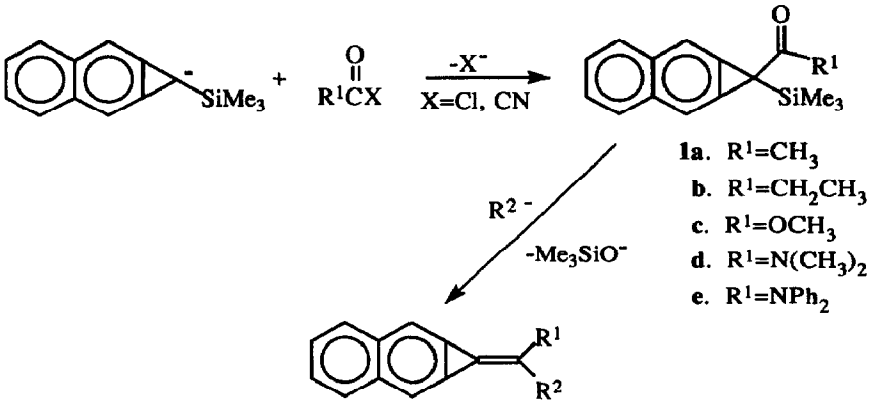
Abstract: ***The general preparation of several new alkylidenecycloproparenes containing functional groups at the exocyclic (C8) position is described.***

The alkylidenecycloproparenes, e.g. **2**, are a class of highly strained, yet remarkably stable group of compounds which were first introduced in 1984.[1a] Since that time, they have attracted considerable attention from both theoretical and experimental chemists.[1-5] We now wish to report the preparation of previously unobtainable 8,8-disubstituted alkylidenecyclopropanaphthalenes via a new, general procedure . This method involves the reaction of the monosilyl cycloproparenyl anion with a carbonyl compound with a good leaving group directly attached, such as an acyl chloride or cyanide. The silyl anion adds in a nucleophilic fashion to the carbonyl. Subsequent elimination of the leaving group then affords **1**. Addition of a second nucleophile, usually as its lithium salt, followed by Peterson olefination yields the desired disubstituted product **2** (Scheme 1).

In a typical experiment, a solution of 1,1-bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene[1b] (284 mg, 1.0 mmol) in dry THF (20 ml) was placed under nitrogen and cooled to -78 °C. A suspension of potassium t-butoxide (134 mg, 1.2 mmol) in THF (10 ml) was added slowly. The mixture was allowed to warm to -42 °C for 1.5 h., then returned to -78 °C. A solution of methyl chloroformate (109 mg, 1.1 mmol) in THF (6 ml) was added dropwise and the reaction mixture was allowed to warm to room temperature slowly. After adding water (30 ml) the mixture was extracted with dichloromethane. The extracts were dried and concentrated. The crude product was then purified via radial chromatography to give **1c** (154 mg, 57%) as a pale orange oil. A solution of **1c** (100 mg, 0.37 mmol) in dry THF (10 ml) was placed under nitrogen and cooled to -42 °C. A solution of lithium cyanide (2 ml of 0.5 M solution, 1.0 mmol) in DMF was added slowly via syringe. The mixture was allowed to warm slowly to room temperature, and stirred for 3 h., then heated to 50 °C for 1.5 h. After cooling, water (10 ml) was added, and the mixture extracted with dichloromethane. The extracts were dried and concentrated. The product was then purified via radial chromatography to give **2f** (128 mg, 62%) as a bright orange solid, m.p. 78-80 °C.



1a. $R^1=CH_3$
b. $R^1=CH_2CH_3$
c. $R^1=OCH_3$
d. $R^1=N(CH_3)_2$
e. $R^1=NPh_2$

2a. $R^1=CH_3$, $R^2=H$
b. $R^1=R^2=CH_3$
c. $R^1=R^2=CH_2CH_3$
d. $R^1=R^2=OCH_3$
e. $R^1=OCH_3$, $R^2=N(CH_3)_2$
f. $R^1=OCH_3$, $R^2=CN$
g. $R^1=R^2=N(CH_3)_2$
h. $R^1=N(CH_3)_2$, $R^2=OCH_3$
i. $R^1=N(CH_3)_2$, $R^2=CN$
j. $R^1=R^2=NPh_2$

