

Regioselective Synthesis of Dialkyl-1,3-cyclopentadienes via Novel 2-Alkyl-6,6-dialkylfulvenes

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Abstract:

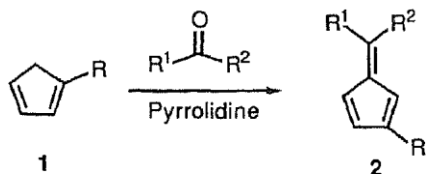
2-Alkyl-6,6-dialkylfulvenes are synthesized by the condensation of monosubstituted 1,3-cyclopentadienes with carbonyl compounds in the presence of pyrrolidine and converted to the corresponding dialkyl-1,3-cyclopentadienes by the addition of nucleophilic reagents lithium aluminum hydride or methyllithium.

Article:

The n^5 -cyclopentadienyl ligand has been one of the most widely used and versatile ligands in organometallic chemistry.¹ Recently, interest in substituted cyclopentadienyl ligands, especially the n^5 -pentamethylcyclopentadienyl ligand has flourished.² Steric constraints and increased electron density at the metal center contribute to novel stoichiometry and reactivity of their transition metal complexes.³ Currently, the number of disubstituted cyclopentadienes available for the preparation of transition metal complexes is very limited. In this paper we report our results on the synthesis of sterically congested 1,3-disubstituted-cyclopentadienes from 2-substituted-6,6-pentafulvenes.

Table 1
Synthesis of 2-Substituted-6,6-dialkylfulvenes. 2.^a

Compound	R	R ¹	R ²	Yield, %
2a	Cyc	-CH ₂ (CH ₂) ₃ CH ₂ -		50
2b	Mecyc	-CH ₂ (CH ₂) ₃ CH ₂ -		56
2c	t-Bu	-CH ₂ (CH ₂) ₃ CH ₂ -		75
2d	Cyc	Me	Me	70
2e	Mecyc	Me	Me	67
2f	t-Bu	Me	Me	93
2g ^b	t-Bu	t-Bu	H	34



Scheme 1

Nucleophilic attack on the highly polarized exocyclic double bond of fulvenes followed by hydrolysis to produce the corresponding monosubstituted-1,3-cyclopentadienes has been known for some time.⁴ We conceived that the addition of nucleophiles to 2-substituted-6,6-dialkylfulvenes would offer a regioselective synthesis of sterically congested disubstituted-1,3-cyclopentadienes. 2-Substituted-6,6-pentafulvenes have been previously synthesized, however a mixture of 1- and 2- positional isomers is often obtained. The condensation of methylcyclopentadiene with acetone and potassium hydroxide in ethanol generates a mixture of the 1 and 2 substituted fulvenes in a 3:1 ratio.⁵ However, monosubstituted-1,3-cyclopentadienes containing bulky

(a) Cyc = cyclohexyl; Mecyc = 1-(1-methyl)

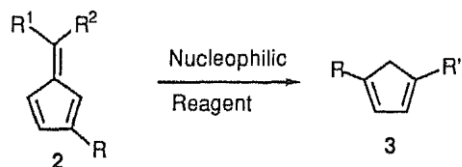
cyclohexyl. (b) Reaction would not proceed at room temperature, reflux was required for 24 h. to obtain appreciable yields.

substituents afford 2-substituted-6,6-pentafulvenes exclusively. This is exemplified by the previous synthesis of 2-iso-propyl-6,6-pentamethylenefulvene in which the regiochemistry was confirmed via the ^1H NMR of its Diels-Alder adduct with methyl propiolate.⁶

A series of 2-substituted-6,6-dialkylfulvenes has been prepared by the condensation of a monosubstituted-1,3-cyclopentadiene with carbonyl compounds in the presence of pyrrolidine⁷ (Scheme 1). The products were obtained in excellent yields and have been characterized by their ^1H NMR, ^{13}C NMR, IR and UV-Vis spectra.⁸ The results are listed in Table 1.

In order to confirm the position of the substituent in 2a-g, the compounds were converted to their Diels-Alder adducts with tetracyanoethylene. In each case, 2-substitution was confirmed via the ^1H NMR of the TCNE adducts.⁹

Nucleophilic addition to the exocyclic double bond of 2-substituted-6,6-dialkylfulvenes provides an exceptional route to disubstituted-1,3-cyclopentadienes with exact regioselectivity. A number of symmetrically and unsymmetrically disubstituted cyclopentadienes were prepared by this method as mixtures of double bond isomers (Scheme 2). These have been characterized by ^1H NMR, IR and UV-Vis spectroscopies.¹⁰ The synthetic details are listed in Table 2.



Scheme 2

Table 2
Synthesis of Disubstituted-1,3-cyclopentadienes¹⁰

	Fulvene Nucleophilic Reagent	1,3-cyclopentadiene, ^a C ₅ H ₄ RR'	Yield, %
2a	LiAlH ₄	3a, R = R' = Cyc	76
2b	CH ₃ Li	3b, R = R' = Mecyc	67
2c	LiAlH ₄	3c, R = <i>i</i> -Bu; R' = Cyc	70
2d	LiAlH ₄	3d, R = Cyc; R' = <i>i</i> -Pr	80
2e	CH ₃ Li	3c, R = Cyc; R' = <i>i</i> -Bu	86
2f	LiAlH ₄	3f, R = <i>i</i> -Bu; R' = <i>i</i> -Pr	70
2g	LiAlH ₄	3g, R = <i>i</i> -Bu; R' = CH ₂ - <i>i</i> -Bu	70

a) Cyc = Cyclohexyl; Mecyc = 1-(1-methyl)cyclohexyl

Compounds 3a-g were obtained in very good yields, for example: The addition of a diethyl ether solution of 2-cyclohexyl-6,6-pentamethylenefulvene to lithium aluminum hydride followed by hydrolysis affords 3a in 76% yield. Compound 3a has been independently synthesized in 35% yield via the method of Neuenschwander *et al.*¹¹ The preparation of fulvenes followed by nucleophilic addition is a more efficient method for the generation of disubstituted-1,3-cyclopentadienes.

In summary, we have shown that a relatively new class of fulvenes, 2-substituted-6,6-dialkylfulvenes, can be prepared in high yield and converted to disubstituted-1,3-cyclopentadienes with exact regioselectivity. These disubstituted-1,3-cyclopentadienes have been used to form transition metal compounds with novel results.¹²

References and Notes

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- (8) Spectral data for 2f, 500 MHz ^1H NMR (benzene d_6) 6.60 (dd, 1H, $J = 5.43, 2.21$), 6.58 (dd, 1H, $J = 5.43, 1.57$), 6.25 (dd, 1H, $J = 2.21, 1.57$), 2.00 (s, 6H), 1.10 (s, 9H). ^{13}C NMR (CDCl₃) 156.5, 146.8, 141.9, 130.5, 121.3, 111.7, 32.1, 29.7, 22.7, 22.6. IR 2980, 1645, 1445 cm^{-1} . UV-Vis (hexanes) 351.2 (2.50), 271.4 (4.28), 264.4 (4.28). MS (m/z) 162 p+, 147, 66.
- (9) A typical reaction involved the 2-alkyl-6,6-dialkylfulvene (1 equivalent) and tetracyanoethylene (1 equivalent) in acetone for 4-8 h. Spectroscopic data for 2-ler1-butyl-7-jmpropylidene-5,5,6,6-tetracyanonorbornene 200 MHz ^1H NMR (CDCl₃) 6.27 (dd, 1H, $J = 3.57, 1.42$), 4.39 (dd, 1H, $J = 1.92, 1.42$), 4.31 (dd, 1H, $J = 3.57, 1.92$), 1.80 (s, 6H), 1.20 (s, 9H).
- (10) Spectroscopic data for 3f, 60 MHz ^1H NMR (CDCl₃) 5.2-6.3 (m, 2H), 2.4 (s, br, 2H), 2.2 (m, 1H), 1.2 (s, 9H), 1.1 (d, 6H). IR 3060, 2960, 2860, 2740, 1620 cm^{-1} . UV-Vis (hexane) 253.4 (3.66). MS (m/z) 164 p+, 149, 121, 107.
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