Scheme 1

Table 1. Synthesis of Alkylidenecyclopropanaphthalenes

R^1	Product[6,7]	Yield(%)	R^2	Product[6,8]	Yield(%)
CH_3	**1a**	65	H	**2a**	41
CH_3	**1a**	65	CH_3	**2b**	54
CH_2CH_3	**1b**	52	CH_2CH_3	**2c**	55
OCH_3	**1c**	57	OCH_3	**2d**	52
OCH_3	**1c**	57	$N(CH_3)_2$	**2e**	43
OCH_3	**1c**	57	CN	**2f**	62
$N(CH_3)_2$	**1d**	50	$N(CH_3)_2$	**2g**	60
$N(CH_3)_2$	**1d**	50	OCH_3	**2h**	58
$N(CH_3)_2$	**1d**	50	CN	**2i**	36
NPh_2	**1e**	63	NPh_2	**2j**	65

In the preparation of **1**, either the appropriately substituted acyl chloride or acyl cyanide may be used with similar yields. Generally, the chlorides were preferred due to the wider availability of various substituted acyl chlorides as well as the lower toxicity of the by-products. This method has provided a wide variety of disubstituted cyclopropanaphthalenes **2a-j** (Table 1). Simple alkyl substituted products are now readily obtainable via the new procedure. In fact, compounds **2a-c** are the simplest alkylidenecyclopropanaphthalenes known.[2] Previous attempts at their synthesis have been unsuccessful.[1b] Since each substituent is added separately, unsymmetrical products, where $R^1 \neq R^2$, may be easily prepared. Thus, many different combinations of substituents are now possible. In most cases, the substituents

may be added in either order with comparable overall yields, as in compounds **2e** and **2h**. However, groups which are good leaving groups, such as cyanide or chloride, must be added second. This appears to be the only major limitation. Perhaps the most interesting of the combinations are those in which one substituent is electron-donating and the other is electron-withdrawing, as in compounds **2f** and **2i**. These exhibit a "push-pull" type effect on the external double bond. Great care must be taken in the preparation of these compounds. They are quite sensitive to reaction conditions, especially temperature. However, both **2f** and **2i** are quite stable solids which, when protected from light, survive indefinitely. In fact, while all of the disubstituted products decompose upon prolonged exposure to light, they are otherwise stable. Only the compounds containing two electron-donating substituents, **2d, e, g, h**, show some thermal instability and decompose gradually at room temperature, but may be stored at lower temperatures.

Each of the disubstituted products **2a-j** exhibit spectral characteristics typical of the alkylidenecyclopropanes. Each has a band in the infrared spectrum at 1760-1775 cm^{-1}, which arises from the exocyclic double bond, as well as those arising from the functional group. The proton NMR spectra are not as informative, with the signals due to the aromatic protons appearing as a complex multiplet in the normal aromatic range, 7.0-8.0 ppm. Most diagnostic are the carbon-13 NMR spectral data. The aromatic carbons C2 and C7 adjacent to the three-membered ring are shifted far upfield from the normal aromatic position, namely at 99-112 ppm, typical of the cyclopropanes.[4] The carbons of the exocyclic double bond are also shifted significantly upfield, with the exact shifts dependent upon the substituents.

In conclusion, we have developed a new method for the preparation of remarkably stable, brightly colored 8,8-disubstituted alkylidenecyclopropanaphthalenes containing various functional groups. The procedure has the potential to provide numerous, diverse, previously unobtainable alkylidenecyclopropanes.

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6. All new compounds were fully characterized by elemental analysis, mass spectrometry, infrared and multinuclear NMR spectroscopy. Selected physical and spectral data are given in references 7 and 8

7. **1a**: pale yellow solid, m.p. 102-103 °C; ^{1}H ($CDCl_3$) δ 0.17 (s, 9H), 1.7 (s, 3H), 7.3-7.8 (m, 6H); $^{13}C\{^1H\}$ ($CDCl_3$) δ -0.79, 19.3, 21.1, 108.4, 110.2, 126.4, 127.3, 127.8, 131.2, 134.1, 138.3, 176.3. **1b**: pale yellow solid, m.p. 107-109 °C; ^{1}H ($CDCl_3$) δ 0.16 (s, 9H), 1.0 (t, 3H), 2.1 (q, 2H), 7.3-7.7 (m, 6H); $^{13}C\{^1H\}$ ($CDCl_3$) δ -0.65, 10.3, 22.1, 28.4, 109.2, 109.0, 125.8, 126.9, 127.4, 132.1, 134.4, 139.4, 179.2. **1c**: pale orange oil; ^{1}H ($CDCl_3$) δ 0.21 (s, 9H), 3.43 (s, 3H), 7.1-7.6 (m, 6H); $^{13}C\{^1H\}$ ($CDCl_3$) δ -0.12, 23.2, 44.3, 105.3, 106.0, 125.3, 128.2, 128.7, 133.6, 135.2, 141.3, 165.3. **1d**: reddish-orange oil; ^{1}H ($CDCl_3$) δ 0.15 (s, 9H), 2.7 (s, 6H), 7.1-7.7 (m, 6H); $^{13}C\{^1H\}$ ($CDCl_3$) δ -1.1, 24.5, 32.1, 34.3, 106.3, 108.1, 123.7, 125.9, 126.6, 134.1, 134.6, 143.1, 159.9. **1e**: red solid, m.p. 89-90 °C; ^{1}H ($CDCl_3$) δ 0.17 (s, 9H), 7.2-8.0 (m, 16H); $^{13}C\{^1H\}$ ($CDCl_3$) δ -0.95, 23.6, 107.1, 124.1, 125.6, 125.9, 127.3, 128.1, 128.4, 135.0, 136.1, 142.6, 161.3.

8. **2a**: pale yellow solid, m.p. 65-67 °C; ^{1}H ($CDCl_3$) δ 1.5 (s, 3H), 6.5 (broad s, 1H), 7.2-7.7 (m, 6H); $^{13}C\{^1H\}$ ($CDCl_3$) δ 18.1, 106.2, 108.1, 109.2, 114.2, 122.3, 123.1, 125.0, 126.1, 126.5, 128.9, 130.1, 140.2, 142.1. **2b**: yellow solid, m.p. 89 °C; ^{1}H ($CDCl_3$) δ 1.6 (s, 6H), 7.2-7.8 (m, 6H); $^{13}C\{^1H\}$ ($CDCl_3$) δ 23.3, 107.3, 112.1, 120.2, 124.9, 126.2, 130.0, 139.1 **2c** yellow solid, m.p. 95-96 °C; ^{1}H ($CDCl_3$) δ 1.2 (t, 6H), 1.8 (q, 4H), 7.2-7.7 (m, 6H); $^{13}C\{^1H\}$ ($CDCl_3$) δ 12.2, 20.5, 108.2, 111.5, 119.3, 125.4, 126.1, 129.3, 140.6. **2d**: bright orange, heat sensitive solid, m.p. 81-83 °C (dec.); ^{1}H ($CDCl_3$) δ 3.6 (s, 6H), 7.1-7.6 (m, 6H); $^{13}C\{^1H\}$ ($CDCl_3$) δ 47.8, 102.1, 104.3, 115.6, 123.2, 127.1, 129.2, 137.5. **2e**: bright orange, heat sensitive solid, m.p. 61-62 °C (dec.); ^{1}H ($CDCl_3$) δ 2.5 (s, 6H), 3.7 (s, 3H), 7.1-7.8 (m, 6H); $^{13}C\{^1H\}$ ($CDCl_3$) δ 43.2, 47.8, 100.2, 101.4, 106.5, 107.3, 113.2, 124.1, 125.2, 126.6, 127.2, 128.3, 128.9, 135.5, 137.3. **2f**: bright orange solid, m.p. 78-80 °C; ^{1}H ($CDCl_3$) δ 3.9 (s, 3H), 7.0-7.9 (m, 6H); $^{13}C\{^1H\}$ ($CDCl_3$) δ 52.4, 109.2, 110.1, 110.5, 118.3, 121.1, 125.1, 125.6, 127.1, 128.2, 128.5, 129.3, 138.2, 141.2. **2g**: bright orange-red, heat-sensitive solid, m.p. 76-79 °C (dec.); ^{1}H ($CDCl_3$) δ 2.7 (s, 12H), 7.2-7.7 (m, 6H); $^{13}C\{^1H\}$ ($CDCl_3$) δ 45.3, 99.5, 104.5, 112.2, 124.3, 126.5, 128.1, 139.4. **2h**: (same as **2e**). **2i**: bright red solid, m.p. 69-71 °C; ^{1}H ($CDCl_3$) δ 2.9 (s, 6H), 7.0-8.0 (m, 6H); $^{13}C\{^1H\}$ ($CDCl_3$) δ 49.5, 107.6, 111.2, 111.9, 119.5, 124.1, 124.9, 125.7, 126.3, 128.1, 128.8, 131.3, 140.4, 140.9. **2j**: deep red solid, m.p. 98-100 °C; ^{1}H ($CDCl_3$) δ 6.8-8.0 (m, 26H); $^{13}C\{^1H\}$ ($CDCl_3$) δ 101.2, 104.3, 116.4, 124.6, 125.7, 126.1, 126.4, 127.5, 128.4, 131.2, 137.5.

